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Stormwater Treatment At Critical Areas

Vol. 1: The Multi-Chambered Treatment Train (MCTT)

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Notice

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Foreword

Today’s rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts and search for solutions.

The National Risk Management Research Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensive engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and user community.

The purpose of this project was to investigate the sources of critical stormwater pollutants and to test a device for the treatment of stormwater toxicants. This is the first volume for this report series and describes the work conducted during the early years of this project through recent full-scale tests. It describes the field activities investigating the sources of critical pollutants, the detailed laboratory tests evaluating the performance of various unit processes in their ability to remove stormwater toxicants, and the development and testing of a specialized stormwater management practice that can be used at critical source areas. The information provided in this report can be used to develop other critical source area treatment devices. Other volumes in this report series describe the results of field investigations of storm drain inlet devices and the use of filter media for stormwater treatment.

A combination of complementary unit processes was determined to provide the most effective stormwater control. The multi-chambered treatment train (MCTT) was designed to include a number of these unit processes. Pilot-scale and full-scale installations have shown excellent pollutant reductions with this device. These field monitoring activities showed high reductions for SS (83 to 98%), COD (60 to 86%), turbidity (40 to 94%), phosphorus (80 to 88%), lead (93 to 96%), zinc (90 to 91%), and for many organic toxicants (generally 65 to 100%). The reductions of dissolved heavy metals (filtered through 0.45 µm filters) were also all greater than 65% during the full-scale tests.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

This is the first volume for this report series and describes the work conducted during the early years of this project through recent full-scale tests. Other volumes in this report series describe the results of field investigations of storm drain inlet devices and the use of filter media for stormwater treatment.

The first project phase investigated typical toxicant concentrations in stormwater, the origins of these toxicants, and storm and land-use factors that influenced these toxicant concentrations. Nine percent of the 87 stormwater source area samples analyzed were considered extremely toxic (using the Microtox™ toxicity screening procedure). Thirty-two percent of the samples exhibited moderate toxicity, while fifty-nine percent of the samples had no evidence of toxicity. Only a small fraction of the organic toxicants analyzed were frequently detected, with 1,3-dichlorobenzene and fluoranthene the most commonly detected organics investigated (present in 23 percent of the samples). Vehicle service and parking area runoff samples had many of the highest observed concentrations of organic toxicants. All metallic toxicants analyzed were commonly found in all samples analyzed.

The second project phase investigated the control of stormwater toxicants using a variety of conventional bench-scale treatment processes. Toxicity changes were monitored using the Azur Environmental Microtox™ bioassay screening test. The most beneficial treatment tests included settling for at least 24 h (up to 90 percent reductions), screening and filtering through at least 40 µm screens (up to 70 percent reductions), and aeration and/or photo-degradation for at least 24 h (up to 80 percent reductions). Because many samples exhibited uneven toxicity reductions for the different treatment tests, a treatment train approach was selected for testing during the third project phase.

The third project phase included testing of a prototype treatment device (the multi-chambered treatment train, or MCTT). However, the information provided in this report can also be used to develop other stormwater treatment devices. This device, through pilot and initial full-scale testing, has been shown to remove more than 90% of many of the stormwater toxicants, in both particulate and filtered forms. The MCTT is most suitable for use at relatively small and isolated paved critical source areas, from about 0.1 to 1 ha (0.25 to 2.5 acre) in area. These areas would include vehicle service facilities (gas stations, car washes, oil change stores, etc.), convenience store parking areas and areas used for equipment storage, along with salvage yards. The MCTT is an underground device that has three main chambers: an initial grit chamber for trapping of the largest sediment and release of most volatile materials; a main settling chamber (providing initial aeration and sorbent pillows) for the trapping of fine sediment and associated toxicants and floating hydrocarbons; and a sand and peat mixed media “filter” (sorption-ion exchange) unit for the reduction of filterable toxicants. A typical MCTT requires between 0.5 and 1.5 percent of the paved drainage area, which is about 1/3 of the area required for a well-designed wet detention pond.

A pilot-scale MCTT was constructed in Birmingham, AL, and tested over a six month monitoring period. Two additional full-scale MCTT units have recently been constructed and are currently being monitored as part of Wisconsin’s 319 grant from the U.S. EPA. During monitoring of 13 storms at a parking facility, the pilot-scale MCTT was found to have the following overall median reduction rates: 96% for total toxicity, 98% for filtered toxicity, 83% for SS, 60% for COD, 40% for turbidity, 100% for lead, 91% for zinc, 100% for n-Nitro-di-n-proplamine, 100% for pyrene, and 99% for bis (2-ethyl hexyl) phthalate. The color was increased by about 50% due to staining from the peat and the pH decreased by about one-half pH unit, also from the peat media. Ammonia nitrogen was increased by several times, and nitrate nitrogen had low reductions (about 14%). The MCTT therefore operated as intended: it had very effective reduction rates for both filtered and particulate stormwater toxicants and SS. Increased filterable toxicant reductions were obtained in the peat/sand mixed media sorption-ion exchange chamber, at the expense of increased color, lowered pH, and depressed COD and nitrate reduction rates. The preliminary full-scale test results substantiate the excellent reductions found during the pilot-scale tests, while showing better control of COD, filterable heavy metals, and nutrients, and less detrimental effects on pH and color.

Contents

Tables

Page

Figures

Page

Acknowledgments

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Many UAB graduate students and staff freely gave of their time to support this project, especially Olga Mirov, Michael Richards, Lyn Lewis, Jay Day, Janice Lanthrop, Joe Farmer, Tim Awtrey, Niki Beckom, Melissa Lilburn, and Holly Ray. Four MSCE theses in the Department of Civil and Environmental Engineering at the University of Alabama at Birmingham were also prepared by graduate students working on this EPA sponsored project:

- Shirley Clark's *Evaluation of Filtration Media for the Treatment of Stormwater* (1996),
- Brian Robertson's *Evaluation of a Multi-Chambered Treatment Train for Treatment of Stormwater Runoff from Critical Pollutant Source Areas* (1995).
- Ali Ayyoubi's *Physical Treatment of Urban Storm Water Runoff Toxicants* (1993), and
- Patricia Barron's *Characterization of Polynuclear Aromatic Hydrocarbons in Urban Runoff* (1990).

Much of the material in this report was previously presented in these theses, which also contain considerable additional supporting information.

The author would also like to thank the following for donation of materials to the project: Jaeger Products, Inc. of Houston, Texas for donating column packing spheres, Polar Supply Company, Inc. of Anchorage, Alaska for donating filter fabric material, and Sherman Industries of Birmingham, Alabama for donating filtering media.

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Chapter 1
Introduction and Conclusions

Past studies have identified urban runoff as a major contributor to the degradation of many urban streams and rivers (Field and Turkeltaub 1981; Pitt and Bozeman 1982; Pitt and Bissonnette 1984, and Pitt 1994, which includes an extensive literature review). Previous studies also found organic and metallic toxicants in urban storm induced discharges (EPA 1983a; Hoffman, *et al*. 1984; Fram, *et al*. 1987) which can contribute to receiving water degradation. Appendix D contains a summary of basic receiving water problems associated with urban stormwater, stressing recent research that supplements the above referenced studies and reviews.

The Nationwide Urban Runoff Program (NURP) monitored stormwater toxicant discharges from 28 cities and concluded that urban areas were responsible for substantial discharges of toxicants (EPA 1983a). The NURP data were collected mostly from residential areas and did not consider snowmelt. Furthermore, only a few commercial and light industrial areas were represented. NURP did not identify any significant regional differences in toxicants found, or in their concentrations. However, other information indicates that industrial stormwater, snowmelt runoff, and dry weather discharges (including illegal discharges into storm drainage) can all contribute significant amounts of toxicants to receiving waters (Pitt and McLean 1986).

The objective of this research was to further characterize stormwater toxicants, confirm the source areas of concern, and investigate the effectiveness of treatment processes to control the toxicants. A parallel EPA sponsored research project resulted in a user's guide for the investigation of inappropriate discharges into storm drainage systems (Pitt, *et al*. 1993) and a comprehensive review of groundwater impacts from stormwater infiltration (Pitt, *et al*. 1994 and 1996). Clearly, an effective urban runoff control program must consider all seasonal flow phases and sources of critical pollutants. If warm weather stormwater runoff was the only source considered, storm drainage control programs in many areas would be disappointingly deficient. A complete control program must consider dry weather flows, plus snow melt in northern areas, in addition to stormwater runoff. The results of the research reported here is only one component of this complete control program approach.

Conclusions

Previous studies have indicated that urban stormwater runoff contains a variety of conventional and potentially toxic pollutants that can degrade receiving waters and impair beneficial uses. Receiving water impacts are due to many variables, including: the magnitude of the dry and wet weather discharges; the transport and fate mechanisms of the toxicants; and effects from other discharges and receiving water conditions. These factors, and the unknown and site specific relationships between them, make the prediction of receiving water effects difficult, if not impossible, especially if one only relies on water column quality measurements. *In situ* biological community structure studies can give an indication of the receiving water effects, especially if pre-development or control conditions are known for comparison purposes. However it will generally be difficult to relate any identified impacts to any specific pollutant, but an in-stream biological community structure and habitat study will indicate whether the receiving water is being adversely effected.

Phase 1 of this research detected only a small fraction of the organic toxicants analyzed (as is typical for stormwater evaluations), but detected heavy metals in the majority of the samples analyzed. The study also confirmed that many toxicants are associated with particulate matter in the runoff. Industrial/commercial areas are likely to be the most significant pollutant source areas, with the highest toxicant concentrations and most frequent occurrences found at vehicle service and parking/storage areas. The duration of the antecedent dry period before a storm and the intensity of the storm event were found to be significant factors influencing the concentrations of most of the toxicants detected. These critical areas were sampled for the phase 2 treatability tests.

The treatability study (phase 2) found that settling, screening, and aeration and/or photo-degradation treatments showed the greatest potential for toxicant reductions, as measured by the reduction in toxicity of the samples, using the Microtox™ toxicity screening test. Studies to measure the actual toxicant reductions in full-scale applications are needed to confirm the real benefit of the potential treatment processes. The results from the second study phase, in conjunction with results from the first project phase, will enable the modification of treatment devices and system designs (for new installations and for retrofitting existing installations) to optimize toxicant reductions from critical stormwater runoff source areas. The third project phase examined the toxicant reduction benefits of large-scale applications of the most suitable treatment unit processes investigated.

The third phase of this research examined the use of a multi-chambered treatment tank (MCTT) to collect and treat runoff from critical stormwater source areas, including gas stations, oil change facilities, transmission repair shops, and other auto repair facilities. The collected runoff is first treated in a catchbasin chamber where larger particles are removed by settling. The water then flows into a main settling chamber containing oil sorbent material where it undergoes a much longer treatment period (24 to 72 h) to remove finer particles and associated pollutants. The final chamber contains a mixed media filter material comprising equal amounts of sand and peat. This final chamber acts as a polishing "filter" to remove some of the filterable toxicants from the runoff by other processes, such as ion exchange and sorption.

The pilot- and full-scale test results show that the MCTT is providing substantial reductions in stormwater toxicants (both in particulate and filtered phases) and suspended solids. Increases in color and a slight decrease in pH also occurred during the final treatment step when using peat as part of the filtering/ion-exchange media.

The main settling chamber provided substantial reductions in total and dissolved toxicity, lead, zinc, certain organic toxicants, SS, COD, turbidity, and color. The sand-peat chamber also provided additional filterable toxicant reductions. However, the catchbasin/grit chamber did not provide any significant improvements in water quality, although it is an important element in reducing maintenance problems by trapping bulk material.

Zinc and toxicity are examples where the use of the final chamber was needed to provide high levels of control. Otherwise, it may be tempting to simplify the MCTT by removing the last chamber. Another option would be to remove the main settling chamber and only use the pre-treating capabilities of the catchbasin as a grit chamber before the peat "filtration" chamber (similar to many stormwater filter designs). This option is not recommended because of the short life that the filter would have before it would clog (Clark and Pitt 1997). In addition, the bench-scale tests showed that a treatment train was needed to provide some redundancy because of frequent variability in sample treatability storm to storm, even for a single sampling site.

It is important not to confuse the MCTT with an oil/water separator or a grit chamber. Oil/water separators are mainly industrial wastewater treatment devices that work well for removing high concentrations of relatively large droplets of oil from wastewater. Stormwaters rarely have such levels of hydrocarbon contamination. If an area did produce stormwater having these hydrocarbon contamination conditions, then oil/water separators should be used, but further treatment may also be needed to remove other pollutants. Unfortunately, the available literature does not contain many examples of successful applications of oil/water separators for stormwater control. Common problems include lack of maintenance and under-sized separators for the flows encountered. Scouring of previously captured material is also common.

Several proprietary stormwater treatment devices have recently been marketed throughout North America. These devices can also be located underground. Unfortunately, comprehensive testing with actual stormwater is not available for most of these devices. The designs and demonstrations are mostly based on reduction of relatively large particles that rarely occur in stormwater. As indicated in this report, the suspended solids in stormwater is mostly in the range of 1 to 100 µm, with only a small fraction of the mass (usually <10%) associated with particles greater than

100 µm. These devices are designed to capture particle sizes that have typically been found on streets, not in the runoff water (Pitt 1987). These devices are excellent grit chambers (and can probably capture floating oils) and can be used to prevent sand-sized particles from accumulating in sewerage. Very little scour of the captured grit material is also likely with these devices. However, they are not likely to provide important reductions of most stormwater pollutants, especially the toxicants. The MCTT was designed to remove pollutants of a specific class of concern in stormwater: particulates as small as a few µm and associated particulate bound toxicants, plus filterable toxicants. If a site is grossly contaminated with oils or grit, then a proprietary oil/water separator or grit chamber is needed, but further treatment will also likely be necessary.

The MCTT is capable of reducing a broad range of stormwater pollutants that cause substantial receiving-water problems (Pitt 1995). The MCTT has a high potential for cost-effective use as an integrated component in watershed management programs designed to protect and enhance receiving waters.

Organization of Report

This report includes discussions pertaining to the major issues that must be addressed when developing a stormwater management plan. These issues include a knowledge of the receiving water problems caused by stormwater (Appendix D), a knowledge of the problem pollutants and where they originate in the watershed (Chapter 2), and a knowledge of the control of these critical pollutants (Chapters 3, 4, 5 and 6). This EPA sponsored cooperative agreement with UAB included three research phases reported in this report covering these basic elements. The first phase included investigating sources of critical stormwater pollutants, the second phase included conducting bench-scale treatability tests to identify the effectiveness of many unit processes, while the third project phase included testing of a pilot-scale treatment device containing many of the most promising unit processes. These project phases are all presented in this report, along with preliminary information from full-scale testing conducted by the state of Wisconsin. The project research information is also substantially supported by information from the literature, especially on effects of stormwater (Appendix D) and sources of pollutants (Chapter 2).

Chapter 1 contains a brief discussion of the conclusions from the research, while Chapter 2 includes much literature information, plus the results of source area characterization studies conducted during this research project. Chapter 3 presents the results of the bench-scale treatability tests. Chapter 4 begins with a discussion of oil/water separators for stormwater control, and then discusses the development of the MCTT. Chapter 5 presents the results of the pilot-scale tests of the MCTT conducted in Birmingham and the preliminary test results from the full-scale tests being conducted in Wisconsin. Chapter 6 includes the general design procedure for the MCTT, including an example design for a Detroit site. Appendices A, B, and C include detailed observations obtained during this research. Appendix D reviews receiving effects from stormwater, while Appendix E is an excerpt from the project Quality Assurance Project Plan (QAPP) describing the laboratory analytical methods used during this project.

This is one of three project reports prepared for this cooperative agreement. The other two volumes describe tests of stormwater inlets and stormwater filtering media for their ability to reduce concentrations of stormwater pollutants. Previous reporting efforts of this cooperative agreement included an earlier report (and a book published by Ann Arbor Press) on groundwater effects of stormwater infiltration, a soon-to-be published book (CRC/Lewis) on conducting receiving water studies, and numerous technical conference presentations and published articles, many through the Engineering Foundation/ASCE series of stormwater conferences.

Chapter 2
Sources of Urban Stormwater Pollutants

Urban runoff is comprised of many separate source area flow components that are combined within the drainage area and at the outfall before entering the receiving water. It may be adequate to consider the combined outfall conditions alone when evaluating the long term, areawide effects of many separate outfall discharges to a receiving water. However, if better predictions of outfall characteristics (or the effects of source area controls) are needed, then the separate source area components must be characterized. The discharge at the outfall is made up of a mixture of contributions from different source areas. The "mix" depends on the characteristics of the drainage area and the specific rain event. The effectiveness of source area controls is therefore highly site and storm specific.

Various urban source areas all contribute different quantities of runoff and pollutants, depending on their specific characteristics. Impervious source areas may contribute most of the runoff during small rain events. Examples of these source areas include paved parking lots, streets, driveways, roofs, and sidewalks. Pervious source areas become important contributors for larger rain events. These pervious source areas include gardens, lawns, bare ground, unpaved parking areas and driveways, and undeveloped areas. The relative importance of the individual sources is a function of their areas, their pollutant washoff potentials, and the rain characteristics.

The washoff of debris and soil during a rain is dependent on the energy of the rain and the properties of the material. Pollutants are also removed from source areas by winds, litter pickup, or other cleanup activities. The runoff and pollutants from the source areas flow directly into the drainage system, onto impervious areas that are directly connected to the drainage system, or onto pervious areas that will attenuate some of the flows and pollutants, before they discharge to the drainage system .

Sources of pollutants on paved areas include on-site particulate storage that cannot be removed by usual processes e.g., rain, wind, street cleaning, etc. Atmospheric deposition, deposition from activities on these paved surfaces (auto traffic, material storage, etc.) and the erosion of material from upland areas that directly discharge flows onto these areas, are the major sources of pollutants to the paved areas. Pervious areas contribute pollutants mainly through erosion processes where the rain energy dislodges soil from between plants. The runoff from these source areas enter the storm drainage system where sedimentation in catchbasins or in the sewerage may affect their ultimate discharge to the outfall. In-stream physical, biological, and chemical processes affect the pollutants after they are discharged to the ultimate receiving water.

It is important to know when the different source areas become "active" (when runoff initiates from the area, carrying pollutants to the drainage system). If pervious source areas are not contributing runoff or pollutants, then the prediction of urban runoff quality is much simplified. The mechanisms of washoff, and delivery yields of runoff and pollutants from paved areas, is much better known than from pervious urban areas (Novotny and Chesters 1981). In many cases, pervious areas are not active except during rain events greater than at least five or ten mm. For smaller rain depths, almost all of the runoff and pollutants originate from impervious surfaces (Pitt 1987). However, in many urban areas, pervious areas may contribute the majority of the runoff, and some pollutants, when rain depths are greater than about 20 mm. The actual importance of the different source areas is highly dependent on the specific land use and rainfall patterns. Obviously, in areas having relatively low density development, especially where moderate and large sized rains occur frequently (such as in the Southeast), pervious areas typically dominate outfall discharges. In contrast, in areas having significant paved areas, especially where most rains are relatively small (such as in the arid west), the impervious areas would dominate outfall discharges. The effectiveness of different source controls would therefore be quite different for different land uses and climatic patterns.

If the number of events exceeding a water quality objective are important, then the small rain events are of most concern. Stormwater runoff typically exceeds some water quality standards for practically every rain event (especially for bacteria and some heavy metals). In the upper Midwest, the median rain depth is about 6 mm, while in the Southeast, the median rain depth is about twice this depth. For these small rain depths and for most urban land uses, directly connected paved areas usually contribute most of the runoff and pollutants. However, if annual mass discharges are more important, e.g. for long-term effects, then the moderate rains are more important. Rains from about 10 to 50 mm produce most of the annual runoff volume in many areas of the U.S. Runoff from both impervious and pervious areas can be very important for these rains. The largest rains (greater than 100 mm) are relatively rare and do not contribute significant amounts of runoff pollutants during normal years, but are very important for drainage design. The specific source areas that are most important (and controllable) for these different conditions vary widely.

The remaining portions of this chapter describe sources of urban runoff flows and pollutants as reported from many past studies as found in the literature. This chapter also reports on the specific source area sampling activities conducted as part of this EPA funded research.

Sources and Characteristics of Urban Runoff Pollutants

It has been known for many years that the vast majority of stormwater toxicants and much of the conventional pollutants are associated with automobile use and maintenance activities and that these pollutants are strongly associated with the particulates suspended in the stormwater (the non-filterable components, or suspended solids). It has been difficult to reduce or modify automobile use to reduce the use of these compounds, with the notable exception of the phasing out of leaded gasoline. Current activities, concentrated in the San Francisco area, are trying to encourage brake pad manufactures to reduce the use of copper. The effectiveness of most stormwater control practices is therefore dependent on their ability to remove these particles from the water, or possibly from intermediate accumulating locations (such as streets or other surfaces) and not through source reduction. The removal of these particles from stormwater is dependent on various characteristics of these particles, especially their size and settling rates. Some source area controls (most notably street cleaning) affect the particles before they are washed-off and transported by the runoff, while others remove the particles from the flowing water. This discussion therefore summarizes the accumulation and washoff of these particulates and the particle size distribution of the suspended solids in stormwater runoff to better understand the effectiveness of source area control practices.

Table 2.1 shows that most of the organic compounds found in stormwater are associated with various human-related activities, especially automobile and pesticide use, or are associated with plastics (Verschueren 1983). Heavy metals found in stormwater also mostly originate from automobile use activities, including gasoline combustion, brake lining, fluids (brake fluid, transmission oil, anti-freeze, grease, etc.), undercoatings, and tire wear (Durum 1974, Koeppe 1977, Rubin 1976, Shaheen 1975, Solomon and Natusch 1977, and Wilbur and Hunter 1980). Auto repair, pavement wear, and deicing compound use also contribute heavy metals to stormwater (Field, *et al*. 1973, and Shaheen 1975). Shaheen (1975) found that eroding area soils are the major source of the particulates in stormwater. The eroding area soil particles, and the particles associated with road surface wear, become contaminated with exhaust emissions and runoff containing the polluting compounds. Most of these compounds become tightly bound to these particles and are then transported through the urban area and drainage system (or removed) with the particulates. Stormwater concentrations of zinc, fluoranthene, 1,3-dichlorobenzene, and pyrene are unique in that substantial fractions of these compounds remain in the water and are less associated with the particulates.

All areas are affected by atmospheric deposition, while other sources of pollutants are specific to the activities conducted on the areas. As examples, the ground surfaces of unpaved equipment or material storage areas can become contaminated by spills and debris, while undeveloped land remaining relatively unspoiled by activities can still contribute runoff solids, organics, and nutrients, if eroded. Atmospheric deposition, deposition from activities on paved surfaces, and the erosion of material from upland unconnected areas are the major sources of pollutants in urban areas.

Table 2.1. Uses and Sources for Organic Compounds found in Stormwater (Source: Verschueren 1983)

COMPOUND	EXAMPLE USE/SOURCE
Phenol	gasoline, exhaust
N-Nitroso-di-n-propylamine	contaminant of herbicide Treflan
Hexachloroethane	plasticizer in cellulose esters, minor use in rubber and insecticide
Nitrobenzene	solvent, rubber, lubricants
2,4-Dimethylphenol	asphalt, fuel, plastics, pesticides
Hexachlorobutadiene	rubber and polymer solvent, transformer and hydraulic oil
4-Chloro-3-methylphenol	germicide; preservative for glues, gums, inks, textile, and leather
Pentachlorophenol	insecticide, algaecide, herbicide, & fungicide mfg., wood preservative
Fluoranthene	gasoline, motor and lubricating oil, wood preservative
Pyrene	gasoline, asphalt, wood preservative, motor oil
Di-n-octylphthalate	general use of plastics

There have been many studies in the past that have examined different sources of urban runoff pollutants. These references have been reviewed as part of this study and the results are summarized in this section. These significant pollutants have been shown to have a potential for creating various receiving water impact problems, as described in Appendix D of this report. Most of these potential problem pollutants typically have significant concentration increases in the urban feeder creeks and sediments, as compared to areas not affected by urban runoff.

The important sources of these pollutants are related to various uses and processes. Automobile related potential sources usually affect road dust and dirt quality more importantly than other particulate components of the runoff system. The road dust and dirt quality is affected by vehicle fluid drips and spills (gasoline, oils, etc.) and vehicle exhaust, along with various vehicle wear, local soil erosion, and pavement wear products. Urban landscaping practices potentially affecting urban runoff include vegetation litter, fertilizer and pesticide. Miscellaneous sources of urban runoff pollutants include firework debris, wildlife and domestic pet wastes and possibly industrial and sanitary wastewaters. Wet and dry atmospheric contributions both affect runoff quality. Pesticide use in an urban area can contribute significant quantities of various toxic materials to urban runoff. Many manufacturing and industrial activities, including the combustion of fuels, also affects urban runoff quality.

Natural weathering and erosion products of rocks contribute the majority of the hardness and iron in urban runoff pollutants. Road dust and associated automobile use activities (gasoline exhaust products) historically contributed most of the lead in urban runoff. However, the decrease of lead in gasoline has resulted in current stormwater lead concentrations being about 1/10 of the levels found in stormwater in the early 1970s (Bannerman, *et al.* 1993). In certain situations, paint chipping can also be a major source of lead in urban areas. Road dust contaminated by tire wear products, and zinc plated metal erosion material, contribute most of the zinc to urban runoff. Urban landscaping activities can be a major source of cadmium (Phillips and Russo 1978). Electroplating and ore processing activities can also contribute chromium and cadmium.

Many pollutant sources are specific to a particular area and on-going activities. For example, iron oxides are associated with welding operations and strontium, used in the production of flares and fireworks, would probably be found on the streets in greater quantities around holidays, or at the scenes of traffic accidents, The relative contribution of each of these potential urban runoff sources, is, therefore, highly variable, depending upon specific site conditions and seasons.

Specific information is presented in the following subsections concerning the qualities of various rocks and soils, urban and rural dustfall, and precipitation. This information is presented to assist in the interpretation of the source area runoff samples collected as part of this project.

Chemical Quality of Rocks and Soils

The abundance of common elements in the lithosphere (the earth's crust) is shown in Table 2.2 (Lindsay l979). Almost half of the lithosphere is oxygen and about 25 percent is silica. Approximately 8 percent is aluminum and 5 percent is iron. Elements comprising between 2 percent and 4 percent of the lithosphere include calcium, sodium, potassium and magnesium. Because of the great abundance of these materials in the lithosphere, urban runoff transports only a relatively small portion of these elements to receiving waters, compared to natural processes. Iron and aluminum can both cause detrimental effects in receiving waters, if in their dissolved forms. A reduction of the pH substantially increases the abundance of dissolved metals. Table 2.3, also from Lindsay (1979), shows the rankings for common elements in soils. These rankings are quite similar to the values shown previously for the lithosphere. Natural soils can contribute pollutants to urban runoff through local erosion. Again, iron and aluminum are very high on this list and receiving water concentrations of these metals are not expected to be significantly affected by urban activities alone.

Table 2.2 Common Elements in the Lithosphere (Source: Lindsay 1979)

Abundance Rank	Element	Concentration in Lithosphere (mg/kg)
1	O	465,000
2	Si	276,000
3	Al	81,000
4	Fe	51,000
5	Ca	36,000
6	Na	28,000
7	K	26,000
8	Mg	21,000
9	P	1,200
10	C	950
11	Mn	900
12	F	625
13	S	600
14	Cl	500
15	Ba	430
16	Rb	280
17	Zr	220
18	Cr	200
19	Sr	150
20	V	150
21	Ni	100

Table 2.3 Common Elements in Soils (Source: Lindsay 1979)

Abundance Rank	Element	Typical Minimum (mg/kg)	Typical Maximum (mg/kg)	Typical Average (mg/kg)
1	O			490,000
2	Si	230,000	350,000	320,000
3	Al	10,000	300,000	71,000

4	Fe	7,000	550,000	38,000
5	C			20,000
6	Ca	7,000	500,000	13,700
7	K	400	30,000	8,300
8	Na	750	7,500	6,300
9	Mg	600	6,000	5,000
10	Ti	1,000	10,000	4,000
11	N	200	4,000	1,400
12	S	30	10,000	700
13	Mn	20	3,000	600
14	P	200	5,000	600
15	Ba	100	3,000	430
16	Zr	60	2,000	300
17	F	10	4,000	200
18	Sr	50	1,000	200
19	Cl	20	900	100
20	Cr	1	1,000	100
21	V	20	500	100

The values shown on these tables are expected to vary substantially, depending upon the specific mineral types. Arsenic is mainly concentrated in iron and manganese oxides, shales, clays, sedimentary rocks and phosphorites. Mercury is concentrated mostly in sulfide ores, shales and clays. Lead is fairly uniformly distributed, but can be concentrated in clayey sediments and sulfide deposits. Cadmium can also be concentrated in shales, clays and phosphorites (Durum 1974).

Street Dust and Dirt Pollutant Sources

Characteristics

Most of the street surface dust and dirt material (by weight) are local soil erosion products, while some materials are contributed by motor vehicle emissions and wear (Shaheen 1975). Minor contributions are made by erosion of street surfaces in good condition. The specific makeup of street surface contaminants is a function of many conditions and varies widely (Pitt 1979).

Automobile tire wear is a major source of zinc in urban runoff and is mostly deposited on street surfaces and nearby adjacent areas. About half of the airborne particulates lost due to tire wear settle out on the street and the majority of the remaining particulates settle within about 6 meters of the roadway. Exhaust particulates, fluid losses, drips, spills and mechanical wear products can all contribute lead to street dirt. Many heavy metals are important pollutants associated with automobile activity. Most of these automobile pollutants affect parking lots and street surfaces. However, some of the automobile related materials also affect areas adjacent to the streets after being transported by wind after being resuspended from the road surface by traffic-induced turbulence.

Automobile exhaust particulates contribute many important heavy metals to street surface particulates and to urban runoff and receiving waters. The most notable of these heavy metals has been lead. However, since the late 1980s, the concentrations of lead in stormwater has decreased substantially (by about ten times) compared to early 1970 observations. This decrease, of course, is associated with significantly decreased consumption of leaded gasoline. Solomon and Natusch (1977) studied automobile exhaust particulates in conjunction with a comprehensive study of lead in the Champaign-Urbana, Illinois area. They found that the exhaust particulates existed in two distinct morphological forms. The smallest particulates were almost perfectly spherical, having diameters in the range of 0.1 to 0.5 µm. These small particles consisted almost entirely of PbBrCl at the time of emission. Because they are small, they are expected to remain airborne for considerable distances and can be captured in the lungs when inhaled. They concluded that the small particles are formed by condensation of PbBrCl vapor onto small nucleating centers, which are probably introduced into the engine with the filtered engine air.

Solomon and Natusch (1977) also found that the second major form of automobile exhaust particulates were rather large, being roughly 10 to 20 µm in diameter. These had typically irregular shapes, with somewhat smooth surfaces. They found that the elemental compositions of these irregular particles were quite variable, being predominantly iron, calcium, lead, chlorine and bromine. They found that individual particles did contain aluminum, zinc, sulfur, phosphorus and some carbon, chromium, potassium, sodium, nickel and thallium. Many of these elements (bromine, carbon, chlorine, chromium, potassium, sodium, nickel, phosphorus, lead, sulfur, and thallium) are most likely condensed, or adsorbed, onto the surfaces of these larger particles during passage through the exhaust system. They believed that these large particles originate in the engine or exhaust system because of their very high iron content. They found that 50 to 70 percent of the emitted lead was associated with these large particles, which would be deposited within a few meters of the emission point onto the roadway, because of their aerodynamic properties.

Solomon and Natusch (1977) also examined urban particulates near roadways and homes in urban areas. They found that lead concentrations in soils were higher near roads and houses. This indicated the capability of road dust and peeling house paint to contaminate nearby soils. The lead content of the soils ranged from 130 to about 1,200 mg/kg. Koeppe (1977), during another element of the Champaign-Urbana lead study, found that lead was tightly bound to various soil components. However, the lead did not remain in one location, but it was transported both downward in the soil profile and to adjacent areas through both natural and man-assisted processes.

Street Dirt Accumulation

The washoff of street dirt and the effectiveness of street cleaning as a stormwater control practice are highly dependent on the available street dirt loading. Street dirt loadings are the result of deposition and removal rates, plus "permanent storage." The permanent storage component is a function of street texture and condition and is the quantity of street dust and dirt that cannot be removed naturally or by street cleaning equipment. It is literally trapped in the texture, or cracks, of the street. The street dirt loading at any time is this initial permanent loading plus the accumulation amount corresponding to the exposure period, minus the re-suspended material removal by wind and traffic-induced turbulence. Removal of street dirt can occur naturally by winds and rain, or by human activity (by the turbulence of traffic or by street cleaning equipment). Very little removal occurs by any process when the street dirt loadings are small, but wind removal may be very large with larger loadings, especially for smooth streets (Pitt 1979).

Figure 2.1 shows very different street dirt loadings for two San Jose, CA, residential study areas (Pitt 1979). The accumulation and deposition rates (and therefore the amounts lost to air) are quite similar, but the initial loading values (the permanent storage values) are very different. The loading differences we7re almost solely caused by the different street textures. Table 2.4 summarizes many accumulation rate measurements obtained from throughout North America. In the earliest studies (APWA 1969; Sartor and Boyd 1972; and Shaheen 1975) it was assumed that the initial street dirt loading values after a major rain or street cleaning were zero. Calculated accumulation rates for rough streets were therefore very large. Later tests measured the initial loading values close to the end of major rains and street cleaning and found that they could be very high, depending on the street texture. When these starting loadings were considered, the calculated accumulation rates were therefore much lower. The early, uncorrected, Sartor and Boyd accumulation rates that ignored the initial loading values were almost ten times the correct values shown on this table. Unfortunately, most urban stormwater models used these very high early accumulation rates as default values.

The most important factors affecting the initial loading and maximum loading values shown on Table 2.4 were found to be street texture and street condition. When data from many locations are studied, it is apparent that smooth streets have substantially less loadings at any accumulation period compared to rough streets for the same land use. Very long accumulation periods relative to the rain frequency resultant in high street dirt loadings. During these conditions, the wind losses of street dirt (as fugitive dust) may approximate the deposition rate, resulting in relatively constant street dirt loadings. At Bellevue, WA, typical interevent rain periods average about 3 days. Relatively constant street dirt loadings were observed in Bellevue because the frequent rains kept the loadings low and very close to the initial storage value, with little observed increase in dirt accumulation over time (Pitt 1985). In Castro Valley, CA, the rain interevent periods were much longer (ranging from about 20 to 100 days) and steady loadings were only observed after about 30 days when the loadings became very high and fugitive dust losses caused by the winds and traffic turbulence moderated the loadings (Pitt and Shawley 1982).

An example of the type of research conducted to obtain the values shown in Table 2.4 was conducted by Pitt and McLean (1986) in Toronto. They measured street dirt accumulation rates and the effects of street cleaning as part of a comprehensive stormwater research project. An industrial street with heavy traffic and a residential street with light traffic were monitored about twice a week for three months. At the beginning of this period, intensive street cleaning (one pass per day for each of three consecutive days) was conducted to obtain reasonably clean streets. Street dirt loadings were then monitored every few days to measure the accumulation rates of street dirt. Street dirt sampling procedures developed by Pitt (1979) were used: powerful industrial vacuums (two units, each having 2 HP, combined with a “Y” connector, and using a 6 in. wide solid aluminum head) were used to clean many separate subsample strips across the roads which were then combined for physical and chemical analyses.

In Toronto, the street dirt particulate loadings were quite high before the initial intensive street cleaning period and were reduced to their lowest observed levels immediately after the last street cleaning. After street cleaning, the loadings on the industrial street increased much faster than for the residential street. Right after intensive cleaning, the street dirt particle sizes were also similar for the two land uses. However, the loadings of larger particles on the industrial street increased at a much faster rate than on the residential street, indicating more erosion or tracking materials being deposited onto the industrial street. The residential street dirt measurements did not indicate that any material was lost to the atmosphere as fugitive dust, likely due to the low street dirt accumulation rate and the short

Figure 2.1 Deposition and accumulation of street dirt (Pitt 1979).

Table 2.4 Street Dirt Loadings and Deposition Rates

periods of time between rains. The street dirt loadings never had the opportunity to reach the high loading values needed before they could be blown from the streets by winds or by traffic-induced turbulence. The industrial street, in contrast, had a much greater street dirt accumulation rate and was able to reach the critical loading values needed for fugitive losses in the relatively short periods between the rains.

Washoff of Street Dirt

The Yalin equation relates the sediment carrying capacity to runoff flow rate (Yalin 1963). Yalin stated that sediment motion begins when the lift force of flow exceeds a critical lift force. Once a particle is lifted, the drag force of the flow moves it downstream until the weight of the particle forces it back down. The Yalin equation is used to predict particle transport, for specific particle sizes, on a weight per unit flow width basis. It is used for fully turbulent channel flow conditions, typical of shallow overland flow in urban areas. The receding limb (tail) of a hydrograph may have laminar flow conditions, and the suspended sediment carried in the previously turbulent flows would settle out. The predicted constant Yalin sediment load would therefore only occur during periods of rain, and, the sediment load would decrease, due to sedimentation, after the rain stops. The critical particle bedload tractive force, the tractive force at which the particle begins to move, can be obtained from the Shield’s diagram. However, Shen (1981) warned that the Shield’s diagram alone cannot be used to predict “self-cleaning” velocities, as it gives only a lower limit below which deposition will occur. It defines the boundary between bed movement and stationary bed conditions. The Shield’s diagram does not consider the particulate supply rate in relationship to the particulate transport rate. Reduced particulate transport occurs if the sediment supply rate is less than the transport rate. The Yalin equation by itself is therefore not sensitive to particulate supply; it only predicts the carrying capacity of flowing waters.

Besides the particulate supply rate, the Yalin equation is also very sensitive to local flow parameters (specifically gutter flow depth). Therefore, a hydraulic model that can accurately predict sheetflow across impervious surfaces and gutter flow is needed. Sutherland and McCuen (1978) statistically analyzed a modified form of the Yalin equation, in conjunction with a hydraulic model for different gutter flow conditions. Except for the largest particle sizes, the effect of rain intensity on particle washoff was found to be negligible.

The Yalin equation is based on classical sediment transport equations, and requires some assumptions concerning the micro-scale aspects of gutter flows and street dirt distributions. The Yalin equation, as typically used in urban stormwater evaluations, assumes that all particles lie within the gutter, and no significant washoff occurs by sheetflows traveling across the street towards the gutter. The early measurements of across-the-street dirt distributions made by Sartor and Boyd (1972) indicated that about 90 percent of the street dirt was within about 30 cm of the curb face (typically within the gutter area). These measurements, however, were made in areas of no parking (near fire hydrants because of the need for water for the sampling procedures that were used), and the traffic turbulence was capable of blowing most of the street dirt against the curb barrier (or over the curb onto adjacent sidewalks or landscaped areas) (Shaheen 1975). In later tests, Pitt (1979) and Pitt and Sutherland (1982) examined street dirt distributions across-the-street in many additional situations. They found distributions similar to Sartor and Boyd’s observations only on smooth streets, with moderate to heavy traffic, and with no on-street parking. In many cases, most of the street dirt was actually in the driving lanes, trapped by the texture of rough streets. If extensive on-street parking was common, much of the street dirt was found on the outside edge of the parking lanes, where much of the resuspended (in air) street dirt blew against the parked cars and settled to the pavement.

Another process that may result in washoff less than predicted by Yalin is bed armoring (Sutherland, *et al*. 1982). As the smaller particulates are removed, the surface is covered by predominantly larger particulates which are not effectively washed-off by rain. Eventually, these larger particulates hinder the washoff of the trapped, under-lying, smaller particulates. Debris on the street, especially leaves, can also effectively armor the particulates, reducing the washoff of particulates to very low levels (Singer and Blackard 1978).

Observations of particulate washoff during controlled tests using actual streets and natural street dirt and debris are affected by street dirt distributions and armoring. The earliest controlled street dirt washoff experiments were conducted by Sartor and Boyd (1972) during the summer of 1970 in Bakersfield, CA. Their data was used in many stormwater models (including SWMM, Huber and Heaney 1981; STORM, COE 1975; and HSPF, Donigian and Crawford 1976) to estimate the percentage of the available particulates on the streets that would wash off during rains of different magnitudes. Sartor and Boyd used a rain simulator having many nozzles and a drop height of 1-1/2 to 2 meters in street test areas of about 5 by 10 meters. Tests were conducted on concrete, new asphalt, and old asphalt, using simulated rain intensities of about 5 and 20 mm/hr. They collected and analyzed runoff samples every 15 minutes for about two hours for each test. Sartor and Boyd fitted their data to an exponential curve, assuming that the rate of particle removal of a given size is proportional to the street dirt loading and the constant rain intensity:

$$dN/dt = krN$$

where: dN/dt = the change in street dirt loading per unit time
k = proportionality constant
r = rain intensity (in/hr)
N = street dirt loading (lb/curb-mile)

This equation, upon integration, becomes:

$$N = N_o e^{-krt}$$

where: N = residual street dirt load (after the rain)
N_o = initial street dirt load
t = rain duration

Street dirt washoff is therefore equal to N_o minus N. The variable combination rt, or rain intensity (in/h) times rain duration (h), is equal to total rain depth (R), in inches. This equation then further reduces to:

$$N = N_o e^{-kR}$$

Therefore, this equation is only sensitive to the total depth of the rain that has fallen since the beginning of the rain, and not rain intensity. Because of decreasing particulate supplies, the exponential washoff curve also predicts decreasing concentrations of particulates with time since the start of a constant rain (Alley 1980 and 1981).

The proportionality constant, k, was found by Sartor and Boyd to be slightly dependent on street texture and condition, but was independent of rain intensity and particle size. The value of this constant is usually taken as 0.18/mm, assuming that 90 percent of the particulates will be washed from a paved surface in 1 h during a 13 mm/h rain. However, Alley (1981) fitted this model to watershed outfall runoff data and found that the constant varied for different storms and pollutants for a single study area. Novotny (as part of Bannerman, *et al*. 1983) also examined "before" and "after" rain event street particulate loading data from the Milwaukee Nationwide Urban Runoff Program (NURP) project and found almost a three-fold difference between the constant value of k for fine (<45 µm) and medium sized particles (100 to 250 µm). The calculated values were 0.026/mm for the fine particles and 0.01/mm for the medium sized particles, both much less than the "accepted" value of 0.18/mm. Jewell, *et al*. (1980) also found large variations in outfall "fitted" constant values for different rains compared to the typical default value. Either the assumption of the high removal of particulates during the 13 mm/hr storm was incorrect or/and the equation cannot be fitted to outfall data (most likely, as this would require that all the particulates are originating from homogeneous paved surfaces during all storm conditions).

This washoff equation has been used in many stormwater models, along with an expression for an availability factor. An availability factor is needed, as N_o is only the portion of the total street load available for washoff. This availability factor (the fraction of the total street dirt loading available for washoff) is generally used as 1.0 for all rain intensities greater than about 18 mm/hr and reduces to about 0.10 for rains of 1 mm/hr.

The Bellevue, WA, urban runoff project (Pitt 1985) included about 50 pairs of street dirt loading observations close to the beginnings and ends of rains. These “before” and “after” loading values were compared to determine significant differences in loadings that may have been caused by the rains. The observations were affected by rains falling directly on the streets, along with flows and particulates originating from non-street areas. The net loading differences were therefore affected by street dirt washoff (by direct rains on the street surfaces and by gutter flows augmented by “upstream” area runoff) and by erosion products that originated from non-street areas that may have settled out in the gutters. When all the data were considered together, the net loading difference was about 10 to 13 g/curb-m removed. This amounted to a street dirt load reduction of about 15 percent, which was much less than predicted using either of the two previously described washoff models. Very large reductions in street dirt loadings during rains were observed in Bellevue for the smallest particles, but the largest particles actually increased in loadings (due to deposited erosion materials originating from off-street areas). The particles were not source limited, but armor shielding may have been important. Most of the particulates in the runoff were in the fine particle sizes (<63 µm). Very few particles greater than 1000 µm were found in the washoff water. Care must be taken to not confuse street dirt particle size distributions with stormwater runoff particle size distributions. The stormwater particle size distributions are much more biased towards the smaller sizes, as described later.

Suspended solids washoff predictions for Bellevue conditions were made using the Sutherland and McCuen modification of the Yalin equation, and the Sartor and Boyd equation. Three particle size groups (<63, 250-500, and 2000-6350 µm), and three rains, having depths of 5, 10, and 20 mm and 3-h durations, were considered. The gutter lengths for the Bellevue test areas averaged about 80 m, with gutter slopes of about 4.5 percent. Typical total initial street dirt loadings for the three particle sizes were: 9 g/curb-m for <63 µm, 18 g/curb-m for 250-500 µm, and 9 g/curb-m for 2000-6350 µm. The actual Bellevue net loading removals during the storms were about 45 percent for the smallest particle size group, 17 percent for the middle particle size group, and -6 percent (6 percent loading increase) for the largest particle size group. The predicted removals were 90 to 100 percent using the Sutherland and McCuen method, 61 to 98 percent using the Sartor and Boyd equation, and 8 to 37 percent using the availability factor with the Sartor and Boyd equation. The ranges given reflect the different rain volumes and intensities only. There were no large predicted differences in removal percentages as a function of particle size. The availability factor with the Sartor and Boyd equation resulted in the closest predicted values, but the great differences in washoff as a function of particle size was not predicted.

The Bellevue street dirt washoff observations included effects of additional runoff water and particulates originating from non-street areas. The additional flows should have produced more gutter particulate washoff, but upland erosion materials may also have settled in the gutters (as noted for the large particles). However, across-the-street particulate loading measurements indicated that much of the street dirt was in the street lanes, not in the gutters, before and after rains. This particulate distribution reduces the importance of these extra flows and particulates from upland areas. The increased loadings of the largest particles after rains were obviously caused by upland erosion, but the magnitude of the settled amounts was quite small compared to the total street dirt loadings.

In order to clarify street dirt washoff, Pitt (1987) conducted numerous controlled washoff tests on city streets in Toronto. These tests were arranged as an overlapping series of 2^3 factorial tests, and were analyzed using standard factorial test procedures described by Box, *et al*. (1978). The experimental factors examined included: rain intensity, street texture, and street dirt loading. The differences between available and total street dirt loads were also related to the experimental factors. The samples were analyzed for total solids (total residue), dissolved solids (filterable residue: <0.45 µm), and SS (particulate residue: >0.45 µm). Runoff samples were also filtered through 0.45 µm filters and the filters were microscopically analyzed (using low power polarized light microscopes to differentiate between inorganic and organic debris) to determine particulate size distributions from about 1 to 500 µm. The runoff flow quantities were also carefully monitored to determine the magnitude of initial and total rain water losses on impervious surfaces.

The total solids concentrations varied from about 25 to 3000 mg/L, with an obvious decrease in concentrations with increasing rain depths during these constant rain intensity tests. No concentrations greater than 500 mg/L occurred after about 2 mm of rain, while all concentrations after about 10 mm of rain were less than 100 mg/L. Total solids concentrations were independent of the test conditions. A wide range in runoff concentrations was also observed for

SS, with concentrations ranging from about 1 to 3000 mg/L. Again, a decreasing trend of concentrations was seen with increasing rain depths, but the data scatter was larger because of the experimental factors. The dissolved solids (<0.45 µm) concentrations ranged from about 20 to 900 mg/L, comprising a surprisingly large percentage of the total solids loadings. For small rain depths, dissolved solids comprised up to 90 percent of the total solids. After 10 mm of rain depth, the filterable residue concentrations were all less than about 50 mg/L.

Manual particle size analyses were also conducted on the suspended solids washoff samples, using a microscope with a calibrated recticle. Figures 2.2 and 2.3 are examples of particle size distributions for two tests. These plots show the percentage of the particles that were less than various sizes, by measured particle volume (assumed to be similar to weight). The plots also indicate median particle sizes of about 10 to 50 µm, depending on when the sample was obtained during the washoff tests. All of the distributions showed surprisingly similar trends of particle sizes with elapsed rain depth. The median size for the sample obtained at about 1 mm of rain was much greater than for the samples taken after more rain. The median particle sizes of material remaining on the streets after the washoff tests were also much larger than for most of the runoff samples, but were quite close to the initial samples' median particle sizes. The washoff water at the very beginning of the test rains therefore contained many more larger particles than during later portions of the rains. Also, a substantial amount of larger particles remained on the streets after the test rains. Most street runoff waters during test rains in the 5 to 15 mm depth category had median suspended solids particle sizes of about 10 to 50 µm. However, dissolved solids (less than 0.45 µm) made up most of the total solids washoff for elapsed rain depths greater than about 5 mm.

These particle size distributions indicate that the smaller particles were much more important than indicated during previous tests. As an example, the Sartor and Boyd (1972) washoff tests (rain intensities of 50 mm/h for 2 h durations) found median particle sizes of about 150 µm which were typically three to five times larger than were found during these tests. They also did not find any significant particle size distribution differences for different rain depths (or rain duration), in contrast to the Toronto tests which were conducted at more likely rain intensities (3 to 12 mm/h for 2 h).

The particulate washoff values obtained during these Toronto tests were expressed in units of grams per square meter and grams per curb-meter, concentrations (mg/L), and the percent of the total initial loading washed off during the test. Plots of accumulative washoff are shown on Figures 2.4 through 2.11. These plots show the asymptotic washoff values observed in the tests, along with the measured total street dirt loadings. The maximum asymptotic values are the "available" street dirt loadings (N_o). The measured total loadings are seen to be several times larger than these "available" loading values. As an example, the asymptotic available total solids value for the HDS (high intensity rain, dirty street, smooth street) test (Figure 2.10) was about 3g/m^2 while the total load on the street for this test was about 14g/m^2, or about five times the available load. The differences between available and total loadings for the other tests were even greater, with the total loads typically about ten times greater than the available loads. The total loading and available loading values for dissolved solids were quite close, indicating almost complete washoff of the very small particles. However, the differences between the two loading values for SS were much greater. Shielding, therefore, may not have been very important during these tests, as almost all of the smallest particles were removed, even in the presence of heavy loadings of large particles.

The actual data are shown on these figures, along with the fitted Sartor and Boyd exponential washoff equations. In many cases, the fitted washoff equations greatly over-predicted suspended solids washoff during the very small rains (usually less than 1 to 3 mm in depth). In all cases, the fitted washoff equations described suspended solids washoff very well for rains greater than about 10 mm in depth.

Table 2.5 presents the equation parameters for each of the eight washoff tests for suspended solids. Pitt (1987) concluded that particulate washoff should be divided into two main categories, one for high intensity rains with dirty streets, possibly divided into categories by street texture, and the other for all other conditions. Factorial tests also found that the availability factor (the ratio of the available loading, N_o, to the total loading) varied depending on the rain intensity and the street roughness, as indicated below:

- Low rain intensity and rough streets: 0.045
- High rain intensity and rough streets, or low rain intensity and smooth streets: 0.075
- High rain intensity and smooth streets: 0.20

Obviously, washoff was more efficient for the higher rain energy and smoother pavement tests. The worst case was for a low rain intensity and rough street, where only about 4.5% of the street dirt would be washed from the pavement. In contrast, the high rain intensities on the smooth streets were more than four times more efficient in removing the street dirt.

Figure 2.2 Particle size distribution of HDS test (high rain intensity, dirty, and smooth street) (Pitt 1987).

Figure 2.3 Particle size distribution for LCR test (light rain intensity, clean, and rough street) (Pitt 1987).

Figure 2.4 Washoff plots for HCR test (high rain intensity, clean, and rough street) (Pitt 1987).

Figure 2.5 Washoff plots for LCR test (light rain intensity, clean, and rough street) (Pitt 1987).

Figure 2.6 Washoff plots for HDR test (high rain intensity, dirty, and rough street) (Pitt 1987).

Figure 2.7 Washoff plots for LDR test (light rain intensity, dirty, and rough street) (Pitt 1987).

Figure 2.8 Washoff plots for HCS test (high rain intensity, clean, and smooth street) (Pitt 1987).

Figure 2.9 Washoff plots for LCS test (light rain intensity, clean, and smooth street) (Pitt 1987).

Figure 2.10 Washoff plots for HDS test (high rain intensity, dirty, and smooth street) (Pitt 1987).

Figure 2.11 Washoff plots for LCS replicate test (light rain intensity, clean, and smooth street)

(Pitt 1987).

Table 2.5 Suspended Solids Washoff Coefficients (Pitt 1987)[1]

Test condition code	Rain intensity category	Street dirt loading category	Street texture category	Calculated k	Standard error for k	Ratio of available load to total initial load
HCR	high	clean	rough	0.832	0.064	0.11
LCR	low	clean	rough	0.344	0.038	0.061
HDR	high	dirty	rough	0.077	0.008	0.032
LDR	low	dirty	rough	0.619	0.052	0.028
HCS	high	clean	smooth	1.007	0.321	0.26
LCS	low	clean	smooth	0.302	0.024	0.047
HDS	high	dirty	smooth	0.167	0.015	0.13
L(D)CS	low	(actually clean)	smooth	0.335	0.031	0.11

[1] Note:

$$N = N_o e^{-kR}$$

where: N = residual street dirt load, after the rain (lb/curb-mile)
N_o = initial street dirt load
R = rain depth (inches)
k = proportionality constant (1/hr)

Observed Particle Size Distributions in Stormwater

The particle size distributions of stormwater greatly affect the ability of most controls in reducing pollutant discharges. This research has included particle size analyses of 121 stormwater samples from three states that were not affected by stormwater controls (southern New Jersey as part of the inlet tests; Birmingham, Alabama as part of the MCTT pilot-scale tests; and in Milwaukee and Minocqua, Wisconsin, as part of the MCTT full-scale tests). These samples represented stormwater entering the stormwater controls being tested. Particle sizes were measured using a Coulter Multi-Sizer IIe and verified with microscopic, sieve, and settling column tests. Figures 2.12 through 2.14 are grouped box and whisker plots showing the particle sizes (in µm) corresponding to the 10th, 50th (median) and 90th percentiles of the cumulative distributions. If 90 percent control of SS was desired, then the particles larger than the 90th percentile would have to be removed, for example. The median particle sizes ranged from 0.6 to 38 µm and averaged 14 µm. The 90th percentile sizes ranged from 0.5 to 11 µm and averaged 3 µm. These particle sizes are all substantially smaller than have been typically assumed for stormwater. In all cases, the New Jersey samples had the smallest particle sizes, followed by Wisconsin, and then Birmingham, AL, which had the largest particles. The New Jersey samples were obtained from gutter flows in a residential semi-xeroscaped neighborhood, the Wisconsin samples were obtained from several source areas, including parking areas and gutter flows mostly from residential, but from some commercial areas, and the Birmingham samples were collected from a long-term parking area.

Atmospheric Sources of Urban Runoff Pollutants

Atmospheric processes affecting urban runoff pollutants include dry dustfall and precipitation quality. These have been monitored in many urban and rural areas. In many instances, however, the samples were combined as a bulk precipitation sample before processing. Automatic precipitation sampling equipment can distinguish between dry periods of fallout and precipitation. These devices cover and uncover appropriate collection jars exposed to the atmosphere. Much of this information has been collected as part of the Nationwide Urban Runoff Program (NURP) and the Atmospheric Deposition Program, both sponsored by the U.S. Environmental Protection Agency (EPA 1983a).

One must be very careful in interpreting this information, however, because of the ability of many polluted dust and dirt particles to be resuspended and then redeposited within the urban area. In many cases, the measured atmospheric deposition measurements include material that was previously residing and measured in other urban runoff pollutant source areas. Also, only small amounts of the atmospheric deposition material would directly contribute to runoff. Rain is subjected to infiltration and the dry fall particulates are likely mostly incorporated with surface soils and

Figure 2.12 Tenth percentile particle sizes for stormwater inlet flows.

Figure 2.13 Fiftieth percentile particle sizes for stormwater inlet flows.

Figure 2.14 Ninetieth percentile particle sizes for stormwater inlet flows.

only small fractions are then eroded during rains. Therefore, mass balances and determinations of urban runoff deposition and accumulation from different source areas can be highly misleading, unless transfer of material between source areas and the effective yield of this material to the receiving water is considered. Depending on the land use, relatively little of the dustfall in urban areas likely contributes to stormwater discharges.

Dustfall and precipitation affect all of the major urban runoff source areas in an urban area. Dustfall, however, is typically not a major pollutant source but fugitive dust is mostly a mechanism for pollutant transport, as previously mentioned. Most of the dustfall monitored in an urban area is resuspended particulate matter from street surfaces or wind erosion products from vacant areas (Pitt 1979). Point source pollutant emissions can also significantly contribute to dustfall pollution, especially in industrial areas. Transported dust from regional agricultural activities can also significantly affect urban stormwater.

Wind transported materials are commonly called “dustfall.” Dustfall includes sedimentation, coagulation with subsequent sedimentation and impaction. Dustfall is normally measured by collecting dry samples, excluding rainfall and snowfall. If rainout and washout are included, one has a measure of total atmospheric fallout. This total atmospheric fallout is sometimes called “bulk precipitation.” Rainout removes contaminants from the atmosphere by condensation processes in clouds, while washout is the removal of contaminants by the falling rain. Therefore, precipitation can include natural contamination associated with condensation nuclei in addition to collecting atmospheric pollutants as the rain or snow falls. In some areas, the contaminant contribution by dry deposition is small, compared to the contribution by precipitation (Malmquist 1978). However, in heavily urbanized areas, dustfall can contribute more of an annual load than the wet precipitation, especially when dustfall includes resuspended materials.

Table 2.6 summarizes rain quality reported by several researchers. As expected, the non-urban area rain quality can be substantially better than urban rain quality. Many of the important heavy metals, however, have not been detected in rain in many areas of the country. The most important heavy metals found in rain have been lead and zinc, both being present in rain in concentrations from about 20 up to several hundred μg/L. It is expected that more recent lead rainfall concentrations would be substantially less, reflecting the decreased use of leaded gasoline since these measurements were taken. Iron is also present in relatively high concentrations in rain (about 30 to 40 μg/L).

Table 2.6. Summary of Reported Rain Quality

	Rural-Northwest (Quilayute, WA)[1]	Rural-Northeast (Lake George, NY)[1]	Urban-Northwest (Lodi, NJ)[2]	Urban-Midwest (Cincinnati, OH)[3]	Other Urban[3]	Continental Avg. (32 locations)[1]
Suspended solids, mg/L				13		
Volatile suspended solids, mg/L				3.8		
Inorganic nitrogen, mg/L as N				0.69		
Ammonia, mg/L as N					0.7	
Nitrates, mg/L as N					0.3	
Total phosphates, mg/L as P					<0.1	
Ortho phosphate, mg/L as P				0.24		
Scandium, μg/L	<0.002	nd				nd
Titanium, μg/L	nd	nd				nd
Vanadium, μg/L	nd	nd				nd
Chromium, μg/L	<2	nd	1			nd
Manganese, μg/L	2.6	3.4				12
Iron, μg/L	32	35				
Cobalt, μg/L	0.04	nd				nd
Nickel, μg/L	nd	nd	3			43
Copper, μg/L	3.1	8.2	6			21
Zinc, μg/L	20	30	44			107
Lead, μg/L			45			

[1] Rubin 1976
[2] Wilbur and Hunter 1980
[3] Manning, *et al*. 1976

The concentrations of various urban runoff pollutants associated with dry dustfall are summarized in Table 2.7. Urban, rural and oceanic dry dustfall samples contained more than 5,000 mg iron/kg total solids. Zinc and lead were present in high concentrations. These constituents can have concentrations of up to several thousand mg of pollutant per kg of dry dustfall. Spring, *et al*. (1978) monitored dry dustfall near a major freeway in Los Angeles. Based on a series of samples collected over several months, they found that lead concentrations on and near the freeway can be about 3,000 mg/kg, but as low as about 500 mg/kg 150 m (500 feet) away. In contrast, the chromium concentrations of the dustfall did not vary substantially between the two locations and approached oceanic dustfall chromium concentrations.

Table 2.7. Atmosphere Dustfall Quality

Constituent, (mg constituent/kg total solids)	Urban[1]	Rural/ suburban[1]	Oceanic[1]	Near freeway (LA)[2]	500' from freeway (LA)[2]
pH				4.3	4.7
Phosphate-Phosphorous				1200	1600
Nitrate-Nitrogen, µg/L				5800	9000
Scandium, µg/L	5	3	4		
Titanium, µg/L	380	810	2700		
Vanadium, µg/L	480	140	18		
Chromium, µg/L	190	270	38	34	45
Manganese, µg/L	6700	1400	1800		
Iron, µg/L	24000	5400	21000		
Cobalt, µg/L	48	27	8		
Nickel, µg/L	950	1400			
Copper, µg/L	1900	2700	4500		
Zinc, µg/L	6700	1400	230		
Lead, µg/L				2800	550

[1] Summarized by Rubin 1976
[2] Spring 1978

Much of the monitored atmospheric dustfall and precipitation would not reach the urban runoff receiving waters. The percentage of dry atmospheric deposition retained in a rural watershed was extensively monitored and modeled in Oakridge, TN (Barkdoll, *et al*. 1977). They found that about 98 percent of the lead in dry atmospheric deposits was retained in the watershed, along with about 95 percent of the cadmium, 85 percent of the copper, 60 percent of the chromium and magnesium and 75 percent of the zinc and mercury. Therefore, if the dry deposition rates were added directly to the yields from other urban runoff pollutant sources, the resultant urban runoff loads would be very much overestimated.

Tables 2.8 and 2.9 report bulk precipitation (dry dustfall plus rainfall) quality and deposition rates as reported by several researchers. For the Knoxville, KY, area (Betson 1978), chemical oxygen demand (COD) was found to be the largest component in the bulk precipitation monitored, followed by filterable residue and nonfilterable residue. Table 2.9 also presents the total watershed bulk precipitation, as the percentage of the total stream flow output for the three Knoxville watersheds studies. This shows that almost all of the pollutants presented in the urban runoff streamflow outputs could easily be accounted for by bulk precipitation deposition alone. Betson concluded that bulk precipitation is an important component for some of the constituents in urban runoff, but the transport and resuspension of particulates from other areas in the watershed are overriding factors.

Rubin (1976) stated that resuspended urban particulates are returned to the earth’s surface and waters in four main ways: gravitational settling, impaction, precipitation and washout. Gravitational settling, as dry deposition, returns most of the particles. This not only involves the settling of relatively large fly ash and soil particles, but also the settling of smaller particles that collide and coagulate. Rubin stated that particles that are less than 0.1 μm in diameter move randomly in the air and collide often with other particles. These small particles can grow rapidly by this coagulation process. These small particles would soon be totally depleted in the air if they were not constantly replenished. Particles in the 0.1 to 1.0 μm range are also removed primarily by coagulation. These larger particles grow more slowly than the smaller particles because they move less rapidly in the air, are somewhat less numerous and, therefore, collide less often with other particles. Particles with diameters larger than 1 μm have appreciable

Table 2.8. Bulk Precipitation Quality

Constituent (all units mg/L except pH)	Urban (average of Knoxville St. Louis & Germany[1]	Rural (Tennessee)[1]	Urban (Guteburg, Sweden)[2]
Calcium	3.4	0.4	
Magnesium	0.6	0.1	
Sodium	1.2	0.3	
Chlorine	2.5	0.2	
Sulfate	8.0	8.4	
pH	5.0	4.9	
Organic Nitrogen	2.5	1.2	
Ammonia Nitrogen	0.4	0.4	2
Nitrite plus Nitrate-N	0.5	0.4	1
Total phosphate	1.1	0.8	0.03
Potassium	1.8	0.6	
Total iron	0.8	0.7	
Manganese	0.03	0.05	
Lead	0.03	0.01	0.05
Mercury	0.01	0.0002	
Nonfilterable residue	16		
Chemical Oxygen Demand	65		10
Zinc			0.08
Copper			0.02

[1] Betson 1978

[2] Malmquist 1978

Table 2.9. Urban Bulk Precipitation Deposition Rates (Source: Betson 1978)[a]

Rank	Constituent	Average Bulk Deposition Rate (kg/ha/yr)	Average Bulk Prec. as a % of Total Streamflow Output
1	Chemical oxygen demand	530	490
2	Filterable residue	310	60
3	Nonfilterable residue	170	120
4	Alkalinity	150	120
5	Sulfate	96	470
6	Chloride	47	360
7	Calcium	38	170
8	Potassium	21	310
9	Organic nitrogen	17	490
10	Sodium	15	270

11	Silica	11	130
12	Magnesium	9	180
13	Total Phosphate	9	130
14	Nitrite and Nitrate-N	5.7	360
15	Soluble phosphate	5.3	170
16	Ammonia Nitrogen	3.2	1,100
17	Total Iron	1.9	47
18	Fluoride	1.8	300
19	Lead	1.1	650
20	Manganese	0.54	270
21	Arsenic	0.07	720
22	Mercury	0.008	250

[a] Average for 3 Knoxville, KY, watersheds.

settling velocities. Those particles about 10 µm in diameter can settle rapidly, although they can be kept airborne for extended periods of time and for long distances by atmospheric turbulence.

The second important particulate removal process from the atmosphere is impaction. Impaction of particles near the earth's surface can occur on vegetation, rocks and building surfaces. The third form of particulate removal from the atmosphere is precipitation, in the form of rain and snow. This is caused by the rainout process where the particulates are removed in the cloud-forming process. The fourth important removal process is washout of the particulates below the clouds during the precipitation event. Therefore, it is easy to see that re-entrained particles (especially from street surfaces, other paved surfaces, rooftops and from soil erosion) in urban areas can be readily redeposited through these various processes, either close to the points of origin or at some distance away.

Pitt (1979) monitored airborne concentrations of particulates near typical urban roads. He found that on a number basis, the downwind roadside particulate concentrations were about 10 percent greater than upwind conditions. About 80 percent of the concentration increases, by number, were associated with particles in the 0.5 to 1.0 µm size range. However, about 90 percent of the particle concentration increases by weight were associated with particles greater than 10 µm. He found that the rate of particulate resuspension from street surfaces increases when the streets are dirty (cleaned infrequently) and varied widely for different street and traffic conditions. The resuspension rates were calculated based upon observed long-term accumulation conditions on street surfaces for many different study area conditions, and varied from about 0.30 to 3.6 kg per curb-km (1 to 12 lb per curb-mile) of street per day.

Murphy (1975) described a Chicago study where airborne particulate material within the city was microscopically examined, along with street surface particulates. The particulates from both of these areas were found to be similar (mostly limestone and quartz) indicating that the airborne particulates were most likely resuspended street surface particulates, or were from the same source. PEDCo (1977) found that the re-entrained portion of the traffic-related particulate emissions (by weight) is an order of magnitude greater than the direct emissions accounted for by vehicle exhaust and tire wear. They also found that particulate resuspensions from a street are directly proportional to the traffic volume and that the suspended particulate concentrations near the streets are associated with relatively large particle sizes. The medium particle size found, by weight, was about 15 µm, with about 22 percent of the particulates occurring at sizes greater than 30 µm. These relatively large particle sizes resulted in substantial particulate fallout near the road. They found that about 15 percent of the resuspended particulates fall out at 10 m, 25 percent at 20 m, and 35 percent at 30 m from the street (by weight). In a similar study Cowherd, *et al*. (1977) reported a wind erosion threshold value of about 5.8 m/s (13 mph). At this wind speed, or greater, significant dust and dirt losses from the road surface could result, even in the absence of traffic-induced turbulence. Rolfe and Reinbold (1977) also found that most of the particulate lead from automobile emissions settled out within 100 m of roads. However, the automobile lead does widely disperse over a large area. They found, through multi-elemental analyses, that the settled outdoor dust collected at or near the curb was contaminated by automobile activity and originated from the streets.

Source Area Sheetflow and Particulate Quality

This chapter section summarizes the source area sheetflow and particulate quality data obtained from several studies conducted in California, Washington, Nevada, Wisconsin, Illinois, Ontario, Colorado, New Hampshire, and New York since 1979. Most of the data obtained was for street dirt chemical quality, but a relatively large amount of parking and roof runoff quality data has also been obtained. Only a few of these studies evaluated a broad range of source areas or land uses.

Source Area Particulate Quality

Particulate potency factors (usually expressed as mg pollutant/kg dry particulate residue) for many samples are summarized on Tables 2.10 and 2.11. These data can help recognize critical source areas, but care must be taken if they are used for predicting runoff quality because of likely differential effects due to washoff and erosion from the different source areas. These data show the variations in chemical quality between particles from different land uses and source areas. Typically, the potency factors increase as the use of an area becomes more intensive, but the variations are slight for different locations throughout the country. Increasing concentrations of heavy metals with decreasing particle sizes was also evident, for those studies that included particle size information. Only the quality of the smallest particle sizes are shown on these tables because they best represent the particles that are removed during rains.

Warm Weather Sheetflow Quality

Sheetflow data, collected during actual rain, are probably more representative of runoff conditions that the previously presented dry particulate quality data because they are not further modified by washoff mechanisms. These data, in conjunction with source area flow quantity information, can be used to predict outfall conditions and the magnitude of the relative sources of critical pollutants. Tables 2.12 through 2.15 summarize warm weather sheetflow observations, separated by source area type and land use, from many locations. The major source area categories are listed below:

- roofs
- paved parking areas
- paved storage areas
- unpaved parking and storage areas
- paved driveways
- unpaved driveways
- dirt walks
- paved sidewalks
- streets
- landscaped areas
- undeveloped areas
- freeway paved lanes and shoulders

Toronto warm weather sheetflow water quality data were plotted against the rain volume that had occurred before the samples were collected to identify any possible trends of concentrations with rain volume (Pitt and McLean 1986). The street runoff data obtained during the special washoff tests reported earlier were also compared with the street sheetflow data obtained during the actual rain events (Pitt 1987). These data observations showed definite trends of solids concentrations verses rain volume for most of the source area categories. Sheetflows from all pervious areas combined had the highest total solids concentrations from any source category, for all rain events. Other paved areas (besides streets) had total solids concentrations similar to runoff from smooth industrial streets. The concentrations of total solids in roof runoff were almost constant for all rain events, being slightly lower for small rains than for large rains. No other pollutant, besides SS, had observed trends of concentrations with rain depths for the samples collected in Toronto. Lead and zinc concentrations were highest in sheetflows from paved parking areas and streets, with some high zinc concentrations also found in roof drainage samples. High bacteria populations were found in sidewalk, road, and some bare ground sheetflow samples (collected from locations where dogs would most likely be "walked").

Some of the Toronto sheetflow contributions were not sufficient to explain the concentrations of some constituents observed in runoff at the outfall. High concentrations of dissolved chromium, dissolved copper, and dissolved zinc in a Toronto industrial outfall during both wet and dry weather could not be explained by wet weather sheetflow observations (Pitt and McLean 1986). As an example, very few detectable chromium observations were obtained in any of the more than 100 surface sheetflow samples analyzed. Similarly, most of the fecal coliform populations observed in sheetflows were significantly lower than those observed at the outfall, especially during snowmelt. It is expected that some industrial wastes, possibly originating from metal plating operations, were the cause of these high concentrations of dissolved metals at the outfall and that some sanitary sewage was entering the storm drainage system.

Table 2.15 summarizes the very little filterable pollutant concentration data available, before this EPA project, for different source areas. Most of the available data is for residential roofs and commercial parking lots.

Table 2.10 Summary of Observed Street Dirt Chemical Quality (means) (mg constituent/kg solids)

	Residential	Commercial	Industrial
P	620 (4)		670 (4)
	540 (6)	400 (6)	
	1100 (5)	1500 (5)	
	710 (1)	910 (1)	
	810 (3)		
TKN	1030 (4)		560 (4)
	3000 (6)	1100 (6)	
	290 (5)	340 (5)	
	2630 (3)	4300 (2)	
	3000 (2)		
COD	100,000 (4)		65,000 (4)
	150,000 (6)	110,000 (6)	
	180,000 (5)	250,000 (5)	
	280,000 (1)	340,000 (1)	
	180,000 (3)	210,000 (2)	
	170,000 (2)		
Cu	162 (4)		360 (4)
	110 (6)	130 (6)	
	420 (2)	220 (2)	
Pb	1010 (4)		900 (4)
	1800 (6)	3500 (6)	
	530 (5)	2600 (5)	
	1200 (1)	2400 (1)	
	1650 (3)	7500 (2)	
	3500 (2)		
Zn	460 (4)		500 (4)
	260 (5)	750 (5)	
	325 (3)	1200 (2)	

	680 (2)		
Cd	<3 (5)	5 (5)	
	4 (2)	5 (2)	
Cr	42 (4)		70 (4)
	31 (5)	65 (5)	
	170 (2)	180 (2)	

References; location; particle size described:

(1) Bannerman, *et al*. 1983 (Milwaukee, WI) <31µm
(2) Pitt 1979 (San Jose, CA) <45 µm
(3) Pitt 1985 (Bellevue, WA) <63 µm
(4) Pitt and McLean 1986 (Toronto, Ontario) <125 µm
(5) Pitt and Sutherland 1982 (Reno/Sparks, NV) <63 µm
(6) Terstrip, *et al*. 1982 (Champaign/Urbana, IL) >63 µm

Table 2.11 Summary of Observed Particulate Quality for Other Source Areas (means for <125 μm particles) (mg constituent/kg solids)

	P	TKN	COD	Cu	Pb	Zn	Cr
Residential/Commercial Land Uses							
Roofs	1500	5700	240,000	130	980	1900	77
Paved parking	600	790	78,000	145	630	420	47
Unpaved driveways	400	850	50,000	45	160	170	20
Paved driveways	550	2750	250,000	170	900	800	70
Dirt footpath	360	760	25,000	15	38	50	25
Paved sidewalk	1100	3620	146,000	44	1200	430	32
Garden soil	1300	1950	70,000	30	50	120	35
Road shoulder	870	720	35,000	35	230	120	25
Industrial Land Uses							
Paved parking	770	1060	130,000	1110	650	930	98
Unpaved parking/storage	620	700	110,000	1120	2050	1120	62
Paved footpath	890	1900	120,000	280	460	1300	63
Bare ground	700	1700	70,000	91	135	270	38

Source: Pitt and McLean 1986 (Toronto, Ontario)

Table 2.12 Sheetflow Quality Summary for Other Source Areas (mean concentration and reference)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets
Total Solids (mg/L)									
Residential:	58 (5) 64 (1) 18 (4)	1790 (5)	73 (5)		510 (5)		1240 (5)	49 (5)	325 (5) 235 (4)
Commercial:	95 (1) 190 (4)	340 (2) 240 (1) 102 (7)							325 (4)
Industrial:	113 (5)	490 (5)	270 (5)	1250 (5)	506 (5)	5620 (5)		580 (5)	1800 (5)
Suspended Solids (mg/L)									
Residential:	22 (1) 13 (5)	1660 (5)	41 (5)		440 (5)		810 (5)	20 (5)	242 (5)
Commercial:		270 (2) 65 (1) 41 (7)							242 (5)
Industrial:	4 (5)	306 (5)	202 (5)	730 (5)	373 (5)	4670 (5)		434 (5)	1300 (5)
Dissolved Solids (mg/L)									
Residential:	42 (10 5 (5)	130 (5)	32 (5)		70 (5)		430 (5)	29 (5)	83 (5) 83 (4)
Commercial:		70 (2) 175 (1) 61 (7)							83 (5)
Industrial:	109 (5)	184 (5)	68 (5)	520 (5)	133 (5)	950 (5)		146 (5)	500 (5)

Table 2.12 Sheetflow Quality Summary for Other Source Areas (mean concentration and reference) (Continued)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets
BOD_5 (mg/L)									
Residential:	3 (4)	22 (4)							13 (4)
Commercial:	7 (4)	11 (1) 4 (8)							
COD (mg/L)									
Residential:	46 (5) 27 (1) 20 (4)	173 (5)	22 (5)		178 (5)			62 (5)	174 (5) 170 (4)
Commercial:	130 (4)	190 (2) 180 (4) 53 (1) 57 (8)							174 (5)
Industrial:	55 (5)	180 (5)	82 (5)	247 (5)	138 (5)	418 (5)		98 (5)	322 (5)
Total Phosphorus (mg/L)									
Residential:	0.03 (5) 0.05 (1) 0.1 (4)				0.36 (5)		0.20 (5)	0.80 (5)	0.62 (5) 0.31 (4)
Commercial:	0.03 (4) 0.07 (4)	0.16 (1) 0.15 (7) 0.73 (5) 0.9 (2) 0.5 (4)							0.62 (5)
Industrial:	<0.06 (5)	2.3 (5)	0.7 (5)	1.0 (5)	0.9 (5)	3.0 (5)		0.82 (5)	1.6 (5)

Table 2.12 Sheetflow Quality Summary for Other Source Areas (mean concentration and reference) (Continued)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets
<u>Total Phosphate (mg/L)</u>									
Residential:	<0.04 (5) 0.08 (4)				<0.2 (5)		0.66 (5)	0.64 (5)	0.07 (5) 0.12 (4)
Commercial:	0.02 (4)	0.03 (5) 0.3 (2) 0.5 (4) 0.04 (7) 0.22 (8)	<0.02 (5)						0.07 (5)
Industrial:	<0.02 (5)	0.6 (5)	0.06 (5)	0.13 (5)	<0.02 (5)	0.10 (5)		0.03 (5)	0.15 (5)
<u>TKN (mg/L)</u>									
Residential:	1.1 (5) 0.71 (4)				3.1 (5)		1.3 (5)	1.1 (5)	2.4 (5) 2.4 (4)
Commercial:	4.4 (4)	3.8 (5) 4.1 (2) 1.5 (4) 1.0 (1) 0.8 (8)							2.4 (5)
Industrial:	1.7 (5)	2.9 (5)	3.5 (5)	2.7 (5)	5.7 (5)	7.5 (5)		4.7 (5)	5.7 (5)
<u>Ammonia (mg/L)</u>									
Residential:	0.1 (5) 0.9 (1) 0.5 (4)	0.1 (5)	0.3 (5)		<0.1 (5)		0.5 (5)	0.3 (5)	<0.1 (5) 0.42 (4)
Commercial:	1.1 (4)	1.4 (2) 0.35 (4) 0.38 (1)							<0.1 (5)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets
Industrial:	0.4 (5)	0.3 (5)	0.3 (5)	<0.1 (5)	<0.1 (5)	<0.1 (5)		<0.1 (5)	<0.1 (5)

Table 2.12 Sheetflow Quality Summary for Other Source Areas (mean concentration and reference) (Continued)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets
<u>Phenols (mg/L)</u>									
Residential:	2.4 (5)	12.2 (5)	30.0 (5)		9.7 (5)		<0.4 (5)	8.6 (5)	6.2 (5)
Industrial:	1.2 (5)	9.4 (5)	2.6 (5)	8.7 (5)	7.0 (5)	7.4 (5)		8.7 (5)	24 (7)
<u>Aluminum (µg/L)</u>									
Residential:	0.4 (5)	3.2 (5)	0.38 (5)		5.3 (5)		<0.03 (5)	0.5 (5)	1.5 (5)
Industrial:	<0.2 (5)	3.5 (5)	3.1 (5)	9.2 (5)	3.4 (5)	41 (5)		1.2 (5)	14 (5)
<u>Cadmium (µg/L)</u>									
Residential:	<4 (5) 0.6 (1)	2 (5)	<5 (5)		5 (5)		<1 (5)	<4 (5)	<5 (5)
Commercial:		5.1 (7) 0.6 (8)							<5 (5)
Industrial:	<4 (5)	<4 (5)	<4 (5)	<4 (5)	<4 (5)	<4 (5)		<4 (5)	<4 (5)
<u>Chromium (µg/L)</u>									
Residential:	<60 (5) <5 (4)	20 (5) 71 (4)	<10 (5)		<60 (5)		<10 (5)	<60 (5)	<60 (5) 49 (4)
Commercial:	<5 (4)	19 (7) 12 (8)							<60 (5)
Industrial:	<60 (5)	<60 (5)	<60 (5)	<60 (5)	<60 (5)	70 (5)		<60 (5)	<60 (5)

Table 2.12 Sheetflow Quality Summary for Other Source Areas (mean concentration and reference) (Continued)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets
Copper (µg/L)									
Residential:	10 (5) <5 (4)	100 (5)	20 (5)		210 (5)		20 (5)	20 (5)	40 (5) 30 (4)
Commercial:	110 (4)	40 (2) 46 (4) 110 (7)							40 (5)
Industrial:	<20 (5)	480 (5)	260 (5)	120 (5)	40 (5)	140 (5)		30 (5)	220 (5)
Lead (µg/L)									
Residential:	<40 (5) 30 (3) 48 (1) 17 (4)	250 (5)	760 (5)		1400 (5)		30 (5)	80 (5)	180 (5) 670 (4)
Commercial:	19 (4) 30 (1)	200 (2) 350 (3) 1090 (4) 146 (1) 255 (7) 54 (8)							180 (5)
Industrial:	<40 (5)	230 (5)	280 (5)	210 (5)	260 (5)	340 (5)		<40 (5)	560 (5)

Table 2.12 Sheetflow Quality Summary for Other Source Areas (mean concentration and reference) (Continued)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets
Zinc (µg/L)									
Residential:	320 (5) 670 (1) 180 (4)	520 (5)	390 (5)		1000 (5)		40 (5)	60 (5)	180 (5) 140 (4)
Commercial:	310 (1) 80 (4)	300 (5) 230 (4) 133 (1) 490 (7)							180 (5)
Industrial:	70 (5)	640 (7)	310 (5)	410 (5)	310 (5)	690 (5)		60 (5)	910 (5)

References:
(1) Bannerman, *et al.* 1983 (Milwaukee, WI) (NURP)
(2) Denver Regional Council of Governments 1983 (NURP)
(3) Pitt 1983 (Ottawa)
(4) Pitt and Bozeman 1982 (San Jose)
(5) Pitt and McLean 1986 (Toronto)
(7) STORET Site #590866-2954309 (Shop-Save-Durham, NH) (NURP)
(8) STORET Site #596296-2954843 (Huntington-Long Island, NY) (NURP)

Table 2.13 Sheetflow Quality Summary for Undeveloped Landscaped and Freeway Pavement Areas (Mean Observed Concentrations and reference)

Pollutants	Landscaped Areas	Undeveloped Areas	Freeway Paved Lane and Shoulder Areas
Total Solids, mg/L	388 (5)	588 (5)	340 (6)
Suspended Solids, mg/L	100 (5)	400 (2) 390 (5)	180 (6)
Dissolved Solids, mg/L	288 (5)	193 (5)	160 (6)
BOD$_5$, mg/L	3 (4)	- - - -	10 (6)
COD, mg/L	70 (4) 26 (5)	72 (2) 54 (5)	130 (6)
Total Phosphorus, mg/L	0.42 (4) 0.56 (5)	0.40 (2) 0.68 (5)	- - - -
Total Phosphate, mg/L	0.32 (4) 0.14 (5)	0.10 (2) 0.26 (5)	0.38 (6)
TKN, mg/L	1.32 (4) 3.6 (5)	2.9 (2) 1.8 (5)	2.5 (6)
Ammonia, mg/L	1.2 (4) 0.4 (5)	0.1 (2) <0.1 (5)	- - - -
Phenols, µg/L	0.8 (5)	- - - -	- - - -
Aluminum, µg/L	1.5 (5)	11 (5)	- - - -
Cadmium, µg/L	<3 (5)	<4 (5)	60 (6)
Chromium, µg/L	10 (4)	<60 (5)	70 (6)
Copper, µg/L	<20 (5)	40 (2) 31 (4) <20 (5)	120 (6)
Lead, µg/L	30 (3) 35 (4) <30 (5)	100 (2) 30 (3) <40 (5)	2000 (6)
Zinc, µg/L	10 (4)	100 (2) 100 (5)	460 (6)

References:
(2) Denver Regional Council of Governments 1983 (NURP)
(3) Pitt 1983 (Ottawa)
(4) Pitt and Bozeman 1982 (San Jose)
(5) Pitt and McLean 1986 (Toronto)
(6) Shelly and Gaboury 1986 (Milwaukee)

Table 2.14 Source Area Bacteria Sheetflow Quality Summary (means)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/ Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets	Land-scaped	Un-developed	Freeway Paved Lane and Shoulders
Fecal Coliforms (#/100 mL)												
Residential:	85 (3) <2 (4) 1400 (5)	250,000 (5)	100 (5)		600 (5)			11,000 (5)	920 (4) 6,900 (5)	3300 (5)	5400 (3) 49 (4)	1500 (9)
Commercial	9 (4)	2900 (3) 350 (4) 210 (1) 480 (7) 23,000 (8)										
Industrial:	1600 (5)	8660 (8)	9200 (5)	18,000 (5)	66,000 (5)	300,000 (5)		55,000 (5)	100,000 (5)			
Fecal Strep (#/100 mL)												
Residential:	170 (3) 920 (4) 2200 (5)	190,000 (5)	<100 (5)		1900 (5)		1800 (5)		>2400 (4) 7300 (5)	43,000 (5)	16,500 (3) 920 (4)	2200 (9)
Commercial:	17 (3)	11,900 (3) >2400 (4) 770 (1) 1120 (7) 62,000 (8)										
Industrial:	690 (5)	7300 (5)	2070 (5)	8100 (5)	36,000 (5)	21,000 (5)		3600 (5)	45,000 (5)			
Pseudo, Aerug (#/100 mL)												
Residential:	30,000 (5) 50 (5)	1900 (5)	100 (5)		600 (5)		600 (5)		570 (5)	2100 (5)		
Industrial:		5800 (5)	5850 (5)	14,000 (5)	14,300 (5)	100 (5)		3600 (5)	6200 (5)			

References:
(1) Bannerman, *et al*. 1983 (Milwaukee, WI) (NURP)
(3) Pitt 1983 (Ottawa)

(4) Pitt and Bozeman 1982 (San Jose)
(5) Pitt and McLean 1986 (Toronto)
(7) STORET Site #590866-2954309 (Shop-Save-Durham, NH) (NURP)
(8) STORET Site #596296-2954843 (Huntington-Long Island, NY) (NURP)
(9) Kobriger, *et al.* 1981 and Gupta, *et al*. 1977

Table 2.15 Source Area Filterable Pollutant Concentration Summary (means)

	Residential			Commercial			Industrial		
	Total	Filterable	% Filt.	Total	Filterable	% Filt.	Total	Filterable	%Filt.
<u>Roof Runoff</u>									
Solids (mg/L)	64	42	66 (1)				113	110	97 (5)
	58	45	77 (5)						
Phosphorus (mg/L)	0.054	0.013	24 (1)						
Lead (µg/L)	48	4	8 (1)						
<u>Paved Parking</u>									
Solids (mg/L)				240	175	73 (1)	490	138	28 (5)
				102	61	60 (7)			
				1790	138	8 (5)			
Phosphorus (mg/L)				0.16	0.03	19 (1)			
				0.9	0.3	33 (2)			
TKN (mg/L)				0.77	0.48	62 (8)			
Lead (µg/L)				146	5	3 (1)			
				54	8.8	16 (8)			
Arsenic (µg/L)				0.38	0.095	25 (8)			
Cadmium (µg/L)				0.62	0.11	18 (8)			
Chromium (µg/L)				11.8	2.8	24 (8)			
<u>Paved Storage</u>									
Solids (mg/L)				73	32	44 (5)	270	64	24 (5)

References:

(1) Bannerman, *et al*. 1983 (Milwaukee) (NURP)
(2) Denver Regional Council of Governments 1983 (NURP)
(5) Pitt and McLean 1986 (Toronto)
(7) STORET Site #590866-2954309 (Shop-Save-Durham, NH) (NURP)
(8) STORET Site #596296-2954843 (Huntington-Long Island, NY) (NURP)

Other Pollutant Contributions to the Storm Drainage System

The detection of pentachlophenols in the relatively few samples previously analyzed indicated important leaching from treated wood. Frequent detections of polycyclic aromatic hydrocarbons (PAHs) during the U.S. Environmental Protection Agency’s Nationwide Urban Runoff Program (EPA 1983a) may possibly indicate leaching from creosote treated wood, in addition to fossil fuel combustion sources. High concentrations of copper, and some chromium and arsenic observations also indicate the potential of leaching from “CCA” (copper, chromium, and arsenic) treated wood. The significance of these leachate products in the receiving waters is currently unknown, but alternatives to these preservatives should be considered. Many cities use aluminum and concrete utility poles instead of treated wood poles. This is especially important considering that utility poles are usually located very close to the drainage system ensuring an efficient delivery of leachate products. Many homes currently use wood stains containing pentachlorophenol and other wood preservatives. Similarly, the construction of retaining walls, wood decks and playground equipment with treated wood is common. Some preservatives (especially creosote) cause direct skin irritation, besides contributing to potential problems in receiving waters. Many of these wood products are at least located some distance from the storm drainage system, allowing some improvement to surface water quality by infiltration through pervious surfaces.

Phase 1 Project Activities - Sources of Stormwater Toxicants

The first project phase of this research project included the collection and analysis of 87 urban stormwater runoff samples from a variety of source areas under different rain conditions (Table 2.16). All of the samples were analyzed in filtered (0.45 µm filter) and non-filtered forms to enable partitioning of the toxicants into “particulate” (non-filterable) and “dissolved” (filterable) forms.

Table 2.16. Numbers of Samples Collected from each Source Area Type

Local Source Areas[a]	Residential	Commercial/ Institutional	Industrial	Mixed
Roofs	5	3	4	
Parking Areas	2	11	3	
Storage Areas	na	2	6	
Streets	1	1	4	
Loading Docks	na	na	3	
Vehicle Service Area	na	5	na	
Landscaped Areas	2	2	2	
Urban Creeks				19
Detention Ponds				12

[a] All collected in Birmingham, AL.

Phase 1 - Analyses and Sampling

The samples listed in Table 2.16 were all obtained from the Birmingham, AL, area. Samples were obtained from shallow flows originating from homogeneous source areas by using several manual grab sampling procedures. For deep flows, samples were collected directly into the sample bottles. For shallow flows, a peristaltic hand operated vacuum pump created a small vacuum in the sample bottle which then gently drew the sample directly into the container through a Teflon™ tube. About one liter of sample was needed, split into two containers: one 500 mL glass bottle with Teflon™ lined lid was used for the organic and toxicity analyses, and another 500 mL polyethylene bottle was used for the metal and other analyses.

An important aspect of the first phase of this research was to evaluate the effects of different land uses and source areas, plus the effects of rain characteristics, on sample toxicant concentrations. Therefore, careful records were obtained of the amount of rain and the rain intensity that occurred before the samples were obtained. Antecedent dry period data were also obtained to compare with the chemical data in a series of statistical tests.

All samples were handled, preserved, and analyzed according to accepted protocols (EPA 1982 and 1983b). The organic pollutants were analyzed using two gas chromatographs, one with a mass selective detector (GC/MSD) and another with an electron capture detector (GC/ECD). The pesticides were analyzed according to EPA method 505, while the base neutral compounds were analyzed according to EPA method 625 (but only using 100 mL samples). The pesticides were analyzed on a Perkin Elmer Sigma 300 GC/ECD using a J&W DB-1 capillary column (30m by 0.32 mm ID with a 1 µm film thickness). The base neutrals were analyzed on a Hewlett Packard 5890 GC with a 5970 MSD using a Supelco DB-5 capillary column (30m by 0.25 mm ID with a 0.2 µm film thickness). Table 2.17 lists the organic toxicants that were analyzed.

Table 2.17. List of Toxic Pollutants Analyzed in Samples

Pesticides DL = 0.3 µg/L	Phthalate Esters DL = 0.5 µg/L	Polynuclear Aromatic Hydrocarbons DL = 0.5 µg/L		Metals DL = 1 µg/L
BHC (Benzene hexachloride)	Bis(2-ethylhexyl) Phthalate	Acenaphthene	Fluoranthene	Aluminum
Heptachlor	Butyl benzyl phthalate	Acenapthylene	Fluorene	Cadmium
Aldrin	Di-n-butyl phthalate	Anthracene	Indeno (1,2,3-cd) pyrene	Chromium
Endosulfan	Diethyl phthalate	Benzo (a) anthracene	Naphthalene	Copper
Heptachlor epoxide	Dimethyl phthalate	Benzo (a) pyrene	Phenanthrene	Lead
DDE (Dichlorodiphenyl dichloroethylene)	Di-n-octyl phthalate	Benzo (b) fluoranthene	Pyrene	Nickel
DDD (Dichlorodiphenyl dichloroethane)		Benzo (ghi) perylene		Zinc
DDT (Dichlorodiphenyl trichloroethane)		Benzo (k) fluoranthene		
Endrin		Chrysene		
Chlordane		Dibenzo (a,h) anthracene		

D.L. = Detection Limit

Metallic toxicants, also listed in Table 2.17, were analyzed using a graphite furnace equipped atomic absorption spectrophotometer (GFAA). EPA methods 202.2 (Al), 213.2 (Cd), 218.2 (Cr), 220.2 (Cu), 239.2 (Pb), 249.2 (Ni), and 289.2 (Zn) were followed in these analyses. A Perkin Elmer 3030B atomic absorption spectrophotometer was used after nitric acid digestion of the samples. Previous research (Pitt and McLean 1986; EPA 1983a) indicated that low detection limits were necessary in order to measure the filtered sample concentrations of the metals, which would not be achieved by use of a standard flame atomic absorption spectrophotometer. Low detection limits would enable partitioning of the metals between the solid and liquid phases to be investigated, an important factor in assessing the fates of the metals in receiving waters and in treatment processes.

The Microtox™ 100% sample toxicity screening test, from Azur Environmental (previously Microbics, Inc.), was selected for this research after comparisons with other laboratory bioassay tests. During the first research phase, twenty source area stormwater samples and combined sewer samples (obtained during a cooperative study being conducted in New York City) were split and sent to four laboratories for analyses using 14 different bioassay tests. Conventional bioassay tests were conducted using freshwater organisms at the EPA's Duluth, MN, laboratory and using marine organisms at the EPA's Narraganssett Bay, RI, laboratory. In addition, other bioassay tests, using bacteria, were also conducted at the Environmental Health Sciences Laboratory at Wright State University, Dayton, Ohio. The tests represented a range of organisms that included fish, invertebrates, plants, and microorganisms.

The conventional bioassay tests conducted simultaneously with the Microtox™ screening test for the 20 stormwater sheetflow and combined sewer overflow (CSO) samples were all short-term tests. However, some of the tests were indicative of chronic toxicity (life cycle tests and the marine organism sexual reproduction tests, for example), whereas the others would be classically considered as indicative of acute toxicity (Microtox™ and the fathead minnow tests, for example). The following list shows the major tests that were conducted by each participating laboratory:

- University of Alabama at Birmingham, Environmental Engineering Laboratory
  - Microtox™ bacterial luminescence tests (10-, 20-, and 35-minute exposures) using the marine *Photobacterium phosphoreum.*

- Wright State University, Biological Sciences Department
  - Macrofaunal toxicity tests:
    - *Daphnia magna* (water flea) survival; *Lemma minor* (duckweed) growth; and *Selenastrum capricornutum* (green alga) growth.
  - Microbial activity tests (bacterial respiration):
    - Indigenous microbial electron transport activity;
    - Indigenous microbial inhibition of β-galactosidase activity;
    - Alkaline phosphatase for indigenous microbial activity;
    - Inhibition of β-galactosidase for indigenous microbial activity; and
    - Bacterial surrogate assay using *O*-nitrophenol-β-D-galactopyranside activity and *Escherichia coli.*

- EPA Environmental Research Laboratory, Duluth, Minnesota
  - *Ceriodaphnia dubia* (water flea) 48-h survival; and
  - *Pimephales promelas* (fathead minnow) 96-h survival.

- EPA Environmental Research Laboratory, Narragansett Bay, Rhode Island
  - *Champia parvula* (marine red alga) sexual reproduction (formation of cystocarps after 5 to 7 d exposure); and
  - *Arbacua punctulata* (sea urchin) fertilization by sperm cells.

Table 2.18 summarizes the results of the toxicity tests. The *C. dubia. P. promelas,* and C. *Parvula* tests experienced problems with the control samples, and those results are therefore uncertain. The *A. pustulata* tests on the stormwater samples also had a potential problem with the control samples. The CSO test results (excluding the fathead minnow tests) indicated that from 50% to 100% of the samples were toxic, with most tests identifying the same few samples as the most toxic. The toxicity tests for the stormwater samples indicated that 0% to 40% of the samples were toxic. The Microtox™ screening procedure gave similar rankings for the samples as the other toxicity tests.

Table 2.18. Fraction of Samples Rated as Toxic

Sample series	Combined sewer overflows, %	Stormwater, %
Microtox™ marine bacteria	100	20
C. Dubia	60	0[a]
P. promelas	0[a]	0[a]

C. parvula	100	0[a]
A. punctulata	100	0[a]
D. magna	63	40
L. minor	50[a]	0

[a] Results uncertain, see text

Laboratory toxicity tests can result in important information on the effects of stormwater in receiving waters, but actual in-stream taxonomic studies should also be conducted. A recently published proceedings of a conference on stormwater impacts on receiving streams (Herricks 1995) contains many examples of actual receiving water impacts and toxicity test protocols for stormwater.

All of the Birmingham samples represented separate stormwater. However, as part of the Microtox™ evaluation, several CSO samples from New York City were also tested to compare the different toxicity tests. These samples were collected from six CSO discharge locations having the following land uses:

- 290 acres, 90% residential and 10% institutional;
- 50 acres, 100% commercial;
- 620 acres, 20% institutional, 6% commercial, 5% warehousing, 5% heavy industrial, and 64% residential;
- 225 acres, 13% institutional, 4% commercial, 2% heavy industrial. and 81% residential:
- 400 acres, 1% institutional and 99% residential; and
- 250 acres, 88% commercial. 6% warehousing, and 6% residential.

Therefore, there was a chance that some of the CSO samples may have had some industrial process waters. However, none of the Birmingham sheetflow samples could have contained any process waters because of how and where they were collected.

The Microtox™ screening procedure gave similar toxicity rankings for the twenty samples as the conventional bioassay tests. It is also a rapid procedure (requiring about one hour) and only requires small (<1 mL) sample volumes. The Microtox™ toxicity test uses marine bioluminescence bacteria and monitors the light output for different sample concentrations. About one million bacteria organisms are used per sample, resulting in highly repeatable results. The more toxic samples produce greater stress on the bacteria test organisms that results in a greater light attenuation compared to the control sample. It should be emphasized that the Microtox™ procedure was not used during this research to determine the absolute toxicities of the samples, or to predict the toxic effects of stormwater runoff on receiving waters, but to compare the relative toxicities of different samples that may indicate efficient source area treatment locations, and to examine changes in toxicity during different treatment procedures.

Phase 1 - Potential Sources

A drainage system captures runoff and pollutants from many source areas, all with individual characteristics influencing the quantity of runoff and pollutant load. Impervious source areas may contribute most of the runoff during small storm events (e.g., paved parking lots, streets, driveways, roofs, sidewalks, etc.). Pervious source areas can have higher material washoff potentials and become important contributors for larger storm events when their infiltration rate capacity is exceeded (e.g., gardens, bare ground, unpaved parking areas, construction sites, undeveloped areas, etc.). Many other factors also affect the pollutant contributions from source areas, including: surface roughness, vegetative cover, gradient, and hydraulic connections to a drainage system; rainfall intensity, duration, and antecedent dry period; and pollutant availability due to direct contamination from local activities, cleaning frequency/efficiency, and natural and regional sources of pollutants. The relative importance of the different source areas is therefore a function of the area characteristics, pollutant washoff potential, and the rainfall characteristics (Pitt 1987).

Important sources of toxicants are often related to the land use (e.g., high traffic capacity roads, industrial processes, and storage area) that are unique to specific land uses activities. Automobile related sources affect the quality and quantity of road dust particles through gasoline and oil drips/spills; deposition of exhaust products; and wear of tire, brake, and pavement materials (Shaheen 1975). Urban landscaping practices potentially produce vegetation cuttings and fertilizer and pesticide washoff. Miscellaneous sources include holiday firework debris, wildlife and domestic pet wastes, and possible sanitary wastewater infiltration. In addition, resuspension and deposition of pollutants/particles via the atmosphere can increase or decrease the contribution potential of a source area (Pitt and Bozeman 1982; Bannerman, *et al*. 1993).

Phase 1 - Results

Table 2.19 summarizes the source area sample data for the most frequently detected organic toxicants and for all of the metallic toxicants analyzed. The organic toxicants analyzed, but not reported, were generally detected in 5, or less, of the non-filtered samples and in none of the filtered samples. Table 2.19 shows the mean, maximum, and minimum concentrations for the detected toxicants. It is important to note that these values are only based on the observed concentrations only. They do not consider the non-detectable conditions. Mean values based on total sample numbers for each source area category would therefore result in much lower concentrations. The frequency of detection is therefore an important consideration when evaluating organic toxicants. High detection frequencies for the organics may indicate greater potential problems than infrequent high concentrations.

Table 2.19 also summarizes the measured pH and SS concentrations. Most pH values were in the range of 7.0 to 8.5 with a low of 4.4 and a high of 11.6 for a roof and concrete plant storage area runoff sample, respectively. This range of pH can have dramatic effects on the speciation of the metals analyzed. The SS concentrations were generally less than 100 mg/L, with impervious area runoff (e.g., roofs and parking areas) having much lower SS concentrations and turbidities compared to samples obtained from pervious areas (e.g., landscaped areas).

Thirteen organic compounds, out of more than thirty-five targeted compounds analyzed, were detected in more than 10 percent of all samples, as shown in Table 2.19. The greatest detection frequencies were for 1,3-dichlorobenzene and fluoranthene, which were each detected in 23 percent of the samples. The organics most frequently found in these source area samples (i.e., polycyclic aromatic hydrocarbons (PAH), especially fluoranthene and pyrene) were similar to the organics most frequently detected at outfalls in prior studies (EPA 1983a).

Roof runoff, parking area and vehicle service area samples had the greatest detection frequencies for the organic toxicants. Vehicle service areas and urban creeks had several of the observed maximum organic compound concentrations. Most of the organics were associated with the non-filtered sample portions, indicating an association with the particulate sample fractions. The compound 1,3-dichlorobenzene was an exception, having a significant dissolved fraction.

In contrast to the organics, the heavy metals analyzed were detected in almost all samples, including the filtered sample portions. The non-filtered samples generally had much higher concentrations, with the exception of zinc which was mostly associated with the dissolved sample portion (i.e., not associated with the SS). Roof runoff generally had the highest concentrations of zinc, probably from galvanized roof drainage components, as previously reported by Bannerman, *et al*. (1983). Parking and storage areas had the highest nickel concentrations, while vehicle service areas and street runoff had the highest concentrations of cadmium and lead. Urban creek samples had the highest copper concentrations, which were probably due to illicit industrial connections or other non-stormwater discharges.

Table 2.20 shows the relative toxicities of the collected stormwaters. A wide range of toxicities were found. About 9% of the non-filtered samples were considered highly toxic using the Microtox™ toxicity screening procedure. About 32% of the samples were moderately toxic and about 59% were considered non-toxic. The greatest percentage of samples considered the most toxic were from industrial storage and parking areas. Landscaped areas also had a high incidence of highly toxic samples (presumably due to landscaping chemicals), and roof runoff had some highly toxic samples (presumably due to high zinc concentrations). The phase 2 treatability study activities indicated that filtering the samples through a range of fine sieves and finally a 0.45µm filter consistently reduced sample toxicities. The chemical analyses also generally found much higher toxicant concentrations in the non-filtered sample portions, compared to the filtered sample portions.

Replicate samples were collected from several source areas at three land uses during four different storm events to statistically examine toxicity and pollutant concentration differences due to storm and site conditions. These data indicated that variations in Microtox™ toxicities and organic toxicant concentrations may be partially explained by rain characteristics. As an example, high concentrations of many of the PAHs were associated with long antecedent dry periods and large rains (Barron 1990).

Table 2.19. Stormwater toxicants detected in at least 10% of the source area sheetflow samples (mg/L, unless otherwise noted).

	Roof areas		Parking areas		Storage areas		Street runoff		Loading docks		Vehicle service areas		Landscaped areas		Urban creeks		Detention ponds	
	N.F.[a]	F.[b]	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.
Total samples	12	12	16	16	8	8	6	6	3	3	5	5	6	6	19	19	12	12
Base neutrals (detection limit = 0.5 mg/L)																		
1,3-Dichlorobenzene detection frequency = 20% N.F. and 13% F.																		
No. detected[C]	3	2	3	2	1	1	1	1	0	0	3	2	3	2	2	0	1	1
Mean[d]	52	20	34	13	16	14	5.4	3.3			48	26	29	5.6	93		27	21
Max.	88	23	103	26							72	47	54	7.5	120			
Min.[e]	14	17	3.0	2.0							6.0	4.9	4.5	3.8	65			
Fluoranthene detection frequency = 20% N.F. and 12% F.																		
No. detected	3	2	3	2	1	0	1	1	0	0	3	2	3	2	1	0	2	1
Mean	23	9.3	37	2.7	4.5		0.6	0.5			39	3.6	13	1.0	130		10	6.6
Max.	45	14	110	5.4							53	6.8	38	1.3			14	
Min.	7.6	4.8	3.0	2.0							0.4	0.4	0.7	0.7			6.6	
Pyrene detection frequency = 17% N,F, and 7% F.																		
No. detected	1	0	3	2	1	0	1	1	0	0	3	2	2	0	1	0	2	1
Mean	28		40	9.8	8		1.0	0.7			44	4.1	5.3		100		31	5.8
Max.			120	20							51	7.4	8.2				57	
Min.			3.0	2.0							0.7	0.7	2.3				6.0	
Benzo(b)fluoranthene detection frequency = 15% N.F. and 0% F.																		
No. detected	4	0	3	0	0	0	1	0	0	0	2	0	1	0	2	0	0	0
Mean	76		53				14				98		30		36			
Max.	260		160								110				64			
Min.	6.4		3.0								90				8.0			
Benzo(k)fluoranthene detection frequency = 11% N.F. and 0% F.																		
No. detected	0	0	3	0	0	0	1	0	0	0	2	0	1	0	2	0	0	0
Mean			20				15				59		61		55			
Max.			1								103				78			
Min.			3.0								15				31			
Benzo(a)pyrene detection frequency = 15% N.F. and 0% F.																		
No. detected	4	0	3	0	0	0	1	0	0	0	2	0	1	0	2	0	0	0
Mean	99		40				19				90		54		73			

Max.	300	120	120	130
Min.	34	3.0	60	19

Table 2.19. Continued).

	Roof areas		Parking areas		Storage areas		Street runoff		Loading docks		Vehicle service areas		Landscaped areas		Urban creeks		Detention ponds	
	N.F.[a]	F.[b]	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.
Total samples	12	12	16	16	8	8	6	6	3	3	5	5	6	6	19	19	12	12
Bis(2-chloroethyl) ether detection frequency = 12% N.F. and 2% F.																		
No. detected	3	1	2	0	0	0	1	0	0	0	1	1	1	0	1	0	1	0
Mean	42	17	20				15				45	23	56		200		15	
Max.	87	2	39															
Min.	20		2.0															
Bis(chloroisopropyl) ether detection frequency = 13% N.F. and 0% F.																		
No. detected	3	0	3	0	0	0	0	0	0	0	2	0	1	0	2	0	0	0
Mean	99		130								120		85		59			
Max.	150		400								160				78			
Min.	68		3.0								74				40			
Naphthalene detection frequency = 11% N.F. and 6% F.																		
No. detected	2	0	1	1	0	0	0	0	0	0	2	1	1	0	1	1	2	2
Mean	17		72	6.6							70	82	49		300	6.7	43	12
Max.	21										100						68	17
Min.	13										37						18	6.6
Benzo(a)anthracene detection frequency = 10% N.F. and 0% F.																		
No. detected	1	0	3	0	0	0	0	0	0	0	2	0	1	0	1	0	0	0
Mean	16		24								35		54		61			
Max.			73								39							
Min.			3.0								31							
Butylbenzyl phthalate detection frequency = 10% N.F. and 4% F.																		
No. detected	1	0	2	1	0	0	0	0	0	0	2	2	1	0	1	0	1	0
Mean	100		12	3.3							26	9.8	130		59		13	
Max.			21								48	16						
Min.			3.3								3.8	3						
Pesticides (detection limit = 0.3 mg/L)																		
Chlordane detection frequency = 11% N.F. and 0% F.																		
No. detected	2	0	2	0	3	0	1	0	0	0	1	0	0	0	0	0	0	0
Mean	1.6		1.0		1.7		0.8				0.8							

Max.	2.2	1.2	2.9
Min.	0.9	0.8	1.0

Table 2.19. Continued).

	Roof areas		Parking areas		Storage areas		Street runoff		Loading docks		Vehicle service areas		Landscaped areas		Urban creeks		Detention ponds	
	N.F.[a]	F.[b]	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.
Total samples	12	12	16	16	8	8	6	6	3	3	5	5	6	6	19	19	12	12
Metals (detection limit = 1 μg/L)																		
Lead detection frequency = 100% N.F. and 54% F.																		
No. detected	12	1	16	8	8	7	6	4	3	1	5	2	6	1	19	15	12	8
Mean	41	1.1	46	2.1	105	2.6	43	2.0	55	2.3	63	2.4	24	1.7	20	1.4	19	1.0
Max.	170		130	5.2	330	5.7	150	3.9	80		110	3.4	70		100	1.6	55	1.0
Min.	1.3		1.0	1.2	3.6	1.6	1.5	1.1	25		27	1.4	1.4		1.4	<1	1	<1
Zinc detection frequency = 99% N.F. and 98% F.																		
No. detected	12	12	16	16	8	7	6	6	2	2	5	5	6	6	19	19	12	12
Mean	250	220	110	86	1730	22	58	31	55	33	105	73	230	140	10	10	13	14
Max.	1580	1550	650	560	13100	100	130	76	79	62	230	230	1160	670	32	23	25	25
Min.	11	9	12	6	12	3.0	4.0	4.0	31	4.0	30	11	18	18	<1	<1	<1	<1
Copper detection frequency = 98% N.F. and 78% F.																		
No. detected	11	7	15	13	8	6	6	5	3	2	5	4	6	6	19	17	12	8
Mean	110	2.9	116	11	290	250	280	3.8	22	8.7	135	8.4	81	4.2	50	1.4	43	20
Max.	900	8.7	770	61	1830	1520	1250	11	30	15	580	24	300	8.8	440	1.7	210	35
Min.	1.5	1.1	10	1.1	10	1.0	10	1.0	15	2.6	1.5	1.1	1.9	0.9	<1	<1	0.2	<1
Aluminum detection frequency = 97% N.F. and 92% F.																		
No. detected	12	12	15	15	7	6	6	6	3	1	5	4	5	5	19	19	12	12
Mean	6850	230	3210	430	2320	180	3080	880	780	18	700	170	2310	1210	620	190	700	210
Max.	71300	1550	6480	2890	6990	740	10040	4380	930		1370	410	4610	1860	3250	500	1570	360
Min.	25	6.4	130	5.0	180	10	70	18	590		93	0.3	180	120	<5	<5	<5	<5
Cadmium detection frequency = 95% N.F. and 69% F.																		
No. detected	11	7	15	9	8	7	6	5	3	3	5	3	4	2	19	15	12	9
Mean	3.4	0.4	6.3	0.6	5.9	2.1	37	0.3	1.4	0.4	9.2	0.3	0.5	0.6	8.3	0.2	2	0.5
Max.	30	0.7	70	1.8	17	10	220	0.6	2.4	0.6	30	0.5	1	1	30	0.3	11	0.7
Min.	0.2	0.1	0.1	0.1	0.9	0.3	0.4	0.1	0.7	0.3	1.7	0.2	0.1	0.1	<0.1	<0.1	0.1	0.4
Chromium detection frequency = 91% N.F. and 55% F.																		
No. detected	7	2	15	8	8	5	5	4	3	0	5	1	6	5	19	15	11	8
Mean	85	1.8	56	2.3	75	11	9.9	1.8	17		74	2.5	79	2.0	62	1.6	37	2.0
Max.	510	2.3	310	5.0	340	32	30	2.7	40		320		250	4.1	710	4.3	230	3.0

Min.	5.0	1.4	2.4	1.1	3.7	1.1	2.8	1.3	2.4	2.4	2.2	1.4	<0.1	<0.1	<0.1	<0.1

Table 2.19. Continued).

	Roof areas		Parking areas		Storage areas		Street runoff		Loading docks		Vehicle service areas		Landscaped areas		Urban creeks		Detention ponds	
	N.F.[a]	F.[b]	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.
Total samples	12	12	16	16	8	8	6	6	3	3	5	5	6	6	19	19	12	12
Nickel detection frequency = 90% N.F. and 37% F.																		
No. detected	10	0	14	4	8	1	5	0	3	1	5	1	4	1	18	16	11	8
Mean	16		45	5.1	55	87	17		6.7	1.3	42	31	53	2.1	29	2.3	24	3.0
Max.	70		130	13	170		70		8.1		70		130		74	3.6	70	6.0
Min	2.6		4.2	1.6	1.9		1.2		4.2		7.9		21		<1	<1	1.5	<1
Other constituents (always detected, analyzed only for non-filtered samples)																		
pH																		
Mean	6.9		7.3		8.5		7.6		7.8		7.2		6.7		7.7		8.0	
Max.	8.4		8.7		12		8.4		8.3		8.1		7.2		8.6		9.0	
Min	4.4		5.6		6.5		6.9		7.1		5.3		6.2		6.9		7.0	
Suspended solids																		
Mean	14		110		100		49		40		24		33		26		17	
Max.	92		750		450		110		47		38		81		140		60	
Min.	0.5		9.0		5.0		7.0		34		17		8.0		5.0		3.0	

[a] N.F.: concentration associated with a nonfiltered sample.

[b] F.: concentration after the sample was filtered through a 0.45 µm membrane filter.

[c] Number detected refers to the number of samples in which the toxicant was detected.

[d] Mean values based only on the number of samples with a definite concentration of toxicant reported (not on the total number of samples analyzed).

[e] The minimum values shown are the lowest concentration detected, they are not necessarily the detection limit.

Table 2.20. Relative Toxicity of Samples Using Microtox ä (Non-filtered)

Local Source Areas	Highly Toxic (%)	Moderately Toxic (%)	Not Toxic (%)	Number of Samples
Roofs	8	58	33	12
Parking Areas	19	31	50	16
Storage Areas	25	50	25	8
Streets	0	67	33	6
Loading Docks	0	67	33	3
Vehicle Service Areas	0	40	60	5
Landscaped Areas	17	17	66	6
Urban Creeks	0	11	89	19
Detention Ponds	8	8	84	12
All Areas	9%	32%	59%	87

Microbics suggested toxicity definitions for 35 minute exposures:

- Highly Toxic - light decrease >60%
- Moderately Toxic - light decrease <60% & >20%
- Not Toxic - light decrease <20%

Chapter 3
Laboratory-Scale Toxicant Reduction Tests

The phase 2 activities of this project examined methods to reduce stormwater toxicity from critical source areas using a variety of conventional bench-scale treatment processes. The data from phase 1 identified the critical source areas which generally had the highest toxicant concentrations for study during this research phase. The critical source areas targeted for this additional study were storage/parking and vehicle service areas.

Phase 2 - Analysis and Sampling

The objective of this second research phase was to quantify improvements in stormwater toxicity using different stages of several bench-scale treatment methods. These data were used to indicate the relative effectiveness of different treatment efforts and processes. To meet this objective and the resource restraints of cost and time, the Azur Environmental (previously Microbics, Inc.) Microtox™ screening toxicity test was chosen to indicate the relative changes in toxicity.

The efficiency of many pollution control devices is affected by the particle sizes and settling velocity distributions of the pollutants in the wastewater. Therefore, settling column tests were conducted to determine the pollutant settling velocities. Standard gravimetric solids analyses (EPA 1983b) were conducted on the settling column samples to calculate the settling velocities and specific gravities of the particulates. Nephelometric turbidity analyses were also conducted (EPA 1983b) for all subsamples during the treatability tests.

Samples were collected in the same manner from the critical source areas selected for testing as described in phase 1, but a larger volume of sample (10 to 20 liters) was collected from each location.

Phase 2 - Experimental Error

The second phase included intensive analyses of samples from twelve sampling locations in the Birmingham, AL, area. Table 3.1 lists the sampling dates, source area categories, and relative toxicity category prior to treatment. These sampled storms represent practically all of the rains that occurred during the field portion of the second project phase (July-November, 1990). Independent replicates (obtained during separate analysis runs) were used to determine the measurement errors associated with the Microtox™ procedure. The total number of Microtox™ analyses that were conducted for all of the treatability tests for each sample is also noted, as are the means, standard deviations, and coefficients of variation of the replicate toxicity values.

The initial toxicity values (before treatability tests) were plotted on normal-probability paper to indicate their probability distribution characteristics. Almost all of the samples had initial toxicity values that were shown to be normally distributed. Therefore, the coefficient of variation (COV = standard deviation/mean) values shown on Table 3.1 can be used as an indication of the confidence intervals of the Microtox™ measurements. The COVs ranged from 2.3 to 9.8 percent, with an average value of 5.1 percent. Therefore, the 95 percent confidence interval (two times the COV values include 95.4 percent of the data, if normally distributed) for the Microtox™ procedure ranged between 5 and 20 percent of the mean values. These confidence intervals are quite narrow for a bioassay test and indicate the good repeatability of the Microtox™ procedure. In all cases, statistical tests were performed on the test results to indicate the significance of the different treatability tests.

Table 3.1 also shows that samples B and D were initially extremely toxic, while the remainder of the samples were moderately toxic. All samples were reduced to “non-toxic” levels after various degrees of treatment.

Table 3.1. Phase 2 Treatability Sample Descriptions

Sample Source	Date	Initial Toxicity[a] (%)	Number of Analyses	Standard Deviation[b]	Coefficient of Variation[b] (%)
Automobile Service Area Samples					
B	7/10/90	78	28	7.6	9.8
C	7/21/90	34	42	2.9	8.5
E	8/19/90	43	74	1.3	3.0
H	10/17/90	50	88	1.5	3.0
Industrial Loading & Parking Area Samples					
D	8/2/90	67	74	2.1	3.1
F	9/12/90	31	88	1.5	4.9
G	10/3/90	53	88	3.0	5.7
I	10/24/90	55	89	1.9	3.4
J	11/5/90	49	89	1.1	2.3
K	11/9/90	28	89	2.2	8.1
Automobile Salvage Yard Samples					
L	11/28/90	26	89	1.4	5.5
M	12/3/90	54	89	1.8	3.4

[a] Toxicity measured as percent light reduction after 35 minute exposure.
[b] Applies to replicate samples only.

Phase 2 - Treatability Tests

The selected source area runoff samples all had elevated toxicant concentrations, compared to the other urban source areas initially examined, allowing a wide range of laboratory partitioning and treatability analyses to be conducted. The treatability tests conducted were:

- Settling column (37 mm x 0.8 m Teflon™ column).
- Floatation (series of eight glass narrow neck 100 mL volumetric flasks).
- Screening and filtering (series of eleven stainless steel sieves, from 20 to 106 µm, and a 0.45 µm membrane filter).
- Photo-degradation (2 liter glass beaker with a 60 watt broad-band incandescent light placed 25 cm above the water, stirred with a magnetic stirrer with water temperature and evaporation rate also monitored).
- Aeration (the same beaker arrangement as above, without the light, but with filtered compressed air keeping the test solution supersaturated and well mixed).
- Photo-degradation and aeration combined (the same beaker arrangement as above, with compressed air, light, and stirrer).
- Undisturbed control sample (a sealed and covered glass jar at room temperature).

Because of the difficulty of obtaining large sample volumes from many of the source areas that were to be examined, these bench-scale tests were all designed to use small sample volumes (about one liter per test). Each test (except for filtration, which was an “instantaneous” test) was conducted over a duration of 3 d. Subsamples (40 mL each) were obtained for toxicity analyses at 0, 1, 2, 3, 6, 12, 24, 48, and 72 h. In addition, settling column samples were also obtained several times within the first hour, at: 1, 3, 5, 10, 15, 25, and 40 minutes.

Phase 2 - Results

The Microtox™ procedure allowed toxicity screening tests to be conducted on each sample partition during the treatment tests. This procedure enabled more than 900 toxicity tests to be made. Turbidity tests were also conducted on all samples.

Figures 3.1 to 3.24 (placed at end of chapter) are graphical data plots of the toxicity reductions observed during each treatment procedure examined, including the control measurements. These figures are grouped in threes for each treatment type. One group contains the treatment responses for the automobile service facility areas (samples B, C, E, and H), another group is for the industrial loading and parking areas (samples D, F, G, I, J, and K), and the last group is for the automobile salvage yards (samples L and M). These plots indicate the reduction in toxicity as the level of treatment increased. As an example, Figures 3.1 through 3.3 show three separate plots for the undisturbed samples undergoing very little change, except for samples F (which increased in toxicity with time) and C (which decreased in toxicity with time). In contrast, Figures 3.4 through 3.6 show the dramatic improvements available with plain physical settling. All samples, except for B, showed dramatic reductions in toxicity with increasing settling times. Even though the data are separated into these three groups, very few consistent differences are noted in the way the different sample types responded to various treatments. As expected, there are greater apparent differences between the treatment methods than between the sample groupings.

Table 3.2 summarizes results from the non-parametric Wilcoxon signed ranks test (using SYSTAT: The System for Statistics, Version 5, SYSTAT, Inc., Evanston, Ill.) for different treatment combinations. This statistical test indicates the two-sided probabilities that the sample groups are the same. A probability of 0.05, or less, is used to indicate significant differences in the data sets (indicated by bold italics in the table). As an example, Table 3.2 indicates that there were significant differences (probabilities of 0.02) for all of the treatment tests done on sample D (an extremely toxic sample), compared to the undisturbed control sample.

Table 3.2. Two-sided Probabilities Comparing Different Treatment Tests

	Auto. Service Area				Industrial Loading & Parking Area						Auto. Salvage	
Undisturbed versus:	B	C	E	H	D	F	G	I	J	K	L	M
settling	n/a	0.25	***0.02***	0.41	***0.02***	0.12	0.09	0.07	***0.01***	***0.01***	***0.02***	***0.02***
aeration	n/a	0.31	0.25	0.07	***0.02***	***0.05***	0.06	***0.04***	***0.01***	***0.01***	***0.02***	***0.03***
photodegradation	n/a	0.12	0.06	0.16	***0.02***	***0.04***	***0.03***	0.07	***0.01***	***0.01***	***0.02***	0.16
aeration & photodegradation.	n/a	0.35	0.24	0.06	***0.02***	***0.05***	***0.03***	0.09	***0.01***	***0.01***	***0.02***	0.09
flotation - top layer	n/a	n/a	0.74	***0.02***	***0.02***	***0.05***	0.13	***0.01***	***0.03***	0.21	***0.01***	0.09
flotation - mid. layer	n/a	n/a	0.31	0.87	***0.02***	0.78	***0.02***	0.26	0.16	0.17	0.59	0.89

The aeration test provided the most samples that had significant probabilities of being different from the control condition. Settling, photo-degradation, and aeration and photo-degradation combined, were similar in providing the next greatest number of samples that had significant probabilities of being different from the control condition. The floatation test had six samples that had significant differences in toxicity between the top floating layer and the control sample. However, the more important contrast between the middle sample layers (below the top floating layer) and the control sample, which would indicate a reduction in toxicity of post-treated water, had only two samples that were significantly different from the control sample.

The absolute magnitudes of toxicity reductions must also be considered. As an example, it may be significant, but unimportant, if a treatment test provided many (and therefore consistent) samples having statistically significant differences compared to the control sample, if the actual toxicity reductions were very small.

As shown on Figures 3.1 to 3.24, important reductions in toxicities were found during many of the treatment tests. The highest toxicant reductions were obtained by settling for at least 24 h (providing at least 50 percent reductions for all but 2 samples), screening through at least a 40 µm screen (20-70 percent reductions), and aeration and/or photo-degradation for at least 24 h (up to 80 percent reductions). Increased settling, aeration or photo-degradation times, and screening through finer meshes, all reduced sample toxicities further. The floatation tests produced floating sample layers that generally increased in toxicity with time and lower sample layers that generally decreased in toxicity with time, as expected; however, the benefits were quite small (less than 30 percent reductions). As shown on Table 3.2, only about 40% of the floatation test toxicity changes were statistically different from the variations found in the control samples.

These tests indicate the wide ranging behavior of these related samples for the different treatment tests. Some samples responded poorly to some tests, while other samples responded well to all of the treatment tests. Any practical application of these treatment unit processes would therefore require a treatment train approach, subjecting critical source area runoff to a combination of processes in order to obtain relatively consistent overall toxicant reduction benefits. The next three chapters describe a treatment train that was evaluated to reduce critical source area stormwater toxicity.

Figure 3.1 Toxicity reduction on control samples - industrial loading and parking areas.

Figure 3.2 Toxicity reduction on control samples - automobile service facilities.

Figure 3.3 Toxicity reduction on control samples - automobile salvage yards.

Figure 3.4 Toxicity reduction from settling treatment - industrial loading and parking areas.

Figure 3.5 Toxicity reduction from settling treatment - automobile service facilities.

Figure 3.6 Toxicity reduction from settling treatment - automobile salvage yards.

Figure 3.7 Toxicity reduction from aeration treatment - industrial loading and parking areas.

Figure 3.8 Toxicity reduction from aeration treatment - automobile service facilities.

Figure 3.9 Toxicity reduction from aeration treatment - automobile salvage yards.

Figure 3.10 Toxicity reduction from sieve treatment - industrial loading and parking areas.

Figure 3.11 Toxicity reduction from sieve treatment - automobile service facilities.

Figure 3.12 Toxicity reduction from sieve treatment - automobile salvage yards.

Figure 3.13 Toxicity reduction from photo-degradation treatment - industrial loading and parking areas.

Figure 3.14 Toxicity reduction from photo-degradation treatment - automobile service facilities.

Figure 3.15 Toxicity reduction from photo-degradation treatment - automobile salvage yards.

Figure 3.16 Toxicity reduction from aeration and photo-degradation treatment - industrial loading and parking areas.

Figure 3.17 Toxicity reduction from aeration and photo-degradation treatment - automobile service facilities.

Figure 3.18 Toxicity reduction from aeration and photo-degradation treatment - automobile salvage yards.

Figure 3.19 Toxicity reduction from floatation treatment (top layer samples) - industrial loading and parking areas.

Figure 3.20 Toxicity reduction from floatation treatment (top layer samples) - automobile service facilities.

Figure 3.21 Toxicity reduction from floatation treatment (top layer samples) - automobile salvage yards.

Figure 3.22 Toxicity reduction from floatation treatment (middle layer samples) - industrial loading and parking areas.

Figure 3.23 Toxicity reduction from floatation treatment (middle layer samples) - automobile service facilities.

Figure 3.24 Toxicity reduction from floatation treatment (middle layer samples) - automobile salvage yards.

Chapter 4
The Development of the MCTT

The information contained in this report can be used to develop new stormwater controls by selecting the most promising unit processes described during the bench-scale tests and applying them in unique combinations, or by adding them to currently utilized stormwater controls. This chapter presents one such application of this information in the development of the Multi-Chambered Treatment Train (MCTT).

Component of a comprehensive urban runoff control program typically include structural practices such as detention ponds, grass swales, infiltration trenches, and other physical devices. The goal of this research was to add additional tools to these other technologies. This research developed and evaluated the effectiveness of the MCTT for the treatment of stormwater toxicants at critical source areas. The target area for use of this particular device includes areas such as vehicle service facilities, parking areas, paved storage areas, and fueling stations. In prior studies and during the first phase of this research project (as summarized in Chapter 2), these areas were found to have some of the highest concentrations of toxicants compared to all source areas (Barron 1990; Pitt, *et al*. 1995). The MCTT device is especially suited for these locations as it is a subterranean unit consuming no land surface area. Space is extremely limited for these typically small areas and these critical source areas are therefore left with few alternatives.

The MCTT consists of three chambers:

1. a catchbasin (or grit chamber) for removal of large particles and litter,
2. a settling chamber for quiescent settling of fine settleable solids,
3. a sand-peat moss “filter” for final polishing.

Figure 4.1 shows a cross section of the MCTT. The catchbasin functions primarily as a protector for the other two units by removing large, grit-sized material. The setting chamber is the primary treatment chamber for removing settleable solids and associated constituents. The sand-peat filter is for final polishing of the effluent, using a combination of sorption and ion exchange for the removal of soluble pollutants, for example. During this research, testing of the pilot-scale MCTT at a typical critical source area found it to significantly reduce urban stormwater pollutants.

The remaining sections of this chapter briefly review oil and water separators, and the development of the MCTT. Chapter 5 presents the results of field trials of the MCTT as a pilot-scale unit in Birmingham., AL, plus as two full-sized units located in Wisconsin. Chapter 6 describes the general procedures for designing an MCTT.

Oil/water separators are discussed in the following section because of their common use in treating stormwater at critical source areas. Information provided from manufactures and from the literature is summarized to indicate their ability to treat stormwater. Several types of commercially available oil/water separators are reviewed in this chapter. Little documentation, however, was located describing the performance of conventional oil/water separators for stormwater treatment. Documentation was also limited as to the proper design and application of these devices for stormwater. These devices are typically used for treating process wastewaters, although some authors describe their use for stormwater treatment. Their short-comings in treating stormwater were a major incentive for the development of the MCTT. The MCTT is somewhat comparable to an oil/water separator, but with enhanced settling and with the addition of a mixed media filter.

Figure 4.1 MCTT cross section.

Oil/Water Separators

This report section briefly examines the most widely available oil/water separation technologies and their expected ability to treat stormwater. These devices include gravity separators (including API separators and separation vaults), coalescing plates separators, and cartridge filters added to oil/water separators. These devices are extensively used to treat industrial wastewaters and have been shown to be effective in those applications for which they were designed. Figure 4.2 summarizes the effectiveness of gravity oil/water separators. These units perform best at very high levels of oil contamination, such as may be found at some industrial locations. This figure shows about 90% reductions in oil, if the influent oil concentrations are greater than about 10,000 mg/L. Reductions of about 50% would occur at influent oil concentrations of about 200 mg/L. Very little reduction is expected at levels less than about 100 mg/L. Little information is available demonstrating their effectiveness in treating stormwater, which usually has oil contamination levels of much less than 100 mg/L.

Other oil/water reduction technologies are used in some industrial applications, including separation tanks (typically small tanks used in shops that produce very small wastewater flows), and centrifuge separators (which require high energy demands and high maintenance, and are utilized in off-shore drilling operations). Neither of these technologies would be appropriate for the diffuse locations and highly irregular stormwater flows from critical source areas and are therefore not addressed in this report.

Factors Relevant to Oil/Water Separator Performance

Many factors affect separator performance, including: the quantity of oil, oil density, water temperature and other wastestream characteristics. The most important characteristic affecting oil removal performance is oil droplet size, from which the critical rise rate can be determined. After determining the rise rate, design flow rate, and effective horizontal separation area, the separator can be appropriately sized.

Oil Droplet Size and Critical Rise Rate

Oil/water mixtures are usually divided into four categories:

- free-floating oil, with oil droplet sizes of 250 µm or more, is evidenced by an oil slick or film on the water surface. In this case, the oil has separated from the water.
- oil droplets and globules ranging in size from 10-300 µm. This range is the most important range when dealing with oil/water separation.
- emulsions, which have sizes in the 1-30 µm range, and
- "dissolved" oil with diameters of less than 10 µm.

The largest oil droplets are easily separated from water using a basic spill trap or separation device. Smaller droplets cause wide ranging differences in performance from different separation devices. Emulsions are of two types: stable and unstable. Stable emulsions are usually the result of surfactants (i.e. soaps and detergents) which hold the droplets in solution. This type of emulsion is often present in cleaning operations and can often be very difficult to remove. Unstable emulsions are created by shearing forces present in mixing: the oil is held in suspension when the interfacial tension of the drops' surface is equal to the force acting on the drops. These will generally separate by physical methods such as extended settling times or filtration methods. Oil/water separators are not able to treat stable emulsions or dissolved oil.

The American Petroleum Institute (API) suggests that the trapping of all oil droplets greater than 60 µm is an appropriate design goal for API oil/water separators (API 1990). The following example was presented by the Local Hazardous Waste Management Program in King County, Washington. The first step is to obtain the oil droplet size distribution, by volume. Droplet size determinations can be made using several techniques, including using a Coulter Counter, manual counting, or using a laser particle counter. The Coulter LS230 is an appropriate laser particle counter, while the Coulter Multi-Sizer IIe measures the oil droplets by sensing their effects on an electrical field. Table 4.1 shows a size distribution of droplets. If the goal is 95% oil reduction, by volume, then all droplets greater than 30 µm should be removed. If the goal was only 65% control, then the critical drop size would be only 90 µm. The critical rise rate (V_T) can be calculated for the critical drop size using Stokes' law and used to select the

Figure 4.2 Performance of API oil/water separators (API 1990).

most appropriate oil/water separator design. The relationship between the number of droplets and the volume of oil is given in the following equation:

$$\text{Volume of Oil} = (\text{number of droplets}) * (\pi/6) * (\text{diameter of droplets})^3$$

Table 4.1. Example Oil Droplet Size Distribution (Source: King Co. 1995)

Drop Diameter (µm)	% in Size Range (by count)	% in Size Range (by volume)
<30	10	<1
31 - 60	40	5
60 - 90	30	30
90 - 120	15	45
>120	5	20

Design Flow Rate

The efficiency of a separator also depends upon the flow rate: as the flow increases, the separator performance decreases. Therefore, a separator must be designed to accommodate the maximum expected flow for a given rainfall event.

Effective Horizontal Separation Area

Once the critical rise-rate and maximum flow have been determined, the effective horizontal area is calculated from the equation $A_H = Q/V_T$. This formula, also known as Hazen's principle, is commonly used in oil/water separator design. Often, large areas are required for effective separation. However, stacked coalescing plates can be used to create the necessary separator area in a limited space.

Other Considerations

Selecting the critical (or design) density of oil is another relevant factor in the design of an oil/water separator. The heaviest oil presumed to be present is used in determining the critical rise velocity. In general, densities range from 0.82-0.95. The separator will be most efficient for the lowest oil densities.

Water temperature also affects oil/water separator performance. At lower temperatures, separation becomes more difficult, and therefore, the lowest temperature routinely encountered should be used in the design. Ambient ground temperatures a few meters below the surface can be used to estimate water temperatures for an underground installation. Also, ambient air temperatures during cooler weather can be used. Highland Tank suggests a conservative value within the 5 – 15°C (40 – 60° F) range, unless actual testing indicates that another value should be used.

The solids content of the wastewater must also be considered for separator design. After the basic dimensions of the separator have been calculated, sufficient volume within the separator must be added for solids storage between cleanings. However, the exact amount of solids that may accumulate is not as important as the knowledge that they do enter the system and that one must design for their removal from the separator (Highland Tank). Therefore, a proper design should include not only the needed storage volumes for both hydrocarbons and solids, but also adequate access so that proper monitoring and cleaning may occur.

Gravity Separation

Gravity separation relies on the density differences between oil and water. Oil will rise to the water surface unless some other contributing factor such as a solvent or detergent interferes with the process. For gravity units, this density difference is the only mechanism by which separation occurs. Other technologies, such as air flotation, coalescing plates, and impingement coalescing filters, enhance the separation process by mechanical means.

Gravity separators are the most basic type of separator and are the most widely used. They have few, if any, moving parts and require little maintenance with regard to the structure or operation of the device. Usually, separators are designed to meet the criteria of the American Petroleum Institute (API), and are fitted with other devices such as coalescing plate interceptors (CPI) and filters. Even though these separators are effective in removing free and unstable oil emulsions, they are ineffective in removing most emulsions and soluble oil fractions (Ford 1978). Furthermore, it is important to remember that no gravity oil/water separation device will have a significant impact on many of the other important stormwater pollutants, requiring additional treatment (Highland Tank).

Conventional American Petroleum Institute (API) Oil/Water Separator

The conventional API oil/water separator consists of a large chamber divided by baffles into three sections. The first chamber acts as an equalization chamber where grit and larger solids settle and turbulent flow slows before entering the main separation chamber (Figure 4.3).

Figure 4.3 API oil/water separator (API 1990).

Often, manufacturers suggest the use of a catchbasin or interceptor tank as a pretreatment device so that coarse material will be kept from entering the oil/water separation tank. After entering the main chamber, solids settle to the bottom and oil rises to the top, according to Stokes' law. Larger API oil/water separators contain a sludge scraper which continually removes the captured settled solids into a sludge pit. The oil is also removed by an oil skimmer operating on the water surface. At the end of the separation chamber, all oil particles having a diameter of larger than the critical size have theoretically risen to the surface and have been removed by an oil skimmer. Small API units usually do not contain an oil skimmer, sludge scrapper, or sludge pit. While they are less costly due to the absence of moving parts, they require more frequent cleaning and maintenance. These smaller units have been shown to be as effective as the larger more expensive units, if they receive proper maintenance at regular intervals.

The API has developed a process by which to design a separator. The following steps describe this process with Figure 4.3 used as a reference:

1. Determine the droplet rise velocity (V_T) of the critical droplet size using Stokes' Law:

$$V_T = (g/18\mu)*(\rho_w - \rho_o)*d^2$$

Where:

V_T = rising velocity (terminal velocity) of oil droplets (cm/sec or ft/s)
g = acceleration due to gravity (cm/sec^2 or ft/s^2)
μ = absolute viscosity of water (g/cm·s or lb$_m$/ft·s)
ρ_w = density of water (g/cm^3 or lbm/ft^3)
ρ_o = density of oil (g/cm^3 or lbm/ft^3)
d = droplet diameter (cm or ft)

2. Calculate the design horizontal velocity (V_H) using the following equation:

$$V_H = 15\ V_T \quad \leq 3 \text{ ft/min}$$

Where:

V_H = horizontal velocity (cm/s or ft/s)

If the calculated velocity is greater than 3 ft/min, then 3 ft/min is used as the appropriate design value.

3. Calculate the minimum vertical cross-sectional area (A_V) using the following equation while using a value for flow rate (Q) that reflects the maximum expected flow:

$$A_V = Q/V_H$$

4. Calculate the channel width (W) and height (H) using the following equation:

$$A_V = H \times W$$

The values H and W will need to conform to the following restraints:

- The depth (d) of the wastewater should be 0.9 – 2.8 m (3 – 8 ft).

- The width (B) of the chamber should be 1.8 – 6.1 m (6 – 20 ft).
- The ratio of depth (d) to width (B) should be 0.3 – 0.5.

Highland Tank notes that these values, as well as the values for horizontal velocity, have a practical basis in that they attempt to limit turbulence within the separation zone and provide a reasonable depth for maintenance while considering construction costs.

5. Calculate the main chamber length (L) using the following equation:

$$L = F * (V_{H)})/(V_T)* H \qquad \geq 5W$$

F is a turbulence and short-circuiting factor, and serves as a correction factor which allows for less than ideal performance. F is a function of V_H and V_T. Values of F are found in American Petroleum Institute publication number 421 (Table 4.2).

Table 4.2. Short-Circuiting Factor (Source: API 1990)

V_H/ V_T	F
20	1.74
15	1.64
10	1.52
6	1.37
3	1.28

6. Finally, the design calculations are checked to see that the actual horizontal surface area is greater that the minimum horizontal area (A_H). If A_H is greater that the actual surface area, then steps 3 through 5 are repeated with different assumptions about height and width. A_H is found by the following equation:

$$A_H = F \times (Q/V_T)$$

The API (1990) stipulates that if these design criteria are met, then the separator will remove all oil droplets greater than about 150 µm in diameter. The API reports that retention times are usually greater than the actual design values since actual flows are usually smaller than design flows, hence smaller droplets are removed most of the time. This finding is confirmed by Ruperd (1993) in a study of an oil/water separator treatment device in the community of Velizy, France. Also, API tanks are known to effectively remove large amounts of oil, including slugs of pure oil, and will not be overwhelmed (Tramier 1983). Studies have also shown that these separators can produce effluents down to 30 ppm (Delaine 1995), routinely at 30-150 ppm, with occasional concentrations above 150 ppm, depending upon the flow rate, and hence the retention times (Ford 1978).

The API has stated that very few separators with ratios of surface area to flow within the API design range achieved effluent oil concentrations lower that 100 ppm (API 1990). Therefore, the API separator is a recommended system for the removal of solids and gross oil as a pretreatment device upstream of another treatment system, if additional pollutants of concern are present, or if more stringent effluent standards are to be met.

The following is a partial list of oil/water separator manufacturers in the U.S.:

- Highland Tank and Manufacturing Co., One Highland, Rd. Stoystown, PA 15563

- McTighe Industries, P.O. Box 928, Mitchell, SD 57301-0928
- Xerxes Corp., 7901 Xerxes Rd. Minneapolis, MN 55431-1253

Separation Vaults

Separation vaults are variations on the API oil/water separator design. They are usually either septic tanks or utility vaults that have been fitted with baffles in the manner of an API separator. They are usually poured in place or manufactured locally. Surveys of these vaults in King County, Washington, revealed that they had main chamber depths of 1.2 – 1.5 m (4 – 5 ft), widths of 1.2 – 1.8 m (4 – 6 ft), and lengths of about 1.8 m (6 ft). These vaults are not necessarily designed according to the previously stated API methods and therefore are termed separation vaults to differentiate them from conventional API oil/water separators (King County 1995).

These vaults can theoretically achieve removal of all oil droplets of 75 µm in size, or greater. The following example is from the Local Hazardous Waste Management Program of King County, Washington. A truck maintenance facility utilizes a separation vault with a depth of 1.2 m (4 ft), width of 1.5 m (5 ft), and an effective length of 1.5 m (5 ft), and which receives runoff at a flow of 0.6 L/s (10 gpm, or 0.02 ft^3/s) from the shop floor and washing pad. It is assumed that the runoff consists of non-emulsified oil and solids. The retention time is therefore 4,500 s (75 min). If the rising time is equal to the retention time ($T_{oil} = T_{water}$), then the critical droplet diameter is found from the following equation:

$$d_{crit} = \{[18\mu H] / [g(\rho_{water} - \rho_{oil})T_{water}]\}^{0.5}$$

This results in a critical droplet size of 75 µm under ideal conditions. This is smaller than the API standard of 150 µm; however, the API separators have been shown to remove particles down to 30 µm under ideal conditions and the value of 150 µm represents what would normally be achieved under practical applications. Here the 75 µm represents an ideal condition; practical removal sizes would probably be in excess of 150 µm.

Coalescing Plate Interceptor Oil/Water Separators

The coalescing plate interceptor (CPI) oil/water separators are simply conventional API oil/water separators and separator vaults with sets of parallel plates added to the main separation chamber. As small droplets of oil enter the plates, they rise until they encounter the next plate. Other drops also rise and coalesce. As the drops become larger, the buoyant forces acting on them become greater, eventually forcing the drops to slide off the plates and to rise quickly to the surface.

The total horizontal separator area requirement is reduced by the use of parallel plates by compacting the effective separation area into a limited space. The total area is the sum of the area of each plate projected on the horizontal plane, along with the open surface area of the separator itself. According to vendors, the use of coalescing plates can reduce spatial requirements of separators up to two-fold on width and ten-fold on length when used in place of a conventional separator without plates. Plates also help to dampen turbulence in the system, thus helping to maintain laminar flow. Oil collected from these systems has a lower water content than from conventional separators. The overall effluent oil content has been reported to be 60% lower for parallel-plate systems, with a higher proportion of small oil droplets recovered (Brunsmann 1962).

The earliest models of CPI separators used horizontal parallel plates. Currently, two types of parallel-plate separators are marketed: the cross-flow inclined plate separator and the down-flow inclined plate separator. Figure 4.4 is a drawing of a downflow parallel plate separator. In the cross-flow separator, flow enters the plates from the side and oil and sludge accumulates above and below the current. As oil and sludge build up, the oil then breaks free and rises, while the sludge descends to the separator bottom. In a down-flow separator, the water flows downward while oil rises to the above plate, and after coalescence, rises counter to the current to the top, while sludge will descend, helped along by the current.

The plates themselves are corrugated to improve oil and sludge collection. Vertical gutters are placed along the sides of the plates themselves at the influent and effluent points to aid in the collection of oils and solids. The plates are tilted at an angle of 45° - 60°, allowing sludge and oil to slide off , preventing clogging and resulting in lower maintenance requirements. A 45° angle has been found to be most effective for oil removal (Thanh and Thipsuwan 1978), but a 60° angle would reduce maintenance requirements further by insuring less clogging. However, a greater angle would also reduce the effective surface area as the effective surface is equal to the projection of the plates onto the horizontal plane (Branion 1978).

Typical sizes for CPI oil/water separators are shown in the Table 4.3. As shown, the spacing between plates usually ranges from 20 – 40 mm (0.75 – 1.5 in.). However, Dull (1984) found that the optimum distance is 20 mm (3/4 in.), based on practical experience. Spacings 13 mm (1/2 in.) and less are prone to clogging and require intensive maintenance. Wider spacings, of up to 50 mm (2 in.) are occasionally used, but this limits the number of plates that can be placed in a separator, thereby decreasing its effectiveness.

Figure 4.4 Downflow parallel plate separator (API 1990).

Table 4.3. Characteristics of coalescing plate interceptor separators (Source: API 1990)

Characteristic	Range
Perpendicular distance between plates	0.75 - 1.5 inches
Angle of plate inclination from the horizontal	45°- 60°
Types of oil removed	free oil only
Direction of wastewater flow	cross-flow, or down-flow

CPI separators have been found to remove droplets down to 30 to 60 μm size (Ryan 1986; Romano 1990), and have been found to produce effluent concentrations in the range of 10 to 20 ppm (Delaine 1995; Dull 1984; Ryan 1986). CPI separators are a good treatment choice if the wastewater contains smaller droplets and possibly some unstable emulsions with larger diameter droplet sizes. Dissolved oil, stable emulsions, or a large amount of unstable emulsions would decrease the performance of the coalescing plate interceptor separators.

The API notes that it is difficult to describe the separation process in a parallel plate separator due to the variability of plate size, spacing, and inclination. They recommend that users rely on the empirically-derived recommendations of the plate unit vendors when selecting a coalescing plate interceptor separator.

Impingement Coalescers and Filtration Devices

Filtration devices are used as post-treatment after separation in coalescing plate separators, and greatly improves the removal efficiency of a system. Many systems utilize these devices for treatment of industrial runoff; however, they are occasionally used in stormwater applications as well (Aires 1995). The most common type used is a vertical tube coalescer which has a random matrix of vertical tubes made of polypropylene fitted together in bundles. These bundles are placed towards the end of the separation tank before the outlet and after the coalescing plates; however, some manufacturers use these devices in place of plate systems. Oleophilic (oil-loving) filters provide a maximum coalescing surface, as well as helping to create a more laminar flow. These types of devices can provide better oil removal than a tank fitted only with coalescing plates, often with effluents suitable for direct discharge into surface waters.

Solids are trapped in sharp turns or crevices while oils are removed by two mechanisms occurring within the filters. First, the small passages in the filters allow the oil droplets to come in contact with each other and coalesce together. Second, the oleophilic properties of the media attract oil droplets and hold them until they coalesce with other trapped droplets until they eventually break free and rise to the surface.

The cartridge bundles can be removed and cleaned for reuse, although disposable filters are sometimes used. Disposable cartridge filters have the benefit of having simple maintenance requirements: when filters become clogged or saturated, they are simply removed and discarded. However, this process in itself may be a drawback in that the cartridges may need to be disposed of as a hazardous waste. Further, the cost of filters may be high and quickly reduce any benefit gained from reduced maintenance. Filters are typically made from fiberglass, nylon, polypropylene, and polyurethane foam; and are normally recommended as a secondary stage of treatment after gross solids and oil have been removed (Webb 1991).

Other problems exist with filter cartridges as well. Filters are easily clogged, even when pretreatment occurs. Also, if stable emulsions are present, surfactants will poison the filter by interfering with the surface-wetting properties of the filter (Tabakin, *et al*. 1978). Despite these problems, filters are known to remove oil to concentrations as low as 10 ppm, with all droplets greater than 20 μm being removed (Xerxes Corp).

Maintenance of Oil/Water Separators

Problems with oil/water separators can be attributed largely to poor maintenance by allowing waste materials to accumulate in the system to levels that hinder performance and to levels that can be readily scoured during intermittent high flows. When excess oil accumulates, it will be forced around the oil retention baffle and make its way into the discharge stream. Also, sludge buildup is a major reason for failure. As waste builds up, the volume in the chamber above the sludge layer is reduced and therefore the retention time is also reduced, allowing oil to be discharged. Therefore, the efficiency of oil/water separators in trapping and retaining solids and hydrocarbons depends largely upon how they are maintained. They must be designed for ease of maintenance and be frequently maintained. Apparently, few oil/water separators built for stormwater control are adequately maintained.

Manufacturers of prefabricated oil/water separators, as well as the American Petroleum Institute, all recommend periodic inspection and maintenance. Some manufacturers advise that these devices be cleaned twice per year, even if the device is apparently working properly. However, it is best if the devices are inspected after every rainfall to determine the rate of hydrocarbon and sludge buildup. The most effective maintenance schedule can then be obtained for each individual device. French researchers also advocate this approach, by developing individual maintenance schedules after intensive observations for six months (Aires 1995).

Ease of maintenance must be considered when designing separators, including providing easy access. Maintenance on these devices is accomplished by using suction equipment, such as a truck mounted vacuum utilized by personnel trained to handle potentially hazardous waste. The vacuum is used to skim off the top oil layer and the device is then drained. In larger devices, the corrugated plates are left in place, but otherwise, they are lifted out along with any other filter devices that are present. The sludge is then vacuumed out or shoveled out and any remaining solids are loosened by spraying hot water at normal pressure.

Maintenance of parallel plate units and coalescing filters is similar. The separator is drained and the plates are washed by spraying. If there is inadequate space, then the plates will need to be lifted from the separator for effective cleaning. Cleaning should occur when coating of the plates is evident and before accumulations begin to clog the spaces. Cleaning of polypropylene coalescing tubes is also accomplished by lifting out the tube bundles and cleaning with a hose or high pressure water spray to remove accumulated oil and grit. Sludge is removed from underneath the coalescer supports and the coalescers are then replaced. No soaps or detergents are used in cleaning polypropylene components as they would destroy the oleophilic nature of the material.

Performance of Oil/Water Separators for Treating Stormwater

Manufacturers state that efficiencies observed during testing of oil/water separators are on the order of 97 – 99% for the removal of oil from wastewater. The test method typically applies oil to a paved washpad, with water added via a sprinkler system to simulate rainfall. Oil is of a specified density (typically 0.72 – 0.95). These synthetic events are necessary to evaluate the performance of a separator but do not necessarily reflect the processes which occur during actual rainfall conditions where rapidly changing flows rates, unknown oil mixtures, and other pollutants are present. Published research is difficult to find on how these units actually perform once placed in operation.

Interception of solid particles through settling, and flotation of oils and other floatables are processes occurring within an oil/water separator. French studies have shown that the average SS removal efficiency of separators is about 50% (Aires 1995). Oil/water separation requires an ascending speed of about 8 m/h, while the settling velocity of solids require descending velocities on the order of 1 to 3 m/h. At rates of 20% of the design flow rate, about 80% of the solids are removed; at 30% of the design flow rate, about 50% of the solids are removed. Negative removals also occur as the result of resuspension of previously settled material (Legrand, *et al*. 1994).

In many instances, pretreatment tanks are placed before the oil/water separator to remove settleable solids before stormwater enters the separator. A study in Velizy, France, found that the SS removal efficiency of a separator, placed downstream of a settling pond, was about 13%. This low value was attributed to the fact that solids had been allowed to settle during pretreatment, and therefore influent to the device had a low content of only the most difficult to remove solids (Ruperd 1993).

When the concentration of the oil in the wastewater is high, the oil removal efficiency increases. In Velizy, France, Ruperd (1993) found that oil/water separators fitted with cross current separators had removal efficiencies ranging from zero to 90%, with an average of 47%. Low efficiencies were associated with low influent levels and greater efficiencies were associated with higher influent levels. This finding supports those of Tramier (1983), stated earlier, that separators are effective in removing large amounts of oil when the oil concentrations are elevated.

The Metropolitan Washington Council of Governments (Washington, D.C.) has conducted a survey of 109 separator vaults in suburban Maryland and subsequently examined 17 in detail to determine their long-term effectiveness (Schueler and Shepp 1993). These separators were used for controlling runoff from areas associated with automobile usage. These separators were either pre-cast or poured in place concrete structures consisting of one, two or three chambers. The results of this study revealed that the amount of trapped sediments within separators varied from month to month and that the contained waters were commonly completely displaced during even minor storms (Shepp and Cole 1992). Figure 4.5 shows the variability in average sediment depth with time for these 17 separators.

Figure 4.5 Monthly changes in sediment in 17 oil/water separators (Schueler and Shepp 1993).

Of the original 109 separators that were observed in the survey, devices less than one year old were effective in trapping sediments. Devices older than one year appeared to lose as much sediment than they retained (Shepp and Cole 1992). Not one of these separators had received maintenance since their installation. Survey observations suggested no net accumulation of sediment over time, in part because they received strong variations in flow. Of the 109 separators surveyed in this suburban Maryland study, 100% had received no maintenance, 1% needed structural repair, 6% were observed to have clogged trash racks, 84% contained high oil concentrations in the sediments trapped in their first chamber, 77% contained high oil concentrations in the sediments trapped in their second chambers, 27% contained high oil and floatables loading in their first chambers, and 23% contained high oil and floatables loading in their second chambers.

Numerous manufacturers have developed small prefabricated separators to remove oils and solids from runoff. These separators are rarely specifically designed and sized for stormwater discharges, but usually consist of modified oil/water separators. Solids are intended to settle and oils are intended to rise within these separators, either by free fall/rise or by counter-current or cross-current lamella separation. Many of these separators have been installed in France, especially along highways (Rupperd 1993). Despite the number of installations, few studies have been carried out in order to assess their efficiency (Aires and Tabuchi 1995).

The historical use of oil/water separators to treat stormwater has been shown to be ineffective for various reasons, especially lack of maintenance and poor design for the relatively low levels of oils present in most stormwaters (Schueler 1994). Stormwater treatment test results from Fourage (1992), Rupperd (1993) and Legrand, *et al*. (1994) show that these devices are usually greatly under-sized. They may possibly work reasonably well at flow rates between 20 and 30% of their published design hydraulic capacities. For higher flow rates, the flow is very turbulent (the Reynolds numbers can be higher than 6000), and improvements in settling by using lamella plates is very poor. These devices need to be cleaned very frequently. If they are not cleaned, the deposits are scoured during storm events, with negative efficiencies. However, the cleaning is usually manually conducted, and expensive. In addition, the maintenance job is not very easy because the separators are very small. Some new devices are equipped with automatic sediment extraction pumps which should be a significant improvement. Currently, these researchers have found that the cleaning frequencies are very insufficient and the stormwater quality benefits from using oil/water separators are very limited.

The Multi-Chambered Treatment Train (MCTT)

Phase 3 - Field Demonstrations of the Multi-Chambered Treatment Train

The Multi-Chambered Treatment Train (MCTT) was developed to specifically address many of the previously stated problems found for oil/water separators used for stormwater treatment at critical source areas. It was developed and tested with specific stormwater conditions in mind, plus it has been tested at several sizes for the reduction of stormwater pollutants of concern. The MCTT is intended to reduce organic and metallic toxicants, plus suspended solids, in the stormwater. Oil/water separators are intended to reduce very large concentrations of floating oils that may be present in industrial wastewaters . The extremely high concentrations of oils that the oil/water separators are most effective in removing are very rare in stormwater, even from critical source areas. If a site has these high levels, then an oil/water separator may be needed, in addition to other controls to reduce the other critical pollutants likely present. The MCTT can remove the typically highest levels of oils that may be present in stormwater from most critical source areas, plus also providing control of the trace toxicants present.

Earlier bench scale treatability studies conducted during this research (Chapter 3) found that the most beneficial treatment for the reduction of stormwater toxicants (as measured using the Microtox™ test) included quiescent settling for at least 24 h (generally 40% to 90% reductions), screening through at least 40 µm screens (20% to 70% reductions), and aeration and/or photo-degradation for at least 24 h (up to 80% reductions). These processes were combined in the MCTT. The MCTT contains aeration, sedimentation, sorption, and sand-peat (or other media) filtration and has been shown to provide excellent toxicant reductions.

The third research phase of this project included pilot- and full-scale tests of the MCTT. A pilot-scale MCTT treatment device was installed at a large parking lot and vehicle maintenance area in Birmingham, AL, on the University of Alabama at Birmingham campus. In addition, the state of Wisconsin Department of Natural Resources (WI DNR) (in conjunction with Region V of EPA, the USGS, and the affected cities) installed full-scale MCTT units at a public works yard in Milwaukee and at a city parking area in Minocqua. These full-scale tests are still in progress, with preliminary results summarized in this report.

The MCTT is most suitable for use at relatively small and isolated paved critical source areas, from about 0.1 to 1 ha (0.25 to 2.5 acre) in area. These areas include vehicle service facilities (gas stations, car washes, oil change stores, etc.), convenience store parking areas and areas used for equipment storage, along with salvage yards. The MCTT is an underground device that has three main chambers: an initial grit chamber for reduction of the largest sediment and most volatile materials; a main settling chamber (containing initial aeration and sorbent pillows) for the trapping of fine sediment and associated toxicants and floating hydrocarbons; and a sand and peat mixed media sorption/ion exchange unit for the removal of filterable toxicants. A typical MCTT requires between 0.5 and 1.5 percent of the paved drainage area, which is about 1/3 of the area required for a well designed wet detention pond.

A pilot-scale MCTT was constructed in Birmingham, AL, and tested over a six month monitoring period, from May to October, 1994. Two additional full-scale MCTT units have recently been constructed and are currently being monitored as part of Wisconsin's 319 grant from the U.S. EPA. Complete organic and metallic toxicant analyses, in addition to conventional pollutants, were included in the analysis program. During monitoring of 13 storms at a parking facility, the Birmingham pilot-scale MCTT was found to have the following overall median reduction rates: 96% for total toxicity (as measured using the Microtox™ screening test), 98% for filtered toxicity, 83% for SS, 60% for COD, 40% for turbidity, 100% for lead, 91% for zinc, 100% for n-Nitro-di-n-proplamine, 100% for pyrene, and 99% for bis (2-ethyl hexyl) phthalate. The color was increased by about 50% due to staining from the peat and the pH decreased by about one-half pH unit, also from the peat media. Ammonia nitrogen was increased by several times, and nitrate nitrogen had very low reductions (about 14%). The MCTT therefore operated as intended: it had very effective reduction rates for both filtered and particulate stormwater toxicants and SS. Increased filterable toxicant reductions were obtained in the peat/sand mixed media sorption/ion exchange chamber, at the expense of increased color, lowered pH, and depressed COD and nitrate reduction rates. The preliminary full-scale test results substantiate the excellent reductions found during the pilot-scale tests, while showing better control of COD and nutrients and less detrimental effects on pH and color. The test results are discussed later in more detail.

Development of the MCTT

The MCTT includes a catchbasin/grit chamber followed by a two chambered tank that is intended to reduce a broad range of toxicants (volatile, particulate, and dissolved). The runoff enters the catchbasin chamber by passing over a flash aerator (small column packing balls with counter-current air flow) to remove highly volatile components, if present, and to capture large debris (such as plastic bags and litter). This catchbasin also serves as a grit chamber to remove the largest (fastest settling) particles. The second chamber serves as an enhanced settling chamber to remove smaller particles and has inclined tube or plate settlers to enhance sedimentation. The tube or plate settlers are mostly used to prevent scour of deposited small particles. This chamber also contains fine bubble diffusers and sorbent pads to further enhance the removal of floatable hydrocarbons and additional volatile compounds. The water is then pumped to the final chamber at a slow rate to maximize pollutant reductions. The final chamber contains a mixed media (usually sand and peat) slow filter (sorption/ion exchange) device, with a filter fabric top layer. The MCTT is typically sized to totally contain all of the runoff from a 6 to 20 mm (0.25 to 0.8 in) rain, depending on interevent time, rain size, and rain intensity patterns for the site.

The treatability and source area information previously described in this report can be used to develop other source area or outfall stormwater controls. As an example, it would be relatively easy to enhance the performance of typical wet detention ponds by adding some of the unit processes investigated. The most important control process would be to enhance the capture of small particles. In addition, water circulation and aeration may also enhance toxicant control by better utilizing photo-degradation and aeration processes. Care obviously needs to be taken to minimize scour of the deposited sediments. Conventional aeration design usually results in a circulation and aeration system than would have about 1/10 of the energy requirements needed for bottom scour. Subsurface discharges would also be an important addition in a wet detention pond to maximize capture of floatable debris and oils. Obviously, many other small units like the MCTT can be conceived and used for stormwater control at critical areas also. Typical goals would be to use a treatment unit having redundant processes, is easy to maintain, is robust for the changing conditions expected, and has the least cost possible for the needed level of stormwater control.

Catchbasin/Grit Chamber

Catchbasins have been found to be effective in removing coarser runoff solids. Moderate reductions in total and suspended solids (SS) (up to 45%, depending on the inflowing water rate) have been indicated by prior studies (Lager, *et al*. 1977, Aronson, *et al*. 1983, Pitt 1979, and Pitt 1985). While relatively few pollutants are associated with these coarser solids, their removal decreases maintenance problems of the other MCTT chambers.

Pitt, *et al*. (1997) (another volume in this series) recently evaluated three storm drain inlet designs in Stafford Township, New Jersey: a conventional catchbasin with a sump, and two representative designs that used filter fabric material. The inlet devices were located in a residential area. Twelve storms were evaluated for each of the three inlet units by taking grab composite samples using a dipper sampler throughout the events. Influent and effluent samples were analyzed for a broad range of conventional pollutants, metals, and organic toxicants, both in total and filtered forms. The catchbasin with the sump was the only device that showed important and significant removals for several pollutants:

> total solids (0 to 50%, average 22%).
> suspended solids (0 to 55%, average 32%).
> turbidity (0 to 65%, average 38%).
> color (0 to 50%, average 24%).

The MCTT catchbasin/grit chamber design is based upon a recommended design from previous studies of catchbasins. This design suggests using a circular catchbasin with the diameter 4 times the diameter of the circular outlet. The outlet is then placed 1.5 times its diameter from the top and 4 times its diameter from the bottom of the catchbasin, thus providing a total depth of 6.5 times the outlet diameter (Lager, *et al*. 1977 and Aronson, *et al*. 1983). The size of the MCTT catchbasin is controlled by three factors: the runoff flow rate, the SS concentration in the runoff, and the desired frequency at which the catchbasin will be cleaned so as not to sacrifice efficiency.

Main Settling Chamber

The main settling chamber mimics the completely mixed settling column bench-scale tests previously conducted and uses a hydraulic loading rate (depth to time ratio) for removal estimates. This loading rate is equivalent to the conventional surface overflow rate (SOR), or upflow velocity, for continuous-flow systems, or the ratio of water depth to detention time for static systems. The MCTT can be operated in both modes. If it uses an orifice, to control the settling chamber outflow, then it operates in a similar mode to a conventional wet detention pond and the rate is the upflow velocity (the instantaneous outflow divided by the surface area of the tank). If the outflow is controlled with a float switch and a pump, then it operates as a static system and the hydraulic loading rate is simply the tank depth divided by the settling time before the pump switches on to remove the settled water. The following discussion describes the development of the this conventional settling tank design parameter.

Upflow Velocity

Linsley and Franzini (1964) stated that in order to get a fairly high percentage removal of particulates, it is necessary that a sedimentation tank be properly designed. In an ideal system, particles that do not settle below the bottom of the tank's outlet will pass through the sedimentation tank, while particles that do settle below/before the outlet will be retained. In the MCTT, the retention of the settled material is enhanced through the use of the inclined tube settlers which prevent scouring velocities from re-suspending previously settled particles.

The path of any particle is the vector sum of the water velocity (V) passing through the tank and the particle settling velocity (v). Therefore, if the water velocity is slow, slowly falling particles can be retained. If the water velocity is fast, then only the heaviest (fastest falling) particles are likely to be retained. The critical ratio of water velocity to particle settling velocity must therefore be equal to the ratio of the sedimentation tank length (L) to depth to the bottom of the outlet (D):

$$\frac{V}{v}=\frac{L}{D}$$

as shown on Figure 4.6.

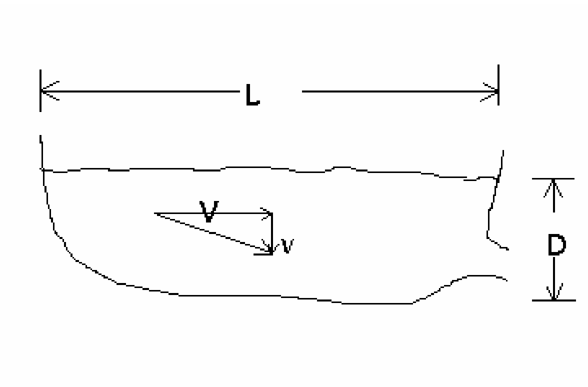

Figure 4.6. Critical Velocity and Settling Tank Dimensions

The water velocity is equal to the discharge rate (Q, such as measured by cubic feet per second) divided by the tank cross-sectional area (a, or depth times width: DW):

$$V = \frac{Q}{a}$$

or

$$V = \frac{Q}{DW}$$

The tank outflow rate equals the tank inflow rate under steady state conditions. The critical time period for steady state conditions is the time of travel from the inlet to the outlet. During critical portions of a storm, the inflow rate (Q_{in}) will be greater than the outflow rate (Q_{out}) due to freeboard storage. The outflow rate is therefore less and controls the water velocity through the tank. By substituting this definition of water velocity into the critical ratio:

$$\frac{Q_{out}}{WDv} = \frac{L}{D}$$

The water depth to the outlet bottom (D) cancels out, leaving:

$$\frac{Q_{out}}{Wv} = L$$

Or

$$\frac{Q_{out}}{v} = LW$$

However, tank length (L) times tank width (W) equals tank surface area (A). Substituting leaves:

$$\frac{Q_{out}}{v} = A$$

and the definition of upflow velocity:

$$v = \frac{Q_{out}}{A}$$

where Q_{out} = tank outflow rate (cubic feet per second),
A = tank surface area (square feet: tank length times tank width), and
v = upflow velocity, or critical particle settling velocity (feet per second).

Therefore, for an ideal sedimentation tank, particles having settling velocities less than this upflow velocity will be removed. Only increasing the surface area, or decreasing the tank outflow rate, will increase particle settling efficiency. Increasing the tank depth lessens the possibility of bottom scour. Deeper tanks may also be needed to provide sacrificial storage volumes for sediment between sediment removal operations.

For slowly changing flow conditions (such as when quiescent settling is provided in the MCTT by a pump and float switch), the following relationships can be shown:

$$t = \frac{Volume}{Flow\ rate}$$

and

$$Flow\ rate\,(Q_{out}) = \frac{Volume}{t}$$

where t = hydraulic detention (residence) time. With

$$v = \frac{Q_{out}}{A}$$

and substituting:

$$v = \frac{Volume}{(t)(A)}$$

but

$$Volume = (A)(depth)$$

therefore,

$$v = \frac{(A)(depth)}{(t)(A)}$$

leaving:

$$v = \frac{depth}{t}$$

It is seen that the overflow rate (Q/A) is equivalent to the ratio of tank depth to detention time, not just detention time alone. Therefore, the MCTT main settling tank can be sized and evaluated using either of these methods. A continuous simulation computer model, presented later, used this relationship to develop storage/treatment design curves for many U.S. cities.

In addition to housing plate or tube settlers, the main settling chamber also contains floating sorbent "pillows" to trap floating oils and a fine bubble aerator that operates during the filling time of the MCTT. Plate settlers (or inclined tubes) increase solids removal by reducing the distance particles travel to the chamber floor and by reducing scour potential. Plate settler theory is described by Davis, *et al*.(1989). The main settling chamber operates much like a settling tank, as described above, but with the plate settlers increasing the effective surface area of the tank. The increase in performance is based on the number of plate diagonals crossing the vertical. If the plates are relatively flat and close together, the increase in performance is greater than if the plates are steeper and wider apart. The effective increase is usually about 3 to 5 fold.

The fine bubble aerator serves two functions: to support aerobic conditions in the settling chamber and to provide dissolved air flotation of particles. Aeration was used during the pilot-scale MCTT tests, but was not used during the full-scale Wisconsin MCTT tests. Flotation has been utilized in industrial applications and combined sewer overflow studies (Gupta, *et al*. 1977). The settling time in the main settling chamber typically ranges from 1 to 3 d, and the settling depth typically ranges from 0.6 to 2.7 m (2 to 9 ft). These depth to time ratios provide for excellent particulate (and associate pollutant) removals in the main settling chamber.

Toxicity Reductions Associated with Particle Settling

Figure 4.7 shows the percent toxicity reductions (compared to the initial toxicity levels) for all samples, plotted against the hydraulic loading (depth/time), for plain settling alone. This hydraulic loading rate is for batch processes which is equivalent to the surface overflow rate (ft/s) for continuous processes, as shown above. The range of possible toxicant reductions can vary greatly, depending on sample characteristics. The settling chamber is therefore supplemented by other processes, including flash aeration, extended aeration, sorbent pillows, sorption and ion exchange, and sand filtration which combine to reduce variations in overall treatment performance.

This figure indicates that depth/time ratios of at least 3×10^{-5} m/s (1×10^{-4} ft/s) are needed to obtain a median toxicity reduction of at least 70 percent in the main settling chamber. If the main settling chamber tank was one meter (3.3 ft) deep, then the required detention time would have to be at least 0.4 days to obtain this level of treatment. If the tank was twice as deep, the required detention time would be 0.8 days. The tank surface area is therefore based on the volume of runoff to be detained and the settling depth desired/available. Shallow tanks require shorter detention times than deeper tanks, but the surface areas are correspondingly larger. Since the MCTT is placed underground, a tank having a large surface area (and a shallower depth) may be much more expensive than

Figure 4.7 Effects of hydraulic loading on toxicity reduction.

a deeper tank requiring a longer detention time. The needed tank dimensions are therefore sensitive to specific site conditions, including:

- available depth before interferences with existing buried utilities that cannot be moved, or bedrock,
- the hydraulic grade line of the drainage system,
- costs for different sizes and shapes of tanks, including structural problems associated with having a large roofed tank in areas having heavy surface traffic, and
- the local rainfall characteristics.

If the rains are infrequent, long detention periods are easily obtained without having "left-over" water in the tank at the beginning of the next event. However, if the rains are frequent, the available holding times are shortened, requiring shallower main settling chamber tanks for the same level of treatment. The discussion of storage/treatment trade-offs later in this chapter presents a computer spreadsheet program that was used to determine the most effective tank sizes and detention periods for different areas of the US. Chapter 6 also includes an example showing how these trade-offs are evaluated for an example design for Detroit, MI.

Filter/Ion exchange Chamber

The final MCTT chamber is a mixed media filter (sorption/ion exchange) device. It receives water partially treated by the grit and the main settling chambers. The initial designs used a 50/50 mix of sand and peat moss, while the Ruby Garage full-scale MCTT in Milwaukee used a 33/33/33 mixture of sand, peat moss, and granulated activated carbon. The MCTT can be easily modified to contain any mixture of media in the last chamber. However, care must be taken to ensure an adequate hydraulic capacity. As an example, peat moss alone was not effective because it compressed quickly, preventing water from flowing through the media. However, when mixed with sand, the hydraulic capacity was much greater and didn't change rapidly with time. The following is a summary of some of the media investigated in prior stormwater treatment devices. Clark and Pitt (1997), another report in this research series, present much more detail pertaining to alternative treatment media for stormwater control. Table 4.4 is a summary of past stormwater treatment benefits from using different filtering media.

Table 4.4. Reported Filtration Media Performance for Stormwater Control

Pollutant	Sand[1]	Leaf Compost[2]	Peat Moss[3]
Suspended Solids	70	95	90
Turbidity	n/a	84	n/a
Total Nitrogen	21	n/a	50
Total Kjeldahl Nitrogen	46	56	n/a

Nitrate - Nitrogen	0	n/a	n/a
Total Phosphorus	33	40	70
BOD_5	70	n/a	90
Fecal Coliform Bacteria	76	n/a	90
COD	n/a	67	n/a
Total Organic Carbon	48	n/a	n/a
Iron	45	89	n/a
Copper	n/a	67	80
Lead	45	n/a	80
Zinc	45	88	80
Petroleum Hydrocarbons	n/a	87	n/a

[1] City of Austin (1988)
[2] W&H Pacific (1992)
[3] Galli (1990)

Sand

Sand filtration for stormwater treatment began in earnest in Austin, Texas (City of Austin 1988). Sand filters in Austin have been used for single sites and for drainage areas less than fifty acres. They are designed to hold and treat the first one-half inch of runoff with very good pollutant reductions. In Washington, D.C., sand filters are used both to improve water quality and to delay the entrance of large slug inputs of runoff into the combined sewer system. Water quality filters are designed to retain and treat 8 – 13 mm (0.3 – 0.5 in.) of runoff, with the specific filter size depending on the amount of impervious area in the watershed (Galli 1990). In the State of Delaware, sand filters are recognized as an acceptable method for achieving the 80% reduction requirements for SS, especially for sites with large impervious areas that drain directly to the filter. The purpose of the filter in many areas is to help prevent or postpone clogging of an infiltration device (Shaver 1991). According to Delaware's specifications, the sand filter should adequately remove particulates (SS reduction efficiency 75 – 85%) but not soluble compounds. Studies of a six year old sand filter in Maryland found that the filter is just now becoming clogged after use in a heavily traversed parking lot. Inspection below the surface of the sand filter shows that oil, grease, and finer sediments have migrated into the filter, but only to a depth of about two to three inches (Shaver 1991).

Peat Moss

Peat is a partially decomposed organic material that forms in water in the absence of air. Generally, the more decomposed the peat is, the lower its hydraulic conductivity (Cohen, *et al*. 1991). Peat is generally light in weight when dry, and is highly adsorptive of water. Peat has a large surface area per unit volume and has a high cation exchange capacity (Clymo 1963). Peat naturally performs an ion exchange with copper, zinc, lead, and mercury, especially at pH levels between 3.0 and 8.5. This capacity to bind and retain cations, though, is finite and reversible and is determined mostly by the pH of the solution. Peat is an excellent substrate for microbial growth and assimilation of nutrients and organic waste materials because of its high C:N:P ratio, which often approaches 100:10:1. Peat’s ability to retain phosphorus in the long-term is related to its calcium, aluminum, iron and ash content. The higher the content of each of the above constituents, the higher the retention capability. Peat is also polar and has a high specific adsorption for dissolved solids such as transition metals and polar organic compounds (Galli 1990). Sorption of organic contaminants is facilitated by the organic content of peat. Polarity is believed to play a strong role in sorption of nonionic organics, although the role of various molecular forces in sorption is not well documented (Chiou and Klle 1994). Cohen, *et al*. (1991) found that more decomposed peat provides slightly greater reductions of selected organics than less decomposed peat.

Combined Sand and Peat Moss Filters

Peat generally has been combined with sand to create a sand-peat moss filter. The sand-peat filter system designed by the Metropolitan Washington Council of Governments (Washington, D.C.) has a grass cover on top underlain by twelve to eighteen inches of peat. The peat layer is supported by a 100 mm (4 in.) mixture of sand and peat which is supported by a 0.5 – 0.6 m (20 – 24 in.) layer of fine to medium sized sand.

Gravel and an underdrain pipe is placed under the sand. The mixture layer is required because it provides the necessary continuous contact between the peat and the sand layers, ensuring a uniform water flow. Because this is a biological filtration system, it works best during the growing season when the grass cover can provide the additional nutrient reduction that will not occur in the rest of the system (Galli 1990). The sand-peat filter is usually an aerobic system. Modifications to the original design by the Metropolitan Washington Council of Governments have been made to account for unusual site conditions or reduction requirements.

Preliminary Filtration Tests with Stormwater

During the initial design of the MCTT, a sand filter alone was expected to permanently retain any particles that it trapped. Preliminary bench-scale tests, however, showed that sand by itself (especially if recently installed) did not permanently retain the stormwater toxicants (which are mostly associated with very fine particles and which were mostly washed from the sand during later events). There were no mechanisms to permanently retain the pollutants in the fresh sand. This lack of ability to retain stormwater toxicants prompted the investigation of other filtration media. Preliminary research has been conducted at the University of Alabama at Birmingham to further evaluate different filter media as part of this U.S. EPA supported cooperative research agreement for this work (Clark and Pitt 1997). The following list shows the preliminary results from filtration of stormwater runoff using the peat-sand filter:

- Toxicity: > 70% toxicity reduction efficiency,
- Turbidity: increase in turbidity (influent turbidity values were low: < 15 NTU),
- Conductivity: no noticeable reduction (influent conditions were between 50 and 175 µS/cm),
- pH: effluent 0.5 - 1.0 pH units lower than influent (influent values were between 6.7 and 7.7),
- Apparent color: slight increase in color (influent color was between 15 and 60 HACH color units),
- Chemical Oxygen Demand: slight increase in COD (influent COD values were between 80 and 100 mg/L),
- Particle size distribution: large reductions throughout size range (most influent particle sizes were between 1 and 50 µm).

Combinations of filtration media, including organic materials (peat moss, activated carbon, composted leaves, and a cotton processing waste material), Zeolite, and sand, were also investigated for their ability to more permanently retain stormwater pollutants (Clark and Pitt 1997). Sand has been mixed with most of these materials in order to maintain adequate hydraulic capacities, especially for peat. Initial clogging tests have shown that channeling still occurred in the Zeolite-sand combination media, significantly decreasing the performance by decreasing the contact time provided by simple gravity flow. The use of a restrictive filter fabric placed on top of the peat-sand filter in the MCTT allows the water to spread over the filter and help prevent preferential channel flow.

The sand-peat filter possesses ion exchange, adsorption, and filtration reduction mechanisms. As the media ages, the performance of these processes will change. Ion exchange capacity and adsorption sites, primarily associated with the peat moss, will be depleted. Filtration, primarily associated with the sand, however, is expected to increase, especially for the trapping of smaller particles. Improved performance of sand filters with age has been documented by Darby, *et al*. (1991). Eventually though, the sand-peat filter will become clogged by solids and the exchange capacity of the peat will be exceeded, requiring replacement of the media. Replacement is expected to be required about every 3 to 5 years.

Site Specific Design Requirements of the MCTT Main Settling Chamber

The design of the MCTT main settling chamber can be separated into the following general steps:

- determine the pollutant removal goal
- conduct a site survey to determine drainage area and character, subsurface conflicts (existing buried utilities and bed rock), and special surface loading conditions (such as from heavy public works

vehicles)

- determine the needed hydraulic grade line for the drainage system receiving the MCTT effluent
- select a series of candidate MCTT tank depths and holding periods for the desired pollutant removal rate from the continuous simulation results for the area nearest to the site that meet the above restraints
- determine critical runoff volumes that need to be captured for the alternative tank depths and holding times
- investigate alternative available tank components and select the most appropriate tank

Of course, the initial catchbasin/grit chamber and the final "filter/sorption" chamber, also need to be designed. Chapter 6 contains an example for the design of a complete MCTT. This chapter is intended to describe the information that was used to develop the main settling chamber design guidelines, the most important pollutant removal component of the MCTT.

A large fraction of the annual runoff volume is generally due to small to moderate sized storm events. In many parts of the country, 85 percent of all the rains are less than 15 mm in depth (and usually last only a few hours in duration). These small rains can generate about 70 percent of the total annual runoff, depending on the land use. The influence of infiltration and initial abstractions is great (being about 1/3 to 2/3 of the total rainfall) for these small rains for typical urban paved areas. Therefore, special small storm hydrology procedures that accurately consider the runoff losses for these small events are needed for water quality investigations, as opposed to conventional large storm hydrology procedures that are used for drainage design (Pitt 1987).

The design of a stormwater treatment device, including the MCTT, is greatly dependent on the rainfall pattern for a specific area. In water quality evaluations, a single "design storm" is not evident because of the many factors comprising runoff quality (runoff volume, runoff flow rate, water temperature, concentrations of many different pollutants, etc.). It is not very clear under which storm condition the combination of these factors is critical for the beneficial uses. In addition, targeting a specific size storm is no guarantee that all storms of lesser magnitude will also be adequately controlled. Continuous simulation is therefore needed to effectively design and evaluate most stormwater quality controls. The following describes the continuous simulation used to develop design guidelines for the MCTT.

Toxicity Reduction through Settling

A critical aspect of the main settling tank design is the reduction of the toxicants through settling. The spreadsheet storage/treatment model used the toxicity reduction values shown in Table 4.5. This table shows the settling rates (m/s) and median toxicity reductions for a 2.1 m (7 ft) deep main settling chamber with the water held for various times (from Figure 4.7). The same settling rates and toxicity reductions would occur if the main settling chamber was half as deep (1.1m or 3.5 ft in this example) and the water was held for half as long. For this shallower example, however, the treatment tank would have to be twice as large in surface area to provide the same volume. The computer simulation shows the significance of having an adequate volume.

Table 4.5. Median Toxicity Reduction for Different Treatment Holding Times

2.1 m Deep Settling Column Holding Period (h)	Equivalent Settling Rate (m/s)	Median Toxicity Reduction (%) per Individual Rain
6	9.8×10^{-5}	46
12	4.9×10^{-5}	60
24	2.5×10^{-5}	75
36	1.6×10^{-5}	84
48	1.2×10^{-5}	92
72	8.2×10^{-6}	100

Storage/Treatment Trade-Offs in MCTT Design

A computer simulation spreadsheet model (shown in Table 4.6) was developed to determine the toxicity reduction for each individual storm (based on storm depth and interevent time available), the amount of annual rainfall treated, and the overall annual toxicity reduction (Ayyoubi 1993). This information was plotted to obtain design curves to enable the selection of the most effective combination of settling period, holding period, and storage volume. A long holding period would result in better treatment than a short holding period, but may result in water remaining in the MCTT at the beginning of the next storm. This will reduce the effective storage volume, with some of the later storm possibly being diverted around the MCTT, without any treatment. Similarly, a holding time can be too short. This would result in very little water held in the tank at the beginning of the next rain, but the short holding time may not provide adequate treatment. In all cases, the smallest storage volume for a specific removal rate would be desired.

The model was run for various storage capacities, holding periods, and settling tank depths for 21 cities throughout the U.S. having annual rains from about 180 – 1500 mm (7 – 60 in.) (design curves presented in Chapter 6). The model used the rain depths and durations, the time interval between the consecutive storm events, the dimensions of the subsurface tank, and the tank pumpout or drainage time. A random set of 100 rain events from the past 5 to 10 years (from EarthInfo CD-ROMs, Boulder, CO,) was used for each city in these simulations.

Table 4.7 is an example use of this computer program for Birmingham, AL, the site of the pilot-scale MCTT tests presented in Chapter 5 (Ayyoubi 1993). This table presents much detail for each individual event, and for the total evaluation period. This analysis was conducted using rain information from the Birmingham 1976 rain year and was used for the design of the pilot-scale MCTT. This year was selected as most representative of the long-term rain conditions for Birmingham, based on annual rain depth, monthly rain depths, and monthly number of individual rains.

The main settling chamber's available volume before each rain is determined by the computer model. Each value in the chamber "occupied before event" column was zero percent if the pump was capable of emptying the chamber before the beginning of the rain since the last rain. The drainage of the main settling chamber for the Birmingham pilot-scale MCTT was controlled with level-actuated float switches connected to a pump. If the pump was not capable of emptying the chamber before the beginning of the rain, then the value used would be the ratio of the volume of water in the tank at the beginning of the storm to the volume of the tank. The numbers in the chamber "occupied during event" column represent the maximum amount of water present in the chamber for each rain. Each value was calculated based on the difference between the average inflow rate during the respective rain event and the pumping rate. A value of 7% was entered if the pumping rate was greater than or equal to the average influent flowrate (the 7% represents 150 mm of water in a 2.1 m deep tank before the pump is activated). If the pumping rate was less than the influent flowrate, a value equal to the difference between the average influent flowrate and the pumping rate multiplied by the rain duration was entered (not exceeding 100%).

Each value in the "treated runoff" column was the same as the runoff amount (for a particular rain event) if the maximum amount of water in the chamber during treatment was less than 100%. If the maximum amount of water in the chamber during treatment was 100%, the depth of treated runoff was then the sum of the runoff depth needed

Table 4.6. Excel® Spreadsheet Model Used to Develop MCTT Design Curves (Ayyoubi 1993)

Table 4.7. Risk Assessment and Design Evaluation of an MCTT for Birmingham, AL, Conditions

Table 4.7. (Continued).

Table 4.7. (Continued).

Table 4.7. (Continued).

Table 4.7. (Continued).

to fill the chamber, plus the amount of water pumped until the chamber was 100% full. The later value was evaluated based on the amount of time it takes to fill the main settling chamber while pumping during a rain event. This time T was determined as:

$$T = V_{av} / (Q_{in} - Q_{out})$$

Where: V_{av} = available volume of the main settling chamber at the beginning of rain event, m^3
Q_{in} = average inflow rate, m^3/hr
Q_{out} = outflow rate (pumping rate), m^3/hr

When the outflow rate exceeds the average inflow rate (T less than zero), the amount of treated runoff is equal to the runoff. If T is positive and less than the rain duration, then the main settling chamber would fill before the rain ends. Therefore, the amount of water pumped until the main settling chamber is 100% full would be equal to the runoff multiplied by the ratio of T to the rain duration. If T is greater than, or equal to, the rain duration, then the rain event would be over before the main settling chamber could fill, and, therefore, the amount of treated runoff is equal to the runoff. Note that it is possible to treat more than the capacity of the chamber during any given storm, because pumping starts when the water level is 6 inches above the permanent storage, and not when the chamber is completely full. Similar drainage behavior would occur if the drainage was controlled with an orifice at this elevation, instead of with a pump, except that the discharge rate would vary with water depth in the main settling chamber.

The values in the “percent toxicity reduction for storm” column were obtained by multiplying the percent toxicity reduction of treated water (fixed at 75.1% for the example shown in Table 4.11) by the ratio of the amount of treated water during each storm to the total runoff of that same storm. The total annual treated runoff (52.1% for this example) was obtained by dividing the accumulative depths of the treated runoff by the total annual runoff, multiplied by one hundred. The total runoff percent toxicity reduction value (39.1%) was based on the runoff treated at different toxicity reduction values for each rain.

The calculations shown in this table were repeated over a range of drainage or pumping rates, and a range of storage volumes and depths available in the main settling chamber. The drainage times evaluated included: 6, 12, 36, 48, and 72 h, the captured runoff depths ranged from 1.8 – 61 mm (0.07 – 2.39 in.) (corresponding to rain depths of 2.5 – 65 mm, or 0.10 – 2.57 in.).

If the MCTT is full from a previous rain (because of the required holding period), the next storm would bypass the MCTT with no treatment. Birmingham rains typically occur about every 3 to 5 d, so it would be desirable to have the holding period less than this value. Similarly, if the storage volume was small, only a small fraction of a large rain would be captured and treated, requiring a partial bypass for most rains. The annual toxicity reductions are calculated by knowing the individual storm median toxicity reductions and the annual percentage of runoff treated. As an example (see Table 4.7), if the holding period was 24 h for a 2.1 m (7 ft) deep settling chamber, the individual median storm toxicity reduction would be about 75%. If the MCTT was large enough to contain the runoff from a 38 mm (1.5 in) rain, then about 98% of the annual runoff would be treated, for an annual expected toxicity reduction of 73% (0.75 X 0.98 = 0.73).

Figure 4.8 is a plot for Birmingham for different annual control levels associated with holding periods from 6 – 72 h and storage volumes from 2.5 – 51 mm (0.1 – 2.0 in.) of runoff for a 2.1 m (7 ft) deep MCTT. This figure can be used to determine the size of the main settling chamber and the minimum required detention time to obtain a desired level of control (toxicity reduction). If the tank is shallower than 2.1 m (7 ft), then the holding periods should be similarly decreased. If the tank is only 1 m (3.5 ft) deep, then the required holding periods would only be half as long, but the surface area would have to be twice as large to obtain the same storage volume. This plot shows that the most effective holding time and storage volume for a 70% toxicity removal goal, is 72 hours and 0.86 inch of runoff. A shorter holding period would require a larger holding tank for the same level of control. Shorter holding periods may only be more cost-effective for small removal goals (<50%). If a 6 hour holding time was used, the maximum toxicant removal would only be about 46% for this depth of tank, irrespective of the tank holding volume.

Figure 4.8 Effects of storage volume and treatment time on annual toxicity reduction, 2.1 m settling depth) .

Additional Considerations in MCTT Design and Construction

The settling depth is the working settling depth and represents the variable water depth range in the main settling chamber. An additional 0.3 m (1 ft) is needed on the bottom of the main settling tank for the inlet flow distribution network and for storage of captured solids, at least. In addition, another 0.15 m (0.5 ft) is needed above this settling depth for the sorbent pillows. Therefore, another 0.45 m (1.5 ft) (minimum) is needed in addition to the settling depth, plus the MCTT top and bottom wall thickness, plus backfill cover, for the complete system depth.

The chambers of the MCTT should be vented, mosquito proofed, and be made easily accessible for maintenance. Maintenance for the MCTT would consist of inspections, cleaning of the catchbasin, and renewing of the sorbent pillows every 6 – 12 mo. The ion exchange/sorption capacity of the sand-peat media should last from 3 – 5 years before requiring replacement. Filter media research being conducted by the

University of Alabama at Birmingham (Clark and Pitt 1997), and later complete results of the full-scale MCTT tests in Wisconsin, will provide more information on likely MCTT maintenance schedules.

Chapter 5
Pilot-Scale and Preliminary Full-Scale Test Results of the MCTT

This chapter describes field tests of the MCTT. Pilot-scale tests were conducted in Birmingham, AL, at a parking lot site on the campus of the University of Alabama at Birmingham. The Birmingham tests included 13 rains, from May through November 1994. The state of Wisconsin has since installed two full-scale MCTT units. One of these is located at the City of Milwaukee public works Ruby Garage, and another is located at a new municipal parking area in Minocqua. The Wisconsin Department of Natural Resources (DNR) monitored seven events in Minocqua and the U.S. Geological Survey, in contract with the DNR, monitored 15 events in Milwaukee that are summarized in this report.

Pilot-Scale MCTT Design

The pilot-scale MCTT that was tested during this research was designed to incorporate all possible features of the full-scale device. The catchbasin/grit chamber is made of a 25 cm (10 in.) diameter vertical PVC pipe containing approximately 6 L of 3 cm (1 in.) diameter plastic Jaeger Products (Houston, Texas) Tri-Packs® packing column spheres. The main settling chamber is 1.3 m^2 (14 ft^2) in area by 1.2 m (4 ft) deep with a total capacity of 1.6 m^3 (55 ft^3) and includes plate settlers, aerators, and PIG® Mat (New Pig Corp., Tipton, Pennsylvania) sorbent pads. During use, the main settling chamber was filled almost to its full 1.2 m depth and was pumped to within a few cm of the bottom when emptying. With a 72 h settling time, the settling rate provided was about 4 X 10^{-6} m/s and was expected to result in a median toxicity reduction of about 90%. The filter chamber is 1.5 m^2 (16 ft^2) in area and contains a 50/50 mixture of sand and peat 0.3 m (1 ft) deep directly on 0.2 m (0.6 ft) of sand placed over a fine plastic screen and coarse gravel that covers the underdrain. Amoco 4557 (Gunderboom™) filter fabric also covers the top of the filter media to distribute the water over the filter surface by reducing the water infiltration rate through the filter and to provide additional pollutant reduction . This extra pollutant reduction is mostly by sorption of very fine particles and oils to the filter fabric material, not by filtering. Any large particles that could be trapped mechanically had already been removed in the main settling chamber. The surface hydraulic loading rate of this filter/ion exchange chamber was between 1.5 and 6 m per day (5 and 20 ft per day). The sand had the following size: 71% finer than #30 sieve (0.6 mm), 65% finer than #40 sieve (0.425 mm), and 0.5% finer than #50 sieve (0.18 mm). The effective size (D_{10}) of the sand was 0.31 mm and the uniformity coefficient (D_{60}/D_{10}) was 1.45.

While the actual MCTT would be an underground unit, the pilot-scale unit was built upon a trailer for mobility. While this necessitated the use of pumps for filling the device with runoff, building a mobile unit offered several advantages. The pilot-scale unit was constructed offsite, it can be moved to any desired location, and maintained and operated with greater ease. Additionally, the cost of this method was much lower than building an underground device. The unit was set up to capture runoff samples from a parking and vehicle service area on the campus of the University of Alabama at Birmingham. This site featured several attributes of critical source areas including paved parking, fueling pumps, and a motorpool garage with vehicle service. Figures 5.1 – 5.4 are photographs of the MCTT located at the UAB parking facility.

Leaching of Materials used for the Construction of Treatability Test Equipment

An important consideration when constructing any treatability apparatus, including the pilot-scale MCTT, is potential contamination of the test solutions by materials used in the construction of the device. Therefore, before the pilot-scale MCTT was constructed, as series of tests were conducted to examine the leachability of different potential construction materials. Samples of the various materials were left to soak in de-ionized water for set periods of time, and then the water was analyzed for a broad list of constituents of interest.

Table 5.1 lists potential contaminants from some materials that may be used in bench-scale and pilot-scale test equipment (Cowgill 1988). Cowgill found that extensive steam cleaning (at least 5 washings using steam produced from distilled water) practically eliminated all contamination problems for sampling equipment. Cemented materials should probably be avoided, as is evident from this table. Threaded or bolted together components are much preferable.

Table 5.1. Potential Sample Contamination from Sampler Material

Material:	Contaminant:
PVC - threaded joints	chloroform
PVC - cemented joints	methylethyl ketone, toluene, acetone, methylene chloride, benzene, ethyl acetate, tetrahydrofuran, cyclohexanone, organic tin compounds, and vinyl chloride
Teflon™	nothing
polypropylene and polyethylene	plasticizers and phthalates
fiberglass reinforced epoxy material (FRE)	nothing
stainless steel	chromium, iron, nickel, and molybdenum
glass	boron and silica

source: Cowgill (1988)

This project included testing the leaching potentials for many materials that may be used in bench-scale and pilot-scale treatment units. Samples of each material were immersed for a period of 72 h in approximately 500 mL of laboratory grade 18 megohm water. A sample blank was also prepared. Analyses conducted on each of these samples, and the sample blank, were the same to be performed for the pilot-scale MCTT, with the exception of solids and metals analysis. Table 5.2 presents the contaminants that were found in the leaching water at the end of the test in high concentrations that may affect the test results. The most serious problems occur with plywood, including both treated and untreated wood. Attempting to seal the wood with Formica and caulking was partially successful, but toxicants were still leached. Covering of the Formica clad plywood with polyethylene plastic sheeting was finally used to eliminate any potential problem. Fiberglass screening material, especially before cleaning, also causes a potential problem with plasticizers and other organics. PVC and aluminum may be acceptable materials, if phthalate esters and aluminum contamination can be tolerated.

These tables indicate that care must be taken when selecting test equipment. The use of Teflon™ reduces most of the problems, but it is quite expensive. Delrin™ is almost as effective, is somewhat less expensive, and is much easier to machine when manufacturing custom equipment. Both of these materials are fragile and cannot withstand rough handling. Glass is not usable for most large treatability test equipment, but is commonly used in bench-scale tests.

Table 5.3 is a summary of the basic materials considered for construction of the pilot-scale MCTT, indicating the relative problems associated with each material and the constituents of greatest concern. Results indicated the plastic screen used to support the filter media to be the only material to be of potential concern. Prior to installation, the screen was rinsed with tap water which was shown by further testing to reduce leaching of toxicants. The plywood used for the MCTT structure showed potential leaching problems, but this was of minimal concern as the plywood was covered by Formica™ and sheet plastic and never contacted the test water.

Pilot-Scale MCTT Operation

During a storm event, runoff from the parking lot drained to an existing storm sewer inlet. A 65 L (15 gal.) tub was mounted inside this inlet which filled with runoff during the event. A float switch within the tub triggered two sump pumps to direct flow into the catchbasin/grit chamber of the unit. Pumped runoff filled the catchbasin storage volume and then discharged into the settling chamber. During filling, an air pump supplied air to aeration stones located in the main settling chamber. When the settling chamber filled to approximately 75 mm (3 in.) from the top of the settling chamber, a float switch cut power to the sump pumps, the air pump, the two automatic samplers, and an analog clock. The clock measured the total amount of time electricity was supplied to the unit and was used for tracking the treatment time. Filling of the settling chamber took a minimum of 30 min. Longer filling times occurred for storm events that produced intermittent runoff. After a quiescent settling period of a nominal 72 h, settling chamber effluent was pumped through the filter media, sampled, and discharged.

Figure 5.1 Pilot-scale MCTT under construction.

Figure 5.2 Pilot-scale MCTT in place at the UAB parking facility.

Figure 5.3 Automatic samplers installed on the pilot-scale MCTT.

Figure 5.4 Pilot-scale MCTT during a storm event.

Table 5.2. Potential Sample Contamination from Materials that may be used in Treatability Test Apparatus

Material:	Contaminant observed:
untreated plywood	toxicity, chloride, sulfate, sodium, potassium, calcium, 2,4-dimethylphenol, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, phenol, N-nitro-so-di-n-propylamine, 4-chloro-3-methylphenol, 2,4-dinitrotoluene, 4-nitrophenol, alpha BHC, gamma BHC, 4,4'-DDE, endosulfan II, methoxychlor, and endrin ketone
treated plywood (CCA)	toxicity, chloride, sulfate, sodium, potassium, hexachloroethane, 2,4-dimethylphenol, bis(2-chloroethoxyl) methane, 2,4-dichlorophenol, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, phenol, 4-chloro-3-methylphenol, acenaphthene, 2,4-dinitrotoluene, 4-nitrophenol, alpha BHC, gamma BHC, beta BHC, 4,4'-DDE, 4,4'-DDD, endosulfan II, endosulfan sulfate, methoxychlor, endrin ketone, and copper (likely), chromium (likely), arsenic (likely)
treated plywood (CCA) and Formica	toxicity, chloride, sulfate, sodium, potassium, **bis(2-chloroethyl) ether***, diethylphthalate, phenanthrene, anthracene, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, **phenol***, N-nitro-so-di-n-propylamine, **4-chloro-3-methylphenol***, 4-nitrophenol, pentachlorophenol, alpha BHC, 4,4'-DDE, endosulfan II, methoxychlor, endrin ketone, and copper (likely), chromium (likely), arsenic (likely)
treated plywood (CCA), Formica and silica caulk	lowered pH, toxicity, **bis(2-chloroethyl) ether***, hexachlorocyclopentadiene, diethylphthalate, bis(2-ethylhexyl) phthalate, **phenol***, N-nitro-so-di-n-propylamine, **4-chloro-3-methylphenol***, alpha BHC, heptachlor epoxide, 4,4'-DDE, endosulfan II, and copper (likely), chromium (likely), arsenic (likely)
Formica and silica caulk	lowered pH, toxicity, 4-chloro-3-methylphenol, aldrin, and endosulfan 1
silica caulk	lowered pH, toxicity, and heptachlor epoxide
PVC pipe	N-nitrosodiphenylamine, and 2,4-dinitrotoluene
PVC pipe with cemented joint	**bis(2-ethylhexyl) phthalate***, acenaphthene, and endosulfan sulfate
plexiglass and plexiglass cement	naphthalene, benzylbutyl phthalate, and bis(2-ethylhexyl) phthalate, and endosulfan II
aluminum	toxicity, and aluminum (likely)
plastic aeration balls	2,6-dinitrotoluene
filter fabric material	acenaphthylene, diethylphthalate, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, and pentachlorophenol
sorbent pillows	diethylphthalate, and bis(2-ethylhexyl) phthalate
black plastic fittings	pentachlorophenol
reinforced PVC tubing	diethylphthalate, and benzylbutyl phthalate
fiberglass window screening	toxicity, dimethylphthalate, **diethylphthalate***, bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, phenol, 4-nitrophenol, pentachlorophenol, and 4,4'-DDD
Delrin™	benzylbutyl phthalate
Teflon™	nothing (likely)
glass	zinc (likely)

note: * signifies that the observed concentrations in the leaching solution were very large compared to the other materials. Not all of the heavy metals had been verified.

Table 5.3. Pilot-Scale MCTT Construction Material Leach Test

MATERIAL	USE	LEACH POTENTIAL
PVC pipe and cement	catchbasin construction and filter effluent piping	LOW
Jaeger Tri-Packs® packing column spheres	stripping column	LOW
polyethylene sheeting	settling chamber liner	LOW (n-nitroso-di-n-propylamine)
Plexiglas™ and cement	lamella plate construction	LOW (conductivity, chloride, sodium)
PIG® Mat absorbent pillow material	settling chamber floating oil absorbent	LOW (chloride)
Formica™ and caulk	sand-peat filter chamber lining	LOW (toxicity, conductivity, pH, nitrobenzene, 4-chloro-3-methylphenol)
aluminum angle bracket	sand- peat filter chamber corner reinforcement	LOW (toxicity, conductivity, chloride, calcium, pentachlorophenol)
Amoco 4557 filter fabric (Gunderboom™)	sand-peat filter cover	LOW (toxicity, conductivity, sulfate, pentachlorophenol)
plastic screen	filter media support	HIGH (toxicity) LOW (phenol, 4-nitrophenol, pentachlorophenol, di-n-octylphthalate)
treated plywood	structural support (non-contact)	HIGH (toxicity, hexachloroethane, 2,4-dimethylphenol, 4-chloro-3-methylphenol, 4-nitrophenol; likely heavy metals)

Pilot-Scale MCTT Sampling and Analytical Techniques

Two automatic samplers, an ISCO 2700 and American Sigma 800 SL, were used to collect time-composited samples from the pilot-scale MCTT in 10 L (2.5 gal.) glass sample containers. During filling of the unit, samples were collected from the influent to the catchbasin and between the catchbasin and settling chamber. During filtration, samples were collected from the settling chamber effluent (or the sand-peat filter influent) and from the filter effluent. All samples collected were promptly transferred to the laboratory for analysis. Table 5.4 lists the analyses conducted and methods used. Table 5.5 shows sample volumes collected for individual analyses. Appendix E contains detailed descriptions of the laboratory methods used for the pilot-scale evaluations.

A reading of pH was conducted immediately when the sample arrived in the laboratory. Within 24 h, a portion of the chilled samples was filtered through a 0.45 µm membrane filter using an all glass filtering apparatus. The filtered and unfiltered sample portions were then divided and preserved as follows:

- unfiltered samples in two 250 mL amber glass bottles (Teflon™ lined lids) (no preservative) for total forms of toxicity, COD, and gas chromatography (GC) analyses (using mass spectrophotometric, MSD, and electron capture, ECD, detectors).
- filtered sample in one 250 mL amber glass bottle (Teflon™ lined lids) (no preservative) for filtered forms of toxicity, COD, and GC analyses (using MSD and ECD detectors).
- unfiltered sample in one 250 mL high density polyethylene (no preservatives) for SS and VSS, turbidity, color, particle size, and conductivity.
- filtered sample in one 250 mL high density polyethylene (no preservatives) for anion and cation analyses (using ion chromatography), hardness, TDS, VDS, and alkalinity.

- unfiltered sample in one 250 mL high density polyethylene (HNO_3 preservative to pH<2) for total forms of heavy metals, using the graphite furnace atomic adsorption spectrophotometer.

- filtered sample in one 125 mL high density polyethylene (HNO_3 preservative to pH<2) for filtered forms of heavy metals, using the graphite furnace atomic adsorption spectrophotometer.

All samples were chilled on ice or in a refrigerator to 4°C (except for the HNO_3 preserved samples for heavy metal analyses) and analyzed within the holding times shown below. The HNO_3 preserved samples were held at room temperature until digested. The following list shows the holding times for the various groups of constituents:

- immediately after sample collection: pH
- within 24 hours: toxicity, ions, alkalinity, color, turbidity
- within 7 days: GC extractions and solids
- within 40 days: GC analyses
- within 6 months: heavy metal digestions and analyses.

Table 5.4. Compounds Analyzed During MCTT Tests

Organic Toxicants by GC/MSD - filtered and unfiltered (1 to 10 µg/L MDL)
  Polycyclic aromatic hydrocarbons
  Phthalate esters
  Phenols

Organic Toxicants by GC/ECD - filtered and unfiltered (0.01 to 0.1 µg/L MDL)
  Chlorinated insecticides

Heavy Metals by graphite furnace–atomic adsorption spectrophotometry (GFAA) - filtered and unfiltered (1 to 5 µg/L MDL)
  Cadmium
  Copper
  Lead
  Zinc

Toxicity Screening by Microtox™ - filtered and unfiltered

Nutrients by Ion Chromatography - filtered (1 mg/L MDL)
  Nitrate
  Nitrite
  Ammonia
  Phosphate

Major Ions by Ion Chromatography - filtered (0.1 to 1 mg/L MDL)
  Cations (calcium, magnesium, potassium, sodium, and lithium)
  Anions (chloride, sulfate, and fluoride)

Conventional Analyses
  COD
  Color
  Specific Conductance
  Hardness
  Alkalinity
  pH
  Turbidity
  Solids (total, suspended, dissolved, and volatile forms)

Particle size (Coulter Counter Multisizer IIe)

Table 5.5. Analytes and Volumes Collected

Constituent	Volume (mL)	Filtered?	Unfiltered?
Microtox™ toxicity screen	10 mL	yes	yes
Turbidity	30 mL	yes	yes
Conductivity	70 mL		yes
pH	25 mL		yes
color	25 mL		yes
hardness	100 mL		yes
alkalinity	50 mL		yes
anions (F^-, Cl^-, NO_2^-, NO_3^{2-}, SO_4^{2-}, and PO_4^{2-})	25 mL	yes	
cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+})	25 mL	yes	
total solids	100 mL		yes
dissolved solids	100 mL	yes	
semi-volatile compounds (by GC/MSD)	315 mL	yes	yes
chlorinated insecticides (by GC/ECD)	315 mL	yes	yes
particle size	20 mL		yes
metals (Pb, Cr, Cd, Cu, and Zn)	70 mL	yes	yes
COD	10 mL	yes	yes

Results of the Pilot-Scale MCTT Evaluation Tests

The pilot-scale MCTT was evaluated for 13 storm events. The performance of the MCTT was found to provide levels of control comparable to those predicted. Based solely upon the design of the settling chamber, percent toxicity reductions were predicted to be near the 90% reduction level. Actual performance of the overall MCTT was found to have a median value of 96%. The median toxicity reduction of the filtered samples was found to be 87%. Tables 5.6 through 5.9 display summarized results for the pilot-scale MCTT. Tables 5.6, 5.7, and 5.8 show results for the catchbasin, the settling chamber, and the sand-peat filter, respectively. Table 5.9 gives summary results for the overall MCTT. Included in these tables are the minimum, maximum, median, standard deviation, and coefficient of variation (COV) for influent concentration conditions and percent reductions. One-sided probability (p) values for the concentration differences across the chamber/device are also displayed. Complete performance data is presented in Appendices A and B.

Exact 1-sided probabilities were calculated by the Wilcoxon Signed Rank Test for paired observations using StatXact-Turbo™ software by Cytel Software Corporation. The exact probability calculated is based upon sign and magnitude of concentration differences occurring across each chamber and across the entire MCTT, while omitting zero differences. The software calculated an exact p value as opposed to a p value obtained asymptotically which would inherently decrease accuracy for the relatively small sample size. The software also expedited data analysis by performing the test in a batch mode. Values of $p < 0.05$, signifying less than a 5% chance that the inlet and outlet values are the same, are typically used to identify significant differences. This research uses a p value of 0.05 as the level of significance, but the tables provide the actual values calculated for individual interpretation.

Table 5.10 shows performance summaries for the settling chamber, sand-peat chamber, and for the overall MCTT for the major constituents of interest. The catchbasin was not found to provide significant toxicity reductions, as expected, and is therefore not included on this table. The catchbasin was used to provide grit and other coarse solids control to reduce maintenance in the other chambers. Significant (1-sided p value $\leq$ 0.05) concentration changes occurring across the MCTT are given in Table 5.11.

By design, the settling chamber was assumed to provide most of the toxicity reductions. The other two chambers and secondary features were added for extra benefit, especially to reduce variations in performance for the highly variable runoff conditions. However, good toxicity reductions occurred in both the settling chamber and the sand-peat filter. The high levels of Microtox^{TM} toxicity reductions observed indicate excellent reductions of critical toxic contaminants by the MCTT.

Table 5.6. MCTT Catchbasin Chamber Performance Summary

Table 5.6. (continued)

Table 5.7. MCTT Settling Chamber Performance Summary

Table 5.7. (continued)

Table 5.8. MCTT Sand-peat Chamber Performance Summary

Table 5.8. (continued)

Table 5.9. Overall MCTT Performance Summary

Table 5.9. (continued)

Table 5.10. Median Percent Reductions by Chamber

Constituent	Main Settling Chamber (percent)	Sand-Peat Chamber (percent)	Overall Device (percent)
Common Constituents			
total solids	***31***[a]	2.6	***32***
suspended solids	***91***	-400	***83***
turbidity	***50***	***-150***	***40***
conductivity	-15	***21***	***11***
apparent color	***16***	***-75***	***-55***
pH	-0.3	***6.7***	***7.9***
COD	***53***	-55	***54***
Nutrients			
nitrate	***27***	-5	***24***
ammonium	***-62***	-7	***-400***
Toxicants			
Microtox™ toxicity (unfiltered)	***18***	***70***	***96***
Microtox™ toxicity (filtered)	***69***	67	***87***
lead	***88***	***18***	***93***
zinc	***39***	62	***91***
n-Nitro-di-n-propylamine	81	64	92
hexachlorobutadiene	29	97	100
pyrene	100	25	100
bis (2-ethylhexyl) phthalate	***99***	N/A	***99***

[a] Note: Bold italics indicate Wilcoxon 1-sided p value ≤0.05

Figures 5.5 through 5.8 are example plots of the concentrations of SS, unfiltered toxicity, unfiltered zinc, and unfiltered bis(2-ethylhexyl) phthalate as the stormwater passed through the MCTT. Appendix A includes similar plots for the remaining constituents tested. The four data locations on these plots correspond to the four sampling locations on the MCTT. The sample location labeled "inlet" is the overall inlet to the MCTT (and the inlet to the catchbasin/grit chamber). The location labeled "catchbasin" is the effluent from the catchbasin (and inlet to the main settling chamber). Similarly, the location labeled "settling chamber" is the outlet from the settling chamber (and the inlet to the sand-peat chamber). Finally, the location labeled "peat-sand" is the outlet from the sand-peat chamber (and the outlet from the MCTT). Individual samples are traced through the MCTT on separate lines. Therefore, the slopes of the lines indicate the relative reduction rates (mg/L reduction) for each sample and for each individual major unit process in the MCTT. If the lines are all parallel between two sampling locations, then the reduction rates are similar. If a line has a positive slope, then a concentration increased occurred. If the lines have close to zero slope, then little reduction has occurred (as for the catchbasin/grit chamber for most constituents and samples).

The suspended solids trends shown on Figure 5.5 show the significant reductions in suspended solids concentrations through the main settling chamber, with little benefit from the catchbasin/grit chamber and the sand-peat chamber. However, the first storm had a significant increase in suspended solids concentration as it passed through the sand and peat due to flushing of fines from the incompletely washed media.

Table 5.11. Significant (1-sided p value < 0.05) Concentration Changes for MCTT

Constituent	Median Percent Reduction
Very High Constituent Reductions (>80%)	
Suspended Solids	83
Toxicity (unfiltered)	96
Toxicity (filtered)	87
Lead	93
Zinc	91
Carbonate	81
Bis(2-ethylhexyl)phthalate	99
High Constituent Reductions (50 to 80%)	
Volatile Suspended Solids	66
Chemical Oxygen Demand	54
Moderate Constituent Reductions (25 to 50%)	
Total Solids	32
Calcium	33
Hardness	30
Bicarbonate	43
Low Constituent Reductions (0 to 25%)	
Volatile Total Solids	19
Conductivity	11
pH	8
Nitrate	24
Constituent Increases	
Turbidity (dissolved)	-92
Apparent Color	-55
Color	-49
Ammonium	-400
Magnesium	-63
Potassium	-23
Chloride	-13
Sulfate	-27

The relative toxicity changes (as measured using a Azur Environmental Microtox™ unit) are shown on Figure 5.6 and indicate significant reductions in toxicity, especially for the moderate and highly toxic samples. No effluent samples were considered toxic (all effluent samples were “non toxic”, or causing less than a 20% light reduction after 25 to 45 minutes of exposure). Figures 5.7 and 5.8 are for zinc and bis(2-

ethylhexl) phthalate, a metallic and an organic toxicant, and show significant and large reductions in concentrations, mostly through the main settling chamber (corresponding to the large fraction of stormwater toxicants found in the particulate sample fraction). Zinc also had further important decreases in concentrations in the peat/sand chamber. Zinc and toxicity are examples where the use of the filtration/sorption chamber was needed to provide the highest levels of control. Otherwise, it may be tempting to simplify the MCTT by removing the last chamber. Another option would be to remove the main settling chamber and only use the pre-treating catchbasin as a grit chamber before the "filtraton" chamber (similar in design to conventional stormwater sand filters). This option is also not recommended because of the short life that the filter would have before it would clog (Clark and Pitt 1997). In addition, the bench-scale tests showed that a treatment train was needed to provide some redundancy, even for a single sampling site, because of frequent storm to storm variability in sample treatability.

Figure 5.5 MCTT performance for suspended solids.

Figure 5.6 MCTT performance for relative toxicity, by Microtox ä , - unfiltered sample.

Figure 5.7 MCTT performance for zinc - unfiltered sample.

Figure 5.8 MCTT performance for bis(2-ethylhexyl)phthalate - unfiltered sample.

Numerous other organic compounds were also analyzed, but only about 15 of the 70 target compounds were detected in sufficient frequency, or at high enough concentrations, to be reported. The organic analyte described above (bis(2-ethylhexl) phthalate) was representative of the 15 compounds that were detected in sufficient concentrations. In all cases, the concentrations observed were representative of stormwater concentrations expected to be found in similar parking areas. However, the frequency of the organic compounds detected were substantially greater (being from 30 to 80% for the 15 primary compounds, compared to 10 to 30% for most past stormwater studies). As expected, few samples had detectable filterable organic toxicant concentrations. The use of the Microtox™ toxicity screening procedure (for both filterable and total sample fractions) was therefore important as an indicator of the "treatability" of the toxic components of the samples.

Appendix A includes plotted data, plotted mean and standard deviation error bars for the data, and summary tables for each parameter. Appendix B includes tabular data with summary tables. Plotted data in Appendix A also displays the instrument detection limit (IDL), where applicable. A definition of the IDL is the "concentration that produces a signal greater than three standard deviations of the mean noise level" for the given instrument. Generally, the IDL is equal to 0.5 of the lower limit of detection, (LLD), 0.25 of the method detection limit (MDL), and 0.1 of the upper limit of quantification (Greenberg, *et al*. 1992). The IDL, as given in the appendices, has been estimated by multiplying the established MDL for each respective analysis by 0.25. The IDL is presented as a reference line in Appendix A to show the relative magnitudes of reported concentrations to respective instrument and method detection capabilities.

Storm events 11 and 12 had missing data due to handling and sampling errors. During event 11, a sampler hose became dislodged, preventing the collection of a sample between the settling chamber and the sand-peat filter. A broken sample bottle resulted in loss of the MCTT/sand-peat effluent sample for event 12. While not initially planned, event 13 was treated by the device to offset the impact of these missing data.

Variability of results may be in part due to the variability of the stormwater runoff treated. In the sand-peat filter, the presence of some constituents likely effects the reduction of others due to interferences and competition for sorption sites. Such competition was observed in a study of sorption of various dyes in a peat bed (Allen, *et al*. 1988). Inconsistent metal reductions in the sand-peat filter may also be due to excessive velocities (hydraulic loadings) through the media not allowing adequate contact time. Research into the area of determining proper velocities has been noted to be lacking (Karamanev, *et al*. 1994).

Preliminary Full-Scale MCTT Test Results

Preliminary results from the full-scale tests of the MCTT in Wisconsin (Corsi, Blake, and Bannerman, personal communication) were encouraging and collaborate the high levels of treatment observed during the Birmingham pilot-scale tests. Table 5.12 shows the treatment levels that have been observed during seven tests in Minocqua (during one year of operation) and 15 tests in Milwaukee (also during one year of operation), compared to the pilot-scale Birmingham test results (13 events). These data indicate high reductions for SS (83 to 98%), COD (60 to 86%), turbidity (40 to 94%), phosphorus (80 to 88%), lead (93 to 96%), zinc (90 to 91%), and for many organic toxicants (generally 65 to 100%). The reductions of dissolved heavy metals (filtered through 0.45 μm filters) were also all greater than 65% during the full-scale tests. None of the organic toxicants were ever observed in effluent water from either full-scale MCTT, even considering the excellent detection limits available at the Wisconsin State Dept. of Hygiene Laboratories that conducted the analyses. The influent organic toxicant concentrations were all less than 5 μg/L and were only found in the unfiltered sample fractions. The Wisconsin MCTT effluent concentrations were also very low for all of the other constituents monitored: <10 mg/L for SS, <0.1 mg/L for phosphorus, <5 μg/L for cadmium and lead, and <20 μg/L for copper and zinc. The pH changes in the Milwaukee MCTT were much less than observed during the Birmingham pilot-scale tests, possibly because of added activated carbon in the final chamber in Milwaukee. Color was also much better controlled in the full-scale Milwaukee MCTT.

The Milwaukee installation is at a public works garage and serves about 0.1 ha (0.25 acre) of pavement. This MCTT was designed to withstand very heavy vehicles driving over the unit. The estimated cost was $54,000 (including a $16,000 engineering cost), but the actual total capital cost was $72,000. The high cost was likely due to uncertainties associated with construction of an unknown device by the contractors and because it was a retro-fit installation. It therefore had to fit within very tight site layout constraints. As an example, installation problems occurred due to sanitary sewerage not being accurately located as mapped. Figures 5.9 – 5.14 are photographs of the MCTT installation at the Ruby Garage site in Milwaukee. Figure 5.9 shows the Ruby garage drainage area, with snow blade storage. Figures 5.10 – 5.12 are photographs of the Ruby garage MCTT being installed. Figure 5.13 shows the catchbasin inlet and connecting piping to the MCTT during construction. Figure 5.14 shows the sorbent pillows on top of the inclined tube settlers in the main settling chamber.

Table 5.12. Preliminary Performance Information for Full-Scale MCTT Tests, Compared to Birmingham Pilot-Scale MCTT Results (median reductions and median effluent quality)

	Milwaukee MCTT (15 events)	Minocqua MCTT (7 events)	Birmingham MCTT (13 events)
suspended solids	98 (<5 mg/L)	85 (10 mg/L)	83 (5.5 mg/L)
volatile suspended solids	94 (<5 mg/L)	na[a]	66 (6 mg/L)
COD	86 (13 mg/L)	na	60 (17 mg/L)
turbidity	94 (3 NTU)	na	40 (4.4 NTU)
pH	-7 (7.9 pH)	na	8 (6.4 pH)
ammonia	47 (0.06 mg/L)	na	-210 (0.31 mg/L)
nitrates	33 (0.3 mg/L)	na	24 (1.5 mg/L)
Phosphorus (total)	88 (0.02 mg/L)	80 (<0.1 mg/L)	nd[b]
Phosphorus (filtered)	78 (0.002 mg/L)	na	nd
Microtox® toxicity (total)	na	na	100 (0%)
Microtox® toxicity (filtered)	na	na	87 (3%)
Cadmium (total)	91 (0.1 µg/L)	na	18 (0.6 µg/L)
Cadmium (filtered)	66 (0.05 µg/L)	na	16 (0.5 µg/L)
Copper (total)	90 (3 µg/L)	65 (15 µg/L)	15 (15 µg/L)
Copper (filtered)	73 (1.4 µg/L)	na	17 (21 µg/L)
Lead (total)	96 (1.8 µg/L)	nd (<3 µg/L)	93 (<2 µg/L)
Lead (filtered)	78 (<0.4 µg/L)	na	42 (<2 µg/L)
Zinc (total)	91 (<20 µg/L)	90 (15 µg/L)	91 (18 µg/L)
Zinc (filtered)	68 (<8 µg/L)	na	54 (6 µg/L)
benzo(a)anthracene	>45 (<0.05 µg/L)	>65 (<0.2 µg/L)	nd
benzo(b)fluoranthene	>95 (<0.1 µg/L)	>75 (<0.1 µg/L)	nd
dibenzo(a,h)anthracene	89 (<0.02 µg/L)	>90 (<0.1 µg/L)	nd
fluoranthene	98 (<0.1 µg/L)	>90 (<0.1 µg/L)	100 (<0.6 µg/L)
indeno(1,2,3-cd)pyrene	>90 (<0.1 µg/L)	>95 (<0.1 µg/L)	nd
phenanthrene	99 (<0.05 µg/L)	>65 (<0.2 µg/L)	nd
pentachlorophenol	na	na	100 (<1 µg/L)
phenol	na	na	99 (<0.4 µg/L)
pyrene	98 (<0.05 µg/L)	>75 (<0.2 µg/L)	100 (<0.5 µg/L)

na[a] : not analyzed
nd[b]: not detected in most of the samples

The Minocqua site is at a 1 ha (2.5 acre) newly paved parking area serving a state park and commercial area. It was located in a grassed area and was also a retro-fit installation, designed to fit within an existing storm drainage system. The installed capital cost of this MCTT was about $95,000. Figures 5.15 – 5.22 show photographs of the MCTT in Minocqua. Figure 5.15 shows the drainage area, a newly paved parking area. Figures 5.16 and 5.17 show the installation of the 3.0 X 4.6 m (10ft X 15ft) box culverts used for the main settling chamber (13 m, or 42 ft long) and the filtering chamber (7.3 m, or 24 ft long). Figure 5.18 shows the placement of the tube settlers and Figure 5.19 shows the filter fabric being unrolled for placement in the final chamber. Figure 5.20 shows the grit chamber (a 7.6 m^3, 2,000 gal. baffled septic tank), and Figure 5.21 shows the interior of the final filtration chamber. Figure 5.22 shows the site after final construction.

It is anticipated that MCTT costs could be substantially reduced if designed to better integrate with a new drainage system and not installed as a retro-fitted stormwater control practice. Plastic tank manufactures have also expressed an interest in preparing pre-fabricated MCTT units that could be sized in a few standard sizes for small critical source areas. It is expected that these pre-fabricated units would be much less expensive and easier to install than the custom built units tested to date.

Figure 5.9 Ruby Garage, Milwaukee, drainage area (WI DNR photo).

Figure 5.10 Ruby Garage, Milwaukee, MCTT installation (WI DNR photo).

Figure 5.11 Ruby Garage, Milwaukee, MCTT installation (WI DNR photo).

Figure 5.12 Ruby Garage, Milwaukee, MCTT installation (WI DNR photo).

Figure 5.13 Ruby Garage, Milwaukee, MCTT catchbasin inlet and piping (WI DNR photo).

Figure 5.14 Ruby Garage, Milwaukee, MCTT main settling chamber inclined tube settlers and sorbent pillows (WI DNR photo).

Figure 5.15 Minocqua, WI, MCTT, drainage area (WI DNR photo).

Figure 5.16 Minocqua, WI, MCTT, installation of box culverts (WI DNR photo).

Figure 5.17 Minocqua, WI, MCTT, installation of box culverts (WI DNR photo).

Figure 5.18 Minocqua, WI, MCTT, placement of tube settlers (WI DNR photo).

Figure 5.19 Minocqua, WI, MCTT, filter fabric being prepared for installation (WI DNR photo).

Figure 5.20 Minocqua, WI, MCTT, grit chamber.

Figure 5.21 Minocqua, WI, MCTT, interior of final filtration chamber.

Figure 5.22 Minocqua, WI, MCTT, site after installation.

Chapter 6
General Design Procedures for the MCTT

Design Procedure

The MCTT consists of three main components, as noted previously. The initial catchbasin inlet/grit chamber design is based on prior catchbasin performance studies (especially Lager, *et al*. 1977, Pitt 1979, and Pitt 1985). The development of the main settling chamber for toxicant control is described in Chapter 4 of this report, based on Ayyoubi's master's thesis (1993). The final "filtration" chamber design is based on Clark's master's thesis (1996). This section summarizes the integrated design of the MCTT, by examining each of these three components separately.

The most critical step in the design of the MCTT is the sizing of the main settling chamber. The design of the filtration/sorption chamber is important as it acts as a polishing unit mainly for the reduction of filterable toxicants. The filtration/sorption chamber also helps to reduce the variability in the overall performance of the MCTT. The catchbasin inlet acts as an initial grit chamber to reduce maintenance problems in the later MCTT components.

The design of the MCTT can be separated into the following general steps:

- determine the pollutant removal goal
- conduct a site survey to determine drainage area and character, subsurface conflicts (existing buried utilities and bedrock), and special surface loading conditions (such as from heavy public works vehicles)
- determine the needed hydraulic grade line for the drainage system receiving the MCTT effluent
- select a series of candidate MCTT tank depths and holding periods for the desired pollutant removal rate in the main settling chamber using the design curves for the area nearest to the site that meets the above site restraints and goals
- determine critical runoff volumes that need to be captured for the alternative tank depths and holding times for the main settling chamber
- investigate alternative available tank components and select the most appropriate tank
- select the most appropriate filtration/sorption media (usually a peat/sand mixture, with activated carbon, if possible)
- size the filtration/sorption chamber to obtain the desired flow rate and mass of media
- size the catchbasin/grit chamber as a pre-treatment unit. This can be located adjacent to the MCTT, or it can be located at inlets upstream to the MCTT.

The following sections of this chapter address the major steps: selecting the pollutant removal goal, sizing the initial catchbasin/grit chamber, selecting alternative main settling tank sizes, and sizing the sorption/filtration chamber. This chapter also illustrates the design processes with an example for Detroit, MI. The chapter also contains material specifications that were used during this research for the construction of the pilot- and full-scale MCTT units.

Pollutant Removal Goal

The first major step in the specific design of any stormwater control device is establishing the pollutant removal goal. This goal should be based on an understanding of the receiving water problems and the sources of the problems. As noted, the MCTT was developed to control toxicant pollutants at critical source areas. In most cases, a desired pollutant removal goal would be fairly large. The MCTT units tested during this project all had very high removals of organic and metallic toxicants and suspended solids (mostly >90% reductions), with smaller removals of nutrients. The design curves presented later in this chapter are used to size the main settling chamber of the MCTT, based on the desired toxicity reduction in that chamber. However, the data from the monitored facilities enable the overall removal of other pollutants to be estimated.

Table 6.1 shows the constituent removal rates for the complete MCTT, compared to the design toxicity reduction for the main settling chamber of the MCTT alone. It is apparent that the overall MCTT provides additional treatment than the main settling chamber alone. As an example, the overall MCTT provides about an additional 30% in toxicity reduction beyond the main settling chamber alone. This additional treatment can be considered in the sizing of the MCTT for a specific removal goal. This table can therefore be used to estimate the removal rates of other critical pollutants for a candidate MCTT design. As an example, if the main settling chamber is designed for a 70% reduction in toxicity, the overall MCTT removals would be approximately:

Microtox® toxicity	91% (1.3 X 70%)
Suspended solids	77% (1.1 X 70%)
Lead	84% (1.2 X 70%)
Zinc	84% (1.2 X 70%)
Most organic toxicants	91% (1.3 X 70%)
COD	50% (0.72 X 70%)
Nitrates	22% (0.32 X 70%)

Similarly, if the desired overall suspended solids removal is 85%, the toxicity removal in the main settling chamber that would be used for MCTT sizing, would be approximately 77% (85%/1.1). The removal estimates for these other pollutants are approximate because of the variability in performance observed. Obviously, no removal can be greater than 100%, and small MCTT units (having small expected toxicity reductions in the main settling chamber alone) have not been tested. Therefore, as the main settling chamber toxicity removal varies from about 75%, these estimates of removal for other pollutants would have increasing errors.

Table 6.1. Full MCTT Pollutant Removals Compared to Design Toxicity Reductions

Constituent	Ratio of Constituent Removal to Design Toxicity Removal Goal (median)
Very High Removals:	
Microtox® toxicity	1.3
Microtox® toxicity (filtered)	1.2
Suspended solids	1.1
Lead	1.2
Zinc	1.2
Fluoranthene	1.3
Pyrene	1.3
Pentachlorophenol	1.3
Phenol	1.3
High Removals:	
Volatile suspended solids	0.87
COD	0.72

Zinc (filtered)	0.72
Moderate Removals:	
Turbidity	0.53
Lead (filtered)	0.56
Low Removals:	
NO_3	0.32
Cadmium	0.24
Cadmium (filtered)	0.21
Copper	0.20
Copper (filtered)	0.23

Catchbasin Inlet Chamber Design

Further background information for catchbasins, including recent field performance trials and summaries of earlier research, is available in another associated report currently being prepared as part of this research project (Pitt, *et al*. 1997). This other report also contains monitoring information from field tests of inlet filters and presents alternative enhanced catchbasin designs. However, the conventional catchbasin, described below, was found to be most effective for almost all conditions. The commercially available inlet filters that were tested performed poorly, with rapid clogging. Some types of inlet screens are useful for trapping litter, however, and may be important in some applications. The conventional catchbasin must contain a sump to trap particulates and to reduce scour losses of previously trapped material. If the sump is too small, very little benefit is realized with a catchbasin. The scour depth of a catchbasin sump is about 0.3 m (1 ft), with deeper sumps needed for sediment storage between cleaning operations.

The geometry of a catchbasin was found to be very important by Lager, *et al*. (1977) and later confirmed by Aronson, *et al*. (1983). The basic catchbasin (having an appropriately sized sump) and an inverted outlet is the most robust configuration for a basic storm drain inlet. In almost all full-scale field investigations, this design has been shown to withstand extreme flows with little scouring losses, no significant differences between supernatant water quality and runoff quality, and minimal insect problems. It will trap the bed-load from the stormwater (especially important in areas using sand for winter traction control) and will trap a moderate amount of SS (about 30 to 45% of the annual loadings). The largest fraction of the sediment in the flowing stormwater will be trapped, in preference to the finer material that has greater amounts of associated pollutants. Their hydraulic capacities are designed using conventional procedures (grating and outlet dimensions), while the sump is designed based on the desired cleaning frequency. Figure 6.1 is this basic recommended configuration for an effective catchbasin.

The size of the catchbasin sump is controlled by three factors: the runoff flow rate, the SS concentration in the runoff, and the desired frequency at which the catchbasin will be cleaned without sacrificing efficiency. Figure 6.2 shows the percent SS removed versus the influent flow rate, as presented by Pitt (1985). The volume of sediment captured in catchbasin sumps was calculated using this relationship for a one acre paved drainage area and for runoff having 50 to 1000 mg/L SS concentrations. The 1976 Birmingham, AL, rain year was used to obtain typical rain depths and flow rates for each rain. The Rv (volumetric runoff coefficient) was obtained from the small storm hydrology tests conducted by Pitt (1987). Figure 6.3 shows the amounts of rainfall treated before the catchbasin sump is 60% full, when the SS deposition is approximately in equilibrium with scour and the capture efficiency is assumed to be reduced to zero (Pitt 1985). The equation for this capture rate is:

$$\%\ \text{SS Reduction} = 44 \text{ x } (0.51)^{Q} \text{ x } (1.1)^{Q\uparrow 2}$$

where Q is the influent flowrate in ft^3/s (CFS). The volume of SS removed was evaluated assuming a specific gravity of 2.5. Table 6.2 shows the approximate accumulation of SS for different total rainfall depths.

An estimate of the required catchbasin sump volume and cleanout frequency can be calculated using this table and specific site conditions. For example, assume the following conditions:

- paved drainage area: 1.3 ha (3.3 acres),
- 250 mg/L SS concentration, and
- 640 mm (25 in.) of rain per year.

The sediment accumulation rate in the catchbasin sump would be about 0.24 m^3/ha (3.4 ft^3/acre) of pavement per year. For a 1.3 ha (3.3 acre) paved drainage area, the annual accumulation would therefore be about 0.3 m^3 (10 ft^3). The catchbasin sump diameter should be at least four times the diameter of the outlet pipe. Therefore, if the outlet from the catchbasin is a 250 mm (10 in.) diameter pipe, the sump should be at least 1 m (40 in.) in diameter (having a surface area of 0.8 m^3, or 9 ft^2). The annual accumulation of sediment in the sump for this situation would therefore be about 0.4 m (1.3 ft). If the sump is to be cleaned about every two years, the total accumulation between cleanings would therefore be about 0.8 m (2.6 ft). An extra 0.3 m (1 ft) of sump depth should be provided as a safety factor because of potential scour during unusual rains. Therefore, a total sump depth of about 1.1 m (3.6 ft) should be used. In no case should the total sump depth be less than about 1 m (3 ft) and the sump diameter less than about

Figure 6.1 Conventional catchbasin with inverted sump (Pitt, *et al.* 1997).

Figure 6.2   Suspended solids capture vs flowrate (Pitt, *et al.* 1997).

Figure 6.3   Amount of rainfall treated before catchbasin sumps are 60% full (Pitt, *et al.* 1997).

Table 6.2 Approximate Suspended Solids Accumulations in Catchbasin Sump (ft^3/acre of pavement)

Total Rainfall (inches)	50 mg/L SS conc.	100 mg/L SS conc.	250 mg/L SS conc.	500 mg/L SS conc.
5	0.13	0.27	0.67	1.3
10	0.27	0.54	1.3	2.7
15	0.40	0.81	2.0	4.0
25	0.67	1.3	3.4	6.7
50	1.3	2.7	6.7	13
100	2.7	5.4	13	27
200	5.4	11	27	54

0.75 m (2.5 ft). This would provide an effective sump volume of about 0.8 m^3 (9 ft^3) assuming a safety factor of about 1.6.

Main Settling Chamber Design

The design of the MCTT is very site specific, as noted previously, being highly dependent on local rains (rain depths, rain intensities, and interevent times). A computer model, described previously, was therefore developed to determine the amount of annual rainfall treated, the toxicity reduction rate for each individual storm, and the overall toxicity reduction associated with a long series of rains for different locations in the U.S. These design guidelines were determined by continuous simulation of the rainfall-runoff process and MCTT performance using 100 random rains (rain depths, rain durations, and interevent periods) obtained over a 5 to 10-year period for each city. Earth-Info™ (Golden, Colorado) CD-ROM rainfall data compilations of National Weather Service data were used to obtain this rain information. Table 6.3 shows the resultant required main settling chamber sizes for 21 cities having rain depths ranging from 180 mm (7.1 in.) (Phoenix) to 1500 mm (60 in.) (New Orleans) per year. Design curves for each of these cities for different MCTT settling depths are shown in Figures 6.4 to 6.23, at the end of this chapter.

Table 6.3. MCTT Main Settling Chamber Required Sizes (all 48 h holding times, except as noted, with 5 foot settling depths).

City	Annual Rain Depth (in.)	Runoff Capacity (in.) for 70% Toxicant Control	Runoff Capacity (in.) for 90% Toxicant Control
Phoenix, AZ	7.1	0.25 (24 h)	0.35
Reno, NV	7.5	0.20 (18 h)	0.20
Bozeman, MT	12.8	0.25	0.40
Los Angeles, CA	14.9	0.30	0.45
Rapid City, SD	16.3	0.20 (18 h)	0.22
Minneapolis, MN	26.4	0.32	0.50
Dallas, TX	29.5	0.50	0.96
Madison, WI	30.8	0.32	0.52
Milwaukee, WI	30.9	0.36	0.65
Detroit, MI	31.0	0.24	0.50
Austin, TX	31.5	0.22 (18 h)	0.32
St. Louis, MO	33.9	0.30	0.49
Buffalo, NY	37.5	0.35	0.50
Seattle, WA	38.8	0.25	0.40
Newark, NJ	42.3	0.48	0.96
Portland, ME	43.5	0.42	0.72
Atlanta, GA	48.6	0.55	0.95
Little Rock, AR	49.2	0.52	0.85
Miami, FL	57.6	0.40	0.73
New Orleans, LA	59.7	0.80	0.92

The overall range in MCTT size varies by more than three times for the same level of treatment for the different cities. The required size of the main settling chamber generally increases as the annual rain depth increases. However, the interevent period and the rain depth for individual rains determines the specific runoff treatment volume requirement. As an example, Seattle requires a much smaller MCTT than other cities having similar annual total rains because of the small rain depths for each rain (it experiences many small rains, of relatively low intensity). Rapid City requires a smaller MCTT, compared to Los Angeles, because Los Angeles has much larger rains when it does rain. Similarly, Dallas requires an unusually large MCTT because of its high rain intensities and large individual rains, compared to upper Midwest cities that have similar annual total rain depths. In all cases, the most effective holding time is 2 d for 90% toxicant control (for the 1.5 m, or 5 ft, settling chamber depth). In most cases, a toxicity reduction goal of about 70% in the main settling chamber is probably the most cost-effective choice, considering the additional treatment that will be provided in the sand-peat chamber.

The required runoff depth storage capacity increases as the depth of the main settling chamber increases. As an example, for 90% toxicant control at Milwaukee, the storage requirement for a 1.5 m (5 ft) settling depth was shown to be 16.5 mm (0.65 in.) on Table 6.3. Figure 6.14 indicates that the required storage volume for a 0.6 m (2 ft) settling chamber would only be 14 mm (0.55 in.) of runoff, while it would increase to 19 mm (0.75 in.) of runoff for a 2.1 m (7 ft) settling depth and to 23 mm (0.9 in.) for a 2.7 m (9 ft) settling depth. The greater runoff depths require more time for the stormwater particulates to settle and be trapped in the chamber, while the shallower tanks require a greater surface area. The best tank design for a specific location is based on site specific conditions, especially the presence of subsurface utilities or groundwater and hydraulic grade line requirements. A large surface tank is usually much more expensive, even though the required volume is less, especially if heavy traffic will be traveling over the tank.

As an example, for a 0.6 m (2 ft) settling depth, a combination of a 48 h holding time and 11 mm (0.45 in.) runoff storage volume would satisfy a 75% treatment goal for Milwaukee (the site of the Ruby Garage full-scale MCTT installation), as shown on Figure 6.14. This 11 mm runoff volume corresponds to a rain depth of about 13 mm (0.51 in.) for pavement (Pitt 1987). The 11 mm runoff storage volume corresponds to a chamber "live" volume of 22 m^3 (770 ft^3) and a surface area of 10 m^2 (110 ft^2) for a 0.2 ha (0.5 acre) paved drainage area. The surface area of the MCTT would therefore be about 0.5 percent of the drainage area. This device would capture and treat about 80% of the annual runoff at a 95% level, resulting in an annual toxicity reduction of about 75% (0.8 X 0.95). The size of the main settling chamber would need to be greater than this because "dead" storage must be added to provided for standing water below the outlet orifice (or pump) which would keep the inclined tubes submerged and to prevent scour.

Drainage of Main Settling Chamber

The main settling chamber needs to be empty at the end of the selected storage time to be able to treat runoff from the next rain. The water leaves the main settling chamber and enters the final filter/sorption chamber. During the pilot-scale MCTT tests, a small pump emptied the main settling chamber after three days of storage. A float switch was used to control the water levels through switching the pump. The pumping rate was selected based on the desired hydraulic loading rate on the filter material. The full-scale MCTT devices in Wisconsin were operated using orifices to control the water drainage from the main settling chamber into the final chamber. Therefore, the full-scale tests included continuous flows from the settling chamber into the last chamber, as long as water was above the orifice. The orifice was located at the desired "dry-weather" depth, close to the top of the tube settlers. The following equation can be used to estimate the orifice diameter for different settling chamber surface areas, settling depths, and desired drainage times:

$$D_o = 0.113\ [(A_t/(C_d)(t)]^{0.5}\ (h_1)^{0.25}$$

where: D_o = orifice diameter, in.,

A_t = surface area of main settling chamber of MCTT, ft^2,
C_d = orifice coefficient,
t = desired MCTT drainage time, h, and
h_1 = settling depth, ft.

The MCTT at Minocqua, WI, has a main settling chamber made of 3.0 m X 4.6 m (10 ft x 15 ft) box culvert sections, having a total length of 13 m (42 ft). The surface area is therefore 59 m^2 (630 ft^2). The settling depth is 1.5 m (5 ft), and the desired drainage time is 72 h. The desired orifice diameter, using the above equation (and an orifice coefficient of 1.0, corresponding to a well-rounded entrance), was calculated to be 13 mm (0.5 in.). In contrast, the MCTT at Ruby Garage in Milwaukee, WI, has a main settling chamber with a surface area 14 m^2 (150 ft^2) and a settling depth of only 0.6 m (2 ft). The desired drainage time was the same as at Minocqua. The calculated orifice diameter for the Milwaukee MCTT was 5 mm (0.2 in.).

These are both small diameter holes through which almost all of the stormwater from the drainage area must eventually pass. Keeping the orifices clear is obviously of great importance. At both full-scale MCTT sites, the orifices are protected with a solid (removable) box covering the orifice with screening on the bottom side where the water enters. The boxes are relatively large to provide a large screened area. The screening holes are smaller than the orifices to help prevent clogging. In addition, the orifices are designed to be inefficient (having C_d coefficients as small as possible) enabling slightly larger diameters than calculated above. The Ruby Garage MCTT experienced clogging once during the first year of operation, requiring manual cleaning. The material clogging the orifice was a mat from a biological growth that was growing on the inside of the MCTT main settling chamber. Care therefore needs to be taken to provide easy access to the orifice for cleaning and to protect the orifice as much as possible from clogging. One of the MCTT access locations should therefore be located directly above the orifice, if possible. An overflow/bypass should also be provided in case the orifice cannot be quickly cleaned.

Final Filtration-Sorption-Ion Exchange Chamber

Additional treatment beyond the level provided in the main settling chamber would result from the filter-sorption-ion exchange chamber. The pumped or drained effluent from the main settling chamber is directed towards a mixed peat-sand chamber, which should provide a surface hydraulic loading rate of between 1.5 and 6 m per day (5 and 20 ft per day), and have a depth of at least 0.5 m (18 in.). In addition to the pumped effluent, any excess runoff after the main settling chamber is full could also be directed towards the filter. Detailed information on stormwater filtration, including information useful for designing the filtration/sorption chamber of the MCTT, is also available in another associated report currently being prepared (Clark and Pitt 1997). The following guidelines are from this other report.

Summarized information from the EPA sponsored filtration experiments (Clark and Pitt 1997) can be used to develop design guidelines for the third “filtration” (sorption-ion exchange) chamber of the MCTT. The design of a stormwater filter needs to be divided into two phases. The first phase is the selection of the filtration media to achieve the desired pollutant reduction goals. The second phase is the sizing of the filter to achieve the desired run time before replacement of the media. The main objective of the associated research reported by Clark and Pitt (1997) was to monitor a variety of filtration media to determine their pollutant reduction capabilities. However, it soon became apparent that the filters were more limited by clogging caused by suspended solids in the stormwater, long before reductions in their pollutant reduction capabilities could be identified. Therefore, measurements in filter run times, including flow rates and clogging parameters, were added to the research activities. Pretreatment of the stormwater so the SS content is about 10 mg/L is likely necessary in order to take advantage of the pollutant retention capabilities of most of the media. The MCTT provides this necessary pretreatment through sedimentation in the main settling chamber.

Selection of Filtration Media for Pollutant Reduction Capabilities

The selection of the filter media needs to be based on the desired pollutant reduction performance and the associated site conditions. If based on a wide range of pollutants for pretreated stormwater (such as provided in the main settling chamber), then the rankings (best media listed first) for the tested media were as follows:

1) peat moss-sand (with degradation in color, turbidity, and pH)
2) activated carbon-sand (no degradation, but fewer benefits)
3) Enretech-sand, forest/sand, filter fabrics, or sand alone (few changes, either good or bad)
4) compost-sand (many negative changes)

(Note: if the stormwater was not pretreated, with associated shortened run times, then the rankings were much different, with compost-sand being near the top of the list). The following list summarizes the likely significant reductions in concentrations observed for the filters:

Sand: With pretreatment, sand filtration has little additional benefit. Likely minimum effluent concentrations: 10 mg/L for SS, 50 HACH color units, 10 NTU for turbidity.

Peat moss-sand: Medium to high levels of control for most pollutants for pre-settled stormwater. Largest range and number of pollutants benefited under pre-settled conditions. Caused increases in color and turbidity, and reductions in pH (by about ½ to 1 pH unit). Likely minimum effluent concentrations: 5 mg/L for SS, 85 HACH color units, 10 - 25 NTU for turbidity.

Activated carbon-sand: Very good control for most pollutants. Caused no adverse changes for any pollutant. Likely minimum effluent concentrations: 5 mg/L for SS, 25 HACH color units, 5 NTU for turbidity.

Zeolite-sand: No likely benefits for pre-settled stormwater. Caused increased color and turbidity on pre-settled stormwater. Likely minimum effluent concentrations: 10 mg/L for SS, 75 HACH color units, 15 NTU for turbidity.

Compost-sand: Worsened water quality for many pollutants if stormwater was pre-settled. Increased color under all conditions and had increased phosphate and potassium in effluent. Likely minimum effluent concentrations: 10 mg/L for SS, 100 HACH color units, 10 NTU for turbidity.

Enretech-sand: Had little effect on pre-settled stormwater. Likely minimum effluent concentrations: 10 mg/L for SS, 80 HACH color units, 10 NTU for turbidity.

Filter fabrics: No significant and/or important reductions for any pollutants using either untreated or pre-settled stormwater.

Design of Filters for Specified Filtration Durations

The filtration durations measured during these tests can be used to develop preliminary filter designs. It is recommended that allowable suspended solids loadings be used as the primary controlling factor in stormwater filtration design. Clogging is assumed to occur when the filtration rate becomes less than about 1 m/day. Obviously, the filter would still function at smaller filtration flow rates, especially for the smallest rains in arid areas, but an excessive amount of filter by-passing would likely occur for moderate rains in humid areas. Tables 6.4 and 6.5 summarize the observed filtration capacities of the different media tested.

Table 6.4. Filtration Capacity as a Function of Suspended Solids Loadings (small-scale tests)

Filtration Media	Capacity to 20 m/day (gSS/m^2)	Capacity to 10 m/day (gSS/m^2)	Capacity to <1 m/day (gSS/m^2)
Sand	150-450	400->2000	1200-4000
Peat-sand	100-300	150-1000	200-1700

Peat	?	?	200
Leaves	?	?	2100
Activated carbon-sand	150-900	200-1100	500->2000
Zeolite-sand	200-700	800-1500	1200->2000
Compost-sand	100-700	200-750	350-800
Enretech-sand	75-300	125-350	400-1500

Table 6.5. Filtration Capacity as a Function of Pretreated Water Loading (influent <10 mg SS /L) (small-scale tests)

Filtration Media	Capacity to 20 m/day (m)	Capacity to 10 m/day (m)	Capacity to <1 m/day (m)
Sand	6-20	8->25	13->40
Peat-sand	3-17	4-22	7-30
Activated carbon-sand	5-25	6->25	15->40
Zeolite-sand	7-25	8->25	14->40
Compost-sand	3-20	4-30	6->30
Enretech-sand	3-11	4-25	15->30

The most restrictive materials (the Enretech and Forest Products media) are very fibrous and still show compaction, even when mixed with sand. The most granular media (activated carbon and the Zeolite) are relatively uniform in shape and size, but have sand interspersed to fill the voids to slow the water to increase the contact time for better pollutant reduction. The sand has the highest filtration rates because it has the most uniform shape and size.

The flow rates through filters that have thoroughly dried between filter runs significantly increases. Our small-scale tests restricted complete drying during normal inter-event periods. Drying may occur more commonly with the full-scale filters in the MCTT. Wetting and drying of filters (especially peat) has been known to produce solution channels through the media that significantly increases the flow. If these solution channels extend too far through the filter, they would reduce pollutant reduction performance. Adequate filter depths will minimize this problem. The filter fabrics did not indicate any flow rate improvements with wetting and drying, while the peat moss/sand filter had the greatest improvement in flow capacity (by about ten times), as expected. The other media showed much more modest improvements (but still about two to three times).

The filter capacity ranges may be grouped into the following approximate categories, as shown on Table 6.6.

Table 6.6. Filter Media Categories and Filtration Capacities (allowing interevent drying of media)

Capacity to <1 m/day (gSS/m^2)	Capacity to 10 m/day (gSS/m^2)	Filtration Media Category
5,000	1,250	Enretech-sand; Forest-sand
5,000	2,500	Compost-sand; Peat-sand
10,000	5,000	Zeolite-sand; Act. Carbon-sand
15,000	7,500	Sand

Filter designs can be made based on the predicted annual discharge of suspended solids to the filtration device and the desired filter replacement interval. As an example, Table 6.7 shows typical volumetric runoff coefficients (Rv) that can be used to approximate the fraction of the annual rainfall that would occur as runoff for various land uses and surface conditions. In addition, Table 6.8 summarizes likely suspended solids concentrations associated with different urban areas and waters.

Table 6.7. Typical Volumetric Runoff Coefficients for Different Land Use Areas

Area	Annual Average Volumetric Runoff Coefficient (Rv)
Low density residential land use	0.15
Medium density residential land use	0.3
High density residential land use	0.5
Commercial land use	0.8
Industrial land use	0.6
Paved areas	0.85
Sandy soils	0.1
Clayey soils	0.3

Table 6.8. Typical Suspended Solids Concentrations for Different Source Areas

Source Area	Suspended Solids Concentration (mg/L)
Roof runoff	4 – 25
Paved parking areas	40 – 1600
Paved storage areas	40 – 200
Paved driveways	400
Streets	250 – 1300
Paved walkways	20 – 400
Unpaved parking and storage areas	700
Landscaped areas	100 – 1000
Detention pond water	20
Mixed stormwater	150
Effluent after high level of pre-treatment of stormwater (such as by the main settling chamber in the MCTT)	5

Using the information in the above tables and the local annual rain depth, it is possible to estimate the annual suspended solids loading from an area. The following three examples illustrate these simple calculations.

1) A 1.0 ha paved parking area, in an area receiving 1.0 m of rain per year:

$$(50 \text{ mg SS/L})\ (0.85 \text{ Rv})\ (1 \text{ m/y})\ (1 \text{ ha})\ (10{,}000 \text{ m}^2/\text{ha})\ (1{,}000 \text{ L/m}^3)\ (\text{g}/1{,}000 \text{ mg}) = 425{,}000 \text{ g SS/y}$$

Therefore, if a peat-sand filter is to be used, having an expected suspended solids capacity of 5,000 g/m^2 before clogging, then 85 m^2 of this filter will be needed for each year of desired operation for this 1.0 ha site. This is about 0.9% of the paved area per year of operation. If this water is pre-treated so the effluent has about 5 mg/L SS, then only about 0.2% of the contributing paved area would be needed for the filter. A sand filter would only be about 1/3 of this size because of its greater capacity before clogging (but with decreased pollutant retention).

2) A 1.0 ha medium density residential area having 1.0 m of rain per year:

(150 mg SS/L) (0.3 Rv) (1 m/y) (1ha) (10,000 m^2/ha) (1,000 L/m^3) (g/1,000 mg) =
450,000 g SS/-y

The unit area loading of suspended solids for this residential area is about the same as in the previous example, requiring about the same percentage of the drainage area dedicated for the filter. The reduced amount of runoff is balanced by the increased suspended solids concentration.

3) A 1.0 ha rooftop in an area having 1.0 m of rain per year:

(10 mg SS/L) (0.85 Rv) (1 m/y) (1 ha) (10,000 m^2/ha) (1,000 L/m^3) (g/1,000 mg) =
85,000 g SS/y

The unit area loading of suspended solids from this area is much less than for the other areas and would only require a filter about 0.2% of the roofed drainage area per year of operation. Pretreatment of this water (such as in the MCTT) would only marginally improve the filter performance and is not recommended for this condition.

It is recommended that the filter media be at least 50 cm in depth and be sized to provide a hydraulic loading rate of between 1.5 and 6 m/d for the MCTT. In addition, it is highly recommended that significant pre-treatment of the water be used to reduce the suspended solids concentrations to about 10 mg/L before filtration for pollutant reduction. This pre-treatment can be accomplished using the main sedimentation chamber in the MCTT. The selection of the specific filtration media should be based on the desired pollutant reductions, but should in all cases include amendments to plain sand if immediate and permanent pollutant reductions are desired.

Example Design of Full-Scale MCTT

The following is an example preliminary design for a full-scale MCTT for a public works garage in Detroit, MI. It was prepared for the Rouge River National Demonstration Project for consideration as a local demonstration project. The design is divided into the major steps, as indicated previously.

Determine the Pollutant Removal Goal

The first step in designing a stormwater management practice is to identify the pollutant removal goal, or range of likely goals for consideration. In the MCTT, this process is based on the toxicity removal goal in the main settling chamber, the control parameter. This value can be estimated, based on the removal goals of other pollutants for the complete MCTT, as shown previously.

The toxicity removal goal in the main settling chamber for this example design was within the range of 70 to 90%. The final removal will be determined based on site constraints and cost. These removals would result in the approximate overall MCTT removals for other pollutants as shown in Table 6.9. Obviously, the high level of treatment associated with the 90% toxicity removal goal in the main settling chamber results in very high removals for most toxicants and many of the conventional pollutants. In most cases, the pollutant reductions associated with the more modest 70% toxicant removal goal for the main settling chamber are adequate. This design example shows the results associated with both of these goals for comparison. It is probably best to consider a range of options for most stormwater management programs. The costs associated with each option, along with their pollutant removal capabilities, can then be used in a decision analysis procedure in order to select the best combination of control practices that should be used in an area.

Table 6.9. Example Pollutant Removals for Example Design Alternatives

Example Constituents	Pollutant Removal if 70% toxicity goal in main settling chamber	Pollutant Removal if 90% toxicity goal in main settling chamber
Very High Removals: Microtox® toxicity, Microtox® toxicity (filtered), suspended solids, lead, zinc, fluoranthene pyrene, pentachlorophenol, and phenol	80 to 90%	Close to 100%
High Removals: Volatile suspended solids, COD, and zinc (filtered)	50 to 60%	65 to 80%
Moderate Removals: Turbidity and lead (filtered)	About 40%	About 50%
Low Removals: Nitrate, cadmium, cadmium (filtered), copper, and copper (filtered)	15 to 25%	20 to 30%

Main Settling Chamber Design

The initial steps, after the pollutant removal goals are identified, include site surveys of candidate MCTT locations. These site surveys include the following, at a minimum:

- conduct a site survey to determine drainage area and character, subsurface conflicts (existing buried utilities and bedrock), and special surface loading conditions (such as from heavy public works vehicles)
- determine the needed hydraulic grade line for the drainage system receiving the MCTT effluent

The following steps are then conducted, using the MCTT design curves for the city of interest:

- select a series of candidate MCTT tank depths and holding periods for the desired pollutant removal rate in the main settling chamber from the continuous simulation results for the area nearest to the site that meet the above restraints and toxicity removal goals
- determine critical runoff volumes that need to be captured for the alternative tank depths and holding times for the main settling chamber
- investigate alternative available tank components and select the most appropriate tank

The filtration/sorption chamber is then designed, using the information previously presented:

- select the most appropriate filtration/sorption media (usually a peat/sand mixture, with activated carbon, if possible)
- size the filtration/sorption chamber to obtain the desired flow rate and mass of media

Finally, the catchbasin/grit chamber is designed, based on existing or new inlet arrangements.

The following paragraphs present these steps for the example Detroit MCTT facility. The discussion describes how the design curve was prepared, using local rain information. Similar processes were used to develop the design curves for the 21 cities throughout the U.S. that are presented as Figures 6.4 through 6.24.

Rainfall for Detroit and Expected Performance of MCTT

The local Detroit rain patterns (depths, durations, and antecedent dry periods) for the past 10 years were examined and used to develop a 100 event random rain set that represents the long-period conditions. Detroit rains from 1950 through 1991 were obtained from the 1993 version of the Earthinfo CD ROM (Boulder, CO) which contained hourly rainfall depths for Detroit. These rains were extracted from the CD ROM and converted into separate rainfall events using the rain utilities in SLAMM (the *Source Loading and Management Model*) (Pitt and Voorhees 1995).

This rain information was used to model MCTT treatment capacity and treatment duration tradeoffs for specific storage and treatment options, using the spreadsheet model previously presented. This model was used to examine the effects of different holding times (6 to 72 hours) and tank capacities (5 mm – 40 mm, or 0.2 – 1.5 inches) for different tank live storage depths (0.6 m – 2.7 m, or 2 – 9 feet). The model was run about 200 times to create a summary for the different options.

The treatment benefits were plotted, as shown in Figure 6.9 for Detroit. These analyses indicated that for a 1.5 m (5 ft) live chamber depth and desired 75% toxicity reductions in the main settling chamber, the smallest MCTT would have a storage capacity of about 9.1 mm (0.36 in.) and should hold the stormwater for 48 hours. Holding the stormwater for longer periods of time would result in better treatment of the water flowing through the MCTT, but a smaller fraction of the annual stormwater would flow through the unit, resulting in less overall annual toxicity reductions. Similarly, holding the water for a shorter period of time would increase the amount of annual stormwater that would pass through the MCTT, but the stormwater would receive less treatment.

Site Surveys

Alternate sites for the proposed MCTT were examined. Site maps were used to estimate the drainage areas at potential locations at the candidate public works yard. Three locations were examined. The upper manhole location would have a relatively small area and the distance from the pavement surface to the pipe crown was only 1.4 m (4.7 ft), too shallow for an effective MCTT. The middle manhole location had a paved yard, plus roof, drainage area of about 0.4 ha (1.0 acres) and the distance from the pavement surface to the pipe crown was 1.8 m (5.9 ft) which would allow a shallow MCTT. The lower manhole location had a drainage area of about 0.6 ha (1.5 acres) and the distance from the pavement surface to the pipe crown was 2.1 m (6.9 ft). The deeper pipe locations were preferred, allowing more efficient MCTT configurations. All existing drainage pipes were 0.3 m (12 inch) in diameter.

The inside vertical dimensions of an MCTT for this site are approximately as follows:

- about 0.15 m (6 in.) for underflow into the main settling chamber (and supports for the inclined tube settlers),
- about 0.6 m (2 ft) for the inclined tube settlers,
- the live settling depth (usually from 0.6 m – 2.7 m, or 2 to 9 ft),
- about 0.15 m (6 in.) freeboard above the live settling depth for absorbent pillows.

Therefore, about 1 m (3 ft) is required, in addition to the live settling depth, for the inside depth of the MCTT. It would be possible to reduce some of the dimensions slightly, but 1.6 m (5 ft) is seen as the likely minimum dimension for an MCTT having a live settling depth of 0.6 m (2 ft). The wall thickness of the bottom and top plates of the MCTT must also be added to these depth requirements. As this is to be located in a heavy weight traffic area, it is expected that 150 mm (6 in.) of heavily reinforced concrete may be needed as the roof of the MCTT (needs to be determined by a structural engineer). With decreasing live settling depths, the surface area of the MCTT must increase to compensate (to obtain the needed tank volume).

MCTT Sizing Options

The following tables summarize the needed MCTT sizes for 70 and 90% toxicity reductions in the main settling chamber for the different main settling chamber heights (the complete MCTT would have increased toxicant reductions, as noted previously). A 70% reduction of toxicants (as indicated by the Azur Environmental Microtox® toxicity screening test) in the main settling chamber would require the capture of

5.1 mm (0.20 in.) of runoff and a holding time of 24 hours, when using a 0.6 m (2 ft) settling depth, as shown on Figure 6.9. In contrast, a 90% reduction would require the capture of 10 mm (0.40 in.) of runoff. The following describes the calculations needed to obtain the actual sizes for the MCTT for the 70% level of treatment in the main settling chamber.

Pavement area: 0.60ha (1.5ac, or 63,600ft^2)

Runoff volume: (0.20in) (63,600ft^2) (ft/12in) = 1,060ft^3 (29 m^3)

Surface area of main settling chamber: 1,060ft^3/2ft depth = 530ft^2 (49 m^2)

Surface area of settling chamber, as a percentage of drainage area: (100) (530ft^2/63,600ft^2) = 0.83%

The sand/peat "filter" size is determined by the following calculations:

Needed average drainage rate: 1,060ft^3/24h = 44ft^3/h (1.2 m^3/h)

The maximum filtration rate is 2 m/d (6 ft/d), or 0.08 m/h (0.25 ft/h) for the filter, based on Austin, TX,
stormwater filtration guidelines

Required area of filtration chamber: (44 ft^3/h)/0.25 ft/h = 176 ft^2 (16 m^2)

Surface area of filtration chamber, as a percentage of drainage area: (100) (176ft^2/63,600ft^2) = 0.28%

The surface area of the main settling chamber plus the "filter" chamber is therefore: 0.83% + 0.28% = 1.11%. The life of the "filtration" media can be estimated knowing the mass of suspended solids that will be discharged from the main settling chamber and directed to the "filtration" chamber. The effluent of the main settling chamber has a suspended solids concentration of approximately 5 mg/L, the volumetric runoff coefficient (Rv) for pavement is about 0.85, and the annual rain depth for Detroit is 790 mm (31 in.). The estimated annual discharge from the main settling chamber is therefore:

(1.5ac)(43,560ft^2/ac)(0.85Rv)(31in/y)(5mgSS/L)(ft/12in)(7.48gal/ft^3)(3.78L/gal) = 21,280,000mgSS/y, or 20,280gSS/y, or 20kgSS/y

The unit area filter loading rate is therefore 1.3kgSS/m^2-y, with a 176ft^2 (16.1m^2) filter area. The peat/sand filter has an estimated lifetime loading capacity, before clogging (flow <1 m/d), of about 5kgSS/m^2. The estimated lifetime of the sand/peat media is therefore about 4 years, before media replacement may be needed. The final filter fabric layer on top of the peat/sand media may extend the lifetime of the media before clogging, requiring replacement of the fabric instead of the media. The preliminary chemical break-through tests (Clark, *et al*. 1997) indicate that clogging, even with the extensive pre-treatment provided by the main settling chamber, will occur before the pollutant removal capacity of the peat/sand will be exceeded. The following tables summarize the calculated sizes for the various MCTT options for this Detroit site:

- 0.6 m (2 ft) live settling depths and 24 h holding times (would require about 1.5 m, or 5 ft, of depth above the drainage pipe crown):

Toxicity Reduction	Settling Chamber Capacity (in. of runoff)	Settling Chamber Area (% of drainage area)	Mixed Media "Filter" Area (% of drainage area)	Total MCTT Area (% of drainage area)
70%	0.20 inch	0.83%	0.28%	1.11%
90%	0.40 inch	1.67%	0.56%	2.22%

If the drainage area was 0.6 ha (1.5 acres or 63,600 ft^2), then the surface area of the MCTT for 70% toxicity reduction would be about 50 m^2 (530 ft^2) for the main settling chamber and about 17 m^2 (180 ft^2) for the "filter" chamber. The inside depth of the chambers would be about 1.5 m (5 ft), and if an 1.5 m X 2.4 m (5 X 8 ft) box culvert was used as the MCTT chambers, 20 m (66 ft) would be required for the length for the main settling chamber and 7 m (23 ft) for the "filter" chamber. The surface areas (and culvert lengths, if still 1.5 m X 2.4 m, or 5 X 8 ft) would be increased by about twice for 90% toxicity reduction in the main settling chamber.

- 1.5 m (5 ft) live settling depths and 48 h holding times (would require about 2.4 m, or 8 ft, of depth above the drainage pipe crown):

Toxicity Reduction	Settling Chamber Capacity (in. of runoff)	Settling Chamber Area (% of drainage area)	Mixed Media "Filter" Area (% of drainage area)	Total MCTT Area (% of drainage area)
70%	0.29 inch	0.48%	0.20%	0.68%
90%	0.51 inch	0.85%	0.35%	1.20%

If the drainage area was 0.6 ha (1.5 acres, or 63,600 ft^2), then the surface area of the MCTT for 70% toxicity reduction would be about 30 m^2 (320 ft^2) for the main settling chamber and about 12 m^2 (130 ft^2) for the "filter" chamber. The inside depth of the chambers would be about 2.4 m (8 ft), and if an 2.4 m X 3.0 m (8 X 10 ft) box culvert was used as the MCTT chambers, 9.8 m (32 ft) would be required for the length for the main settling chamber and 4.0 m (13 ft) for the "filter" chamber. The surface areas (and culvert lengths, if still 2.4 m X 3.0 m, or 8 X 10 ft) would be increased by about 1.8 times for 90% toxicity reduction in the main settling chamber.

- 2.1 m (7 ft) live settling depths and 72 h holding times (would require about 3.0 m, or 10 ft, of depth above the drainage pipe crown):

Toxicity Reduction	Settling Chamber Capacity (in. of runoff)	Settling Chamber Area (% of drainage area)	Mixed Media "Filter" Area (% of drainage area)	Total MCTT Area (% of drainage area)
70%	0.31 inch	0.37%	0.14%	0.51%
90%	0.64 inch	0.76%	0.30%	1.06%

If the drainage area was 0.6 ha (1.5 acres, or 63,600 ft^2), then the surface area of the MCTT for 70% toxicity reduction would be about 22 m^2 (240 ft^2) for the main settling chamber and about 8.4 m^2 (90 ft^2) for the "filter" chamber. The inside depth of the chambers would be about 3.0 m (10 ft), and if a 3.0 m X 3.7 m (10 X 12 ft) box culvert was used as the MCTT chambers, 6.1 m (20 ft) would be required for the length for the main settling chamber and 2.3 m (7.5 ft) for the "filter" chamber. The surface areas (and culvert lengths, if still 3.0 m X 3.7 m, or 10 X 12 ft) would be increased by about 2.1 times for 90% toxicity reduction in the main settling chamber.

- 2.7 m (9 ft) live settling depths and 72 h holding times (would require about 3.7 m, or 12 ft of depth above the drainage pipe crown):

Toxicity Reduction	Settling Chamber Capacity (in. of runoff)	Settling Chamber Area (% of drainage area)	Mixed Media "Filter" Area (% of drainage area)	Total MCTT Area (% of drainage area)
70%	0.36 inch	0.33%	0.17%	0.50%
90%	0.74 inch	0.69%	0.34%	1.03%

If the drainage area was 0.6 ha (1.5 acres, or 63,600 ft^2), then the surface area of the MCTT for 70% toxicity reduction would be about 20 m^2 (210 ft^2) for the main settling chamber and about 10 m^2 (110 ft^2) for the "filter" chamber. The inside depth of the chambers would be about 3.7 m (12 ft), and if a 3.7 m X 4.6 m (12 X 15 ft) culvert was used as the MCTT chambers, 4.3 m (14 ft) would be required for the length for the main settling chamber and 2.3 m (7.5 ft) for the "filter" chamber. The surface areas (and culvert lengths, if still 3.7 m X 4.6 m, or 12 X 15 ft) would be increased by about 2.1 times for 90 % toxicity reduction in the main settling chamber.

Catchbasin/Grit Chamber Design

The last step is to size the catchbasin/grit chamber as a pre-treatment unit. The catchbasin can be located adjacent to the MCTT, or it can be located at inlets upstream to the MCTT. During the pilot-scale Birmingham tests, the catchbasin was located adjacent to the rest of the MCTT units for convenience. However, at the Milwaukee, WI, full-scale MCTT installation, the existing inlet was modified and used as a catchbasin, upstream of the main settling and "filtration" chambers. In Minocqua, WI, the upstream inlets were fitted with the aeration balls in nylon net bags, but a large sump (a 1200 gal precast concrete septic tank) was located before the main settling chamber to serve as the grit chamber/sump.

The general dimensions for a catchbasin/grit chamber were described earlier. For the 305 mm (12 in.) diameter outlet pipe at this site, the catchbasin should be 1.2 m (48 in.) in diameter. The scour depth is about 305 mm (12 in.) for any catchbasin, so the sump should be sized to provide sufficient sacrificial storage capacity. Table 6.2 indicated that the annual sediment accumulation for a site having 790 mm (31 in.) of rain per year, with influent SS concentrations of 100 mg/L, would be about 0.29 m^3/ha-y (4.2 ft^3/ac-y). The 1.2 m (48 in.) diameter sump has a cross-sectional area of about 1.2 m^2 (12.6 ft^2), indicating a sediment accumulation rate of about 100 mm (0.33 ft) per year. If the influent SS concentration was a high 250 mg/L, then the sediment accumulation rate in the sump would be about 240 mm (0.8 ft) per year. A sump depth of 0.6 m (2 ft) (in addition to the 305 mm, 1 ft, scour depth) would therefore provide at least 2 years, to more than 5 years of storage.

Maintenance Activities

No effective stormwater pollution control device can be considered maintenance-free. In order to be effective, the stormwater control device must accumulate pollutants, especially sediment and other debris. As noted previously, the MCTT is designed for reasonable maintenance. The MCTT is intended to be periodically examined about every 6 months, with major maintenance activities every several years.

The chambers of the MCTT should be vented, mosquito proofed, and be made easily accessible for maintenance. Maintenance for the MCTT would consist of inspections, cleaning of the catchbasin, and renewing of the sorbent pillows every 6 – 12 mo. The ion exchange/sorption capacity of the sand-peat media should last from 3 – 5 years before requiring replacement. Specific site conditions may warrant more frequent maintenance, which should be evident after the first few site examinations.

Preliminary Material Specifications

- A removable grid needs to be placed in the catchbasin inlets a few inches above any possible water surface to support a nylon mesh bag (locally available) which contains about a foot thickness of Jaeger 25 mm (1 in.) Tri-Pack High Performance column packing balls (available from W. J. May & Assoc. of Nashville, TN (615) 662-1276, or from Jaeger Products of Houston at (800) 678-0345). Several of these bags need to be made for rotating during cleaning. The support needs to be made of material and constructed so as not to snag and tear the mesh bags.

- The inclined tube settlers can be purchased from Meurer Research (Golden, CO, 303-279-8373) (or alternative). These are about 0.6 m (2 ft) thick and have 0.1 m (4 in.) tubes. The estimated cost for these is about \$25 per ft^2 (for 1.2 m, or 4 ft tall units). They will have to be supported on some type of grid about 0.15 m (6 in.) off the bottom of the tank. Do not use any galvanized metal or treated wood in the installation where water contact is possible (stainless steel, aluminum or plastic are acceptable).

- Floating sorbent pillows can be purchased from New Pig Corp. (Tipton, PA, 800-643-6465) (or alternative). 75 mm X 3.0 m (3 in. X 10 ft) “Spaghetti Socks” float and are about $12 each. About 5 to 10 should be placed in the MCTT main settling chamber at one time.

- The MCTT tank accesses need to be sufficient in size for entry, cleanout and installation. For example, the inclined tube settler sections need to be able to fit through the accesses easily (large 1.8 m X 1.8 m, or 6 ft X 6 ft accesses with hinged steel covers may be better than smaller round manhole covers).

- There should be no direct connection between the main settling chamber and the filtration tank chambers (such as over the top of a tank divider) besides the orifice, because overtopping water would easily scour the filter media. A suitable bypass/overflow should be provided to prevent flooding if the orifice clogs. This bypass/overflow should be around the last filter/sorption chamber, connecting the downstream discharge directly with the main settling chamber.

- The 0.3 – 0.45 m (12 - 18 in.) of mixed filter media is comprised of ½ sand mixed with ½ peat moss. The surface of the mixed filter media is to be covered with a “Gunderboom” fabric material (Amoco 4557, available from Ray Bauer Assoc. in New York at (516) 671-6535 or from Polar Supply, Co. of Anchorage at (907) 563-5000, or from a local Amoco filter fabric distributor). The fabric needs to be one piece (or carefully seamed) and is to cover the top of the media and extend about 0.15 m (6 in.) up the sides of the tank to minimize leakage at the edges. The edges should be anchored to the walls of the MCTT, or weighted with concrete cinder blocks. Do not use loose stone to weigh down the filter fabric (as shown in Figure 5.21) because of difficulties in removing the fabric for cleaning or replacement. The water jet coming from the orifice will need to be directed to some type of splash plate to diffuse the water before it hits the fabric. It can be directed into a perforated pipe laying on the top of the fabric, extending the length of the filter, to serve as a rough flow distributor. The mixed media filter material is laid over another filter fabric and then 0.15 m (6 in.) of sand. The sand is also above another filter fabric and then gravel underdrain material. These bottom two layers of filter fabric also need to extend up the tank several inches and preferably be one piece (or carefully sewn). The top filter fabric acts as a flow distributor and the Amoco fabric also tends to sorb dissolved oils.

- The filter sand material needs to be clean and have an effective size (D_{10}) of about 0.3 mm and an uniformity coefficient (D_{60}/D_{10}) of about 1.5. After the filter media installation is complete, it needs to be carefully rinsed using clean water until the water runs clear to remove any fines.

Figure 6.4 MCTT design curves for Atlanta, GA.

Figure 6.5 MCTT design curves for Austin, TX.

Figure 6.6 MCTT design curves for Bozeman, MT.

Figure 6.7 MCTT design curves for Buffalo, NY.

Figure 6.8 MCTT design curves for Dallas, TX.

Figure 6.9 MCTT design curves for Detroit, MI.

Figure 6.10 MCTT design curves for Little Rock, AR.

Figure 6.11 MCTT design curves for Los Angeles, CA.

Figure 6.12 MCTT design curves for Madison, WI.

Figure 6.13 MCTT design curves for Miami, FL.

Figure 6.14 MCTT design curves for Milwaukee, WI.

Figure 6.15 MCTT design curves for Minneapolis, MN.

Figure 6.16 MCTT design curves for Newark, NJ.

Figure 6.17 MCTT design curves for New Orleans, LA.

Figure 6.18 MCTT design curves for Phoenix, AZ.

Figure 6.19 MCTT design curves for Portland, ME.

Figure 6.20 MCTT design curves for Rapid City, SD.

Figure 6.21 MCTT design curves for Reno, NV.

Figure 6.22 MCTT design curves for Seattle, WA.

Figure 6.23 MCTT design curves for St. Louis, MO.

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Appendix A
Plotted MCTT Performance Data

A-2 A-3 A-4 A-5 A-6 A-7 A-8 A-9

A-10 A-11 A-12 A-13 A-14 A-15 A-16 A-17 A-18 A-19

A-20 A-21 A-22 A-23 A-24 A-25 A-26 A-27 A-28 A-29

A-30 A-31 A-32 A-33 A-34 A-35 A-36 A-37 A-38 A-39

A-40 A-41 A-42 A-43 A-44 A-45 A-46 A-47 A-48 A-49

A-50 A-51 A-52 A-53 A-54 A-55 A-56 A-57 A-58 A-59

A-60 A-61 A-62 A-63 A-64 A-65 A-66 A-67 A-68 A-69 A-70

Table A-54 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #1

Table A-55 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #2

Table A-56 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #3

Table A-57 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #4

Table A-58 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #5

Table A-59 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #6

Table A-60 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #7

Table A-61 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #8

Table A-62 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #9

Table A-63 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #10

Table A-64 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #11

Table A-65 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL Storm Event #12

Table A-66 Particle Size Distributions of MCTT Treated Water – UAB Remote Parking Lot, Birmingham, AL
Storm Event #13

Appendix B

Tabular MCTT Performance Data

B-2 B-3 B-4 B-5 B-6 B-7 B-8 B-9

B-10 B-11 B-12 B-13 B-14 B-15 B-16 B-17 B-18 B-19

B-20 B-21 B-22 B-23 B-24 B-25 B-26 B-27 B-28 B-29

B-30 B-31 B-32 B-33 B-34 B-35 B-36 B-37 B-38 B-39

B-40 B-41 B-42 B-43 B-44 B-45 B-46 B-47 B-48 B-49

B-50 B-51 B-52 B-53 B-54 B-55 B-56 B-57 B-58 B-59

B-64

Table B-54. Observed MCTT Influent Pesticide Concentrations (μg/L)

Continued

Table B-54. Continued

Table B-55. Observed Pesticide Concentrations after Grit Chamber and before Main Settling Chamber (μg/L)

Continued

Table B-55. Continued

Table B-56. Observed Pesticide Concentrations after Main Settling Chamber and before Final MCTT Chamber (μg/L)

Continued

Table B-56. Continued

Table B-57. Observed Pesticide Concentrations in MCTT Effluent (μg/L)

Continued

Table B-57. Continued

Appendix C
Source Area Pollutant Observations

Table C-1. Roof Runoff Sheetflow Quality Observations

	1-Resid. Roof		7-Apt. Roof		23-Resid. Roof		24-Resid. Roof	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	70	86	23	55	2	15	11	31
I35 (% light decrease)	92	98	24	65	15	26	29	48
EC50 (fraction)	0.4	0.4						
Other Constituents								
pH	6.6		7.0		6.7		5.9	
Suspended solids (mg/L)	12		17		3		92	
Turbidity (NTU)	3.8		8.9		1		5.5	
Particle Size								
10% larger (by vol.) than:	59		46		25		69	
25	23		42		16		45	
50	14		39		11		35	
75	12		36		10		18	
85	10		32		9		16	
90	10		30		9		14	
95	9		28		8		11	
99	9		23		8		8	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether			21					
1,3-Dichlorobenzene	14		55	17				
Bis(chloroisopropyl) ether	82		147					
Hexachloroethane								
Naphthalene								
Di-n-butyl phthalate								
Phenanthrene								
Anthracene								
Benzyl butyl phthalate								
Fluoranthene								
Pyrene								
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene	14		6.4					
Benzo(k) fluoranthene	3.4		12					
Benzo(a) pyrene	11		34					
Benzo(g,h,I) perlene								
Pesticides Detected								
Alpha BHC								
Delta BHC								
Aldrin								
DDT	46							
Chlordane	0.9		0.5					
Heavy Metals Detected								
Aluminum	620	230	8370	1550	80	6.4	380	8.7
Cadmium	30	0.3	0.68		0.57		0.32	0.18
Chromium	40	2.3			10			
Copper	170		30	1.3	20	2.6	10	8.7
Lead	70		170		3.1		3.2	
Nickel	7.9		30		4.4		30	

Zinc	1580	1550	60	46	140	140	395	250

Table C-1. Roof Runoff Sheetflow Quality Observations (Continued)

	25-Resid. Roof		10-Car Service Roof		31-Com. Roof		34-Com. Roof	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	40	37	34	39	19	35	25	33
I35 (% light decrease)	46	40	40	45	19	36	29	33
EC50 (fraction)								
Other Constituents								
pH	6.0		7.2		4.4		7.0	
Suspended solids (mg/L)	10		1		<1		7	
Turbidity (NTU)	2		1.2		7.3		1.5	
Particle Size								
10% larger (by vol.) than:	17		84		84		27	
25	15		67		58		21	
50	13		38		32		11	
75	11		22		15		5	
85	11		16		9		5	
90	10		10		8		4	
95	10		8		7		4	
99	9		5		5		3	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether			87	17				
1,3-Dichlorobenzene			88	23				
Bis(chloroisopropyl) ether			68					
Hexachloroethane			56					
Naphthalene			187	13				
Di-n-butyl phthalate	31							
Phenanthrene			22					
Anthracene			24					
Benzyl butyl phthalate			105					
Fluoranthene			45	4.8				
Pyrene			28					
Benzo(a) anthracene			16					
Chrysene			73					
Benzo(b) fluoranthene			266					
Benzo(k) fluoranthene			221					
Benzo(a) pyrene			300					
Benzo(g,h,I) perlene								
Pesticides Detected								
Alpha BHC								
Delta BHC								
Aldrin								
DDT			0.3					
Chlordane								
Heavy Metals Detected								
Aluminum	120	16	270	75	25	11	160	160
Cadmium	0.19	0.13			0.95	0.13	0.28	
Chromium	10		510					
Copper	1.5	1.1	1.7		13	1.6		
Lead	10		1.3		80		5.3	
Nickel	3.6				2.6		70	
Zinc	210	210	410	250	110	110	23	23

Table C-1. Roof Runoff Sheetflow Quality Observations (Continued)

	14-Indus. Roof		49- Indus. Flat Roof		52- Indus. Flat Roof		58- Indus. Flat Roof	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	0	16	13	17	30	13	21	25
I35 (% light decrease)	3	17	16	22	35	21	26	29
EC50 (fraction)								
Other Constituents								
pH	7.3		8.4		8.2		8.2	
Suspended solids (mg/L)	11		6		2		1	
Turbidity (NTU)	8.9		3.5		2		1.5	
Particle Size								
10% larger (by vol.) than:	58		53		16		17	
25	16		42		14		14	
50	9		27		12		8	
75	7		21		11		6	
85	7		18		10		6	
90	6		17		10		6	
95	6		16		9		5	
99	5		15		8		5	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether	20							
1,3-Dichlorobenzene								
Bis(chloroisopropyl) ether								
Hexachloroethane								
Naphthalene	48	21						
Di-n-butyl phthalate								
Phenanthrene								
Anthracene								
Benzyl butyl phthalate								
Fluoranthene	15	14			7.6			
Pyrene								
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene	28							
Benzo(k) fluoranthene	12							
Benzo(a) pyrene	52							
Benzo(g,h,I) perlene								
Pesticides Detected								
Alpha BHC	0.7							
Delta BHC	1.1							
Aldrin	0.7							
DDT								
Chlordane	2.2							
Heavy Metals Detected								
Aluminum	380	30	322	322	420	162	154	154
Cadmium	1.4		1.5	0.6	1.0	0.52	1.0	0.68
Chromium			5		10	1.4	9.1	
Copper	900	1.7	10		30		20	3.7
Lead	80		5.7		50		15	1.1
Nickel			4.9		5.4		5.3	

Zinc	15	15	87	51	11	9	21	12

Table C-2. Parking Area Runoff Sheetflow Quality Observations

	D-Apt.		6-Apt.		2-Inst.		9-Com.	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	61	45	8	26	9	27	0	38
I35 (% light decrease)	66	49	9	27	19	37	0	41
EC50 (fraction)								
Other Constituents								
pH	7.3		6.9		6.7		7.5	
Suspended solids (mg/L)	22		9		27		52	
Turbidity (NTU)	17		14		7.7		7.9	
Particle Size								
10% larger (by vol.) than:	52		52		57		62	
25	40		45		42		51	
50	32		38		30		36	
75	27		32		25		28	
85	25		28		23		26	
90	23		27		22		23	
95	22		24		19		20	
99	18		20		17		17	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether							15	
1,3-Dichlorobenzene	9.6		33				60	17
Bis(chloroisopropyl) ether			81		217		102	
Hexachloroethane					47		41	
Naphthalene							72	6.6
Phenanthrene			41				13	
Benzyl butyl phthalate							21	
Fluoranthene	1		94	4.8			16	
Pyrene	1		80	19			40	
Benzo(a) anthracene	1.8		55				16	
Chrysene			29					
Benzo(b) fluoranthene			132		10		18	
Benzo(k) fluoranthene			11		8		42	
Benzo(a) pyrene			78		21		20	
Benzo(g,h,l) perlene			20					
Pesticides Detected								
DDT			0.3					
Endrin	1.4	0.2						
Chlordane					0.8		1.2	
Heavy Metals Detected								
Aluminum	3420	1110	1580	110	780	230	130	130
Cadmium	70	0.3	0.5		10	0.2	0.72	
Chromium	310		270		40		5.9	1.2
Copper	440	2.8	130	1.3	60		12	
Lead	3.3	1.5	130		130		30	
Nickel			70		60			
Zinc	88	88	40	23	30	25	30	14

Table C-2. Parking Area Runoff Sheetflow Quality Observations (Continued)

	16-Inst. Unpaved		27-Inst. Unpaved		29-Inst. Paved		30-Com.	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	29	13	7	4	9	16	9	29
I35 (% light decrease)	35	13	22	20	10	16	14	29
EC50 (fraction)								
Other Constituents								
pH	8.5		8.0		7.4		7.2	
Suspended solids (mg/L)	750		32		181		69	
Turbidity (NTU)	720		63		67		8	
Particle Size								
10% larger (by vol.) than:	n/a		44		9		59	
25	n/a		41		9		47	
50	n/a		38		8		37	
75	n/a		33		8		29	
85	n/a		30		8		26	
90	n/a		29		7		24	
95	n/a		28		7		21	
99	n/a		25		6		17	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether	24							
1,3-Dichlorobenzene								
Bis(chloroisopropyl) ether								
Hexachloroethane								
Naphthalene								
Phenanthrene								
Benzyl butyl phthalate								
Fluoranthene								
Pyrene								
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene								
Benzo(k) fluoranthene								
Benzo(a) pyrene								
Benzo(g,h,I) perlene								
Pesticides Detected								
DDT								
Endrin								
Chlordane								
Heavy Metals Detected								
Aluminum	22500	120	620	620	6480	480	880	32
Cadmium			0.25		0.24		0.39	0.10
Chromium	>2.4	2.4			30		5.2	
Copper	770	2.6	10	2.0	30	2.7	10	1.6
Lead	130	1.2	1		30		29	
Nickel	20		40		10		50	
Zinc	150	23	13	13	24	18	25	23

Table C-2. Parking Area Runoff Sheetflow Quality Observations (Continued)

	37-Com. Paved		44-Com. Paved		S1-Com. Paved		S2-Com. Paved	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	8	9	11	22	34	30	65	55
I35 (% light decrease)	8	10	16	33	48	43	72	61
EC50 (fraction)							0.25	0.23
Other Constituents								
pH	7.7		8.2		5.6		5.9	
Suspended solids (mg/L)	67		14		50		22	
Turbidity (NTU)	8.8		4.2		20		4.8	
Particle Size								
10% larger (by vol.) than:	66		59		47		73	
25	54		39		42		47	
50	46		18		39		30	
75	39		15		36		23	
85	36		14		34		21	
90	33		13		33		19	
95	29		12		32		18	
99	24		10		28		17	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene								
Bis(chloroisopropyl) ether								
Hexachloroethane								
Naphthalene								
Phenanthrene								
Benzyl butyl phthalate								
Fluoranthene								
Pyrene								
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene								
Benzo(k) fluoranthene								
Benzo(a) pyrene								
Benzo(g,h,I) perlene								
Pesticides Detected								
DDT								
Endrin								
Chlordane								
Heavy Metals Detected								
Aluminum	1530	34	390	91	>222	222	271	14
Cadmium	1.5		2.6	0.23	1.6	1.2	0.63	0.46
Chromium	25		60	1.3	4.6	2.0	11	1.1
Copper	30	9.2			70	31	33	22
Lead	70		5.6		31	2.1	39	2.0
Nickel	50	1.6	4.2		28	3.2	5.4	2.6
Zinc	95	14	12	7	277	259	308	253

Table C-2. Parking Area Runoff Sheetflow Quality Observations (Continued)

	S3-Com. Paved		39-Indus. Unpaved		48-Indus. Unpaved		56-Indus. Unpaved	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	47	35	22	11	18	23	15	22
I35 (% light decrease)	60	58	22	14	26	29	19	22
EC50 (fraction)	0.65	0.38						
Other Constituents								
pH	5.7		7.7		8.7		7.4	
Suspended solids (mg/L)	27		457		39		13	
Turbidity (NTU)	2.0		57		62		8.1	
Particle Size								
10% larger (by vol.) than:	53		51		43		49	
25	46		50		41		45	
50	39		48		39		41	
75	34		44		35		37	
85	33		41		32		34	
90	31		38		30		32	
95	29		35		28		29	
99	26		31		24		25	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene								
Bis(chloroisopropyl) ether								
Hexachloroethane								
Naphthalene								
Phenanthrene								
Benzyl butyl phthalate								
Fluoranthene								
Pyrene								
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene								
Benzo(k) fluoranthene								
Benzo(a) pyrene								
Benzo(g,h,I) perlene								
Pesticides Detected								
DDT								
Endrin								
Chlordane								
Methoxychlor	0.3							
Heavy Metals Detected								
Aluminum	262	<5	4290	2890	4840	100	303	303
Cadmium	3.4	1.8	0.11		1	0.47	1.9	1.0
Chromium	5.0	5.0	4.5	2.1	11		3.8	3.1
Copper	99	61	20	7.9	10	1.8	10	1.1
Lead	29	5.2	60	1.4	14	1.2	10	2.5
Nickel	67	13	130		70		20	
Zinc	647	558	27	27	30	6	28	24

Table C-3. Storage Area Runoff Sheetflow Quality Observations

	43-Com.		46-Com.		13-Indus. Unpaved		51-Indus.	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	0.2	0	21	8	36	57	100	100
I35 (% light decrease)	8	0	26	15	36	57	100	100
EC50 (fraction)							0.1	0.1
Other Constituents								
pH	8.1		7.7		7.6		11.6	
Suspended solids (mg/L)	17		7		453		21	
Turbidity (NTU)	3.5		6.1		260		21	
Particle Size								
10% larger (by vol.) than:	76		48		7		68	
25	58		31		7		53	
50	34		24		6		46	
75	20		20		6		38	
85	17		18		5		35	
90	16		18		5		32	
95	14		17		5		28	
99	10		16		4		23	
Base Neutrals Detected (mg/L)								
1,3-Dichlorobenzene					16	14		
Fluoranthene					4.5			
Bis(2-ethyl hexyl) phthalate	31							
Pyrene					8			
Pesticides Detected								
Chlordane					1.1			
Heavy Metals Detected								
Aluminum	180	54	<5	<5	6990	37	1360	744
Cadmium	2.2	0.72	16	1.6	2.4		10	1.3
Chromium	7.5		3.7		340		90	8.1
Copper	10		10	1.3	300	1.7	30	1
Lead	50	1.6	3.6	1.8	310		9.4	1.6
Nickel	60		1.9		60		30	
Zinc	29	14	103	103	290	9	12	

Table C-3. Storage Area Runoff Sheetflow Quality Observations (Continued)

	53-Indus. Unpaved		54-Indus. Unpaved RR ROW		55-Indus. Unpaved		S6-Junkyard	
	Non-filtered	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**
Microtox Toxicity								
I10 (% light decrease)	36	11	9	8	49	67	100	100
I35 (% light decrease)	38	8	10	6	45	68	100	100
EC50 (fraction)						0.6	0.02	0.07
Other Constituents								
pH	9.0		7.9		10.0		6.5	
Suspended solids (mg/L)	254		10		5		38	
Turbidity (NTU)	119		12		2.4		15	
Particle Size								
10% larger (by vol.) than:	31		31		16		55	
25	30		29		15		49	
50	28		25		13		47	
75	25		23		11		40	
85	23		21		10		38	
90	23		20		10		36	
95	22		18		10		34	
99	18		17		9		30	
Base Neutrals Detected (mg/L)								
1,3-Dichlorobenzene								
Fluoranthene								
Bis(2-ethyl hexyl) phthalate								
Pyrene								
Pesticides Detected								
Chlordane							29	
Heavy Metals Detected								
Aluminum	6040	<5	590	10	480	182	584	33
Cadmium	3.2	0.42	0.91	0.42	10	0.27	17	10
Chromium	20	1.1	60	1.7	69	32	12	12
Copper	120		10	1.5	30	1	1830	1520
Lead	330	5.7	30	1.6	8.4	2.5	99	3.5
Nickel	90		20		7.9		167	87
Zinc	260	8	25	6	21	2	13100	13

Table C-4. Street Runoff Sheetflow Quality Observations (Continued)

	26-Resid.		42-School		A-Indus.		15-Indus.	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	0	12	0	0	27	45	33	10
I35 (% light decrease)	19	30	0	0	32	48	36	10
EC50 (fraction)								
Other Constituents								
pH	6.9		7.4		8.0		7.4	
Suspended solids (mg/L)	7		22		94		52	
Turbidity (NTU)	3.3		7.6		64		83	
Particle Size								
10% larger (by vol.) than:	67		82		20		38	
25	51		55		17		36	
50	34		26		16		34	
75	26		16		15		31	
85	22		15		14		29	
90	20		14		13		27	
95	17		13		12		25	
99	16		11		11		21	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether							15	
1,3-Dichlorobenzene					5.4	3.3		
Fluoranthene					0.6	0.5		
Bis(2-ethyl hexyl) phthalate			305					
Pyrene					1	0.7		
Benzo(b) fluoranthene							14	
Benzo(k) fluoranthene							15	
Benzo(a) pyrene							19	
Pesticides Detected								
Chlordane							0.8	
Heavy Metals Detected								
Aluminum	70	18	292	292	10040	4380	3880	50
Cadmium	0.35	0.10	0.56	0.51	0.40	0.20	220	
Chromium	2.8	1.3	3.2		30	2.7		
Copper	10	1.7	10	0.97	1250	2.1	360	2.9
Lead	30	3.9	1.5	1.5	150		30	
Nickel	3.3		1.2		2.8			
Zinc	58	58	17	3	130	76	80	6

Table C-4. Street Runoff Sheetflow Quality Observations (Continued)

	40-Indus.		50-Indus.	
	Non-filtered	**Filtered**	**Non-filtered**	**Filtered**
Microtox Toxicity				
I10 (% light decrease)	33	43	22	10
I35 (% light decrease)	37	43	32	17
EC50 (fraction)				
Other Constituents				
pH	7.7		8.4	
Suspended solids (mg/L)	105		11	
Turbidity (NTU)	42		3.3	
Particle Size				
10% larger (by vol.) than:	26		51	
25	25		42	
50	22		36	
75	19		31	
85	18		29	
90	17		27	
95	16		24	
99	15		21	
Base Neutrals Detected (mg/L)				
Bis(2-chloroethyl) ether				
1,3-Dichlorobenzene				
Fluoranthene				
Bis(2-ethyl hexyl) phthalate				
Pyrene				
Benzo(b) fluoranthene				
Benzo(k) fluoranthene				
Benzo(a) pyrene				
Pesticides Detected				
Chlordane				
Heavy Metals Detected				
Aluminum	4020	410	>151	151
Cadmium	1.3	0.16	1.0	0.57
Chromium	10	1.3	3.3	2.0
Copper	20	11	10	
Lead	40	1.5	5.0	1.1
Nickel	70		6.3	
Zinc	56	23	>4	4

Table C-5. Loading Dock Runoff Sheetflow Quality Observations

	38-Indus.		47-Indus.		57-Indus.	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity						
I10 (% light decrease)	12	21	31	28	31	9
I35 (% light decrease)	17	21	36	35	37	9
EC50 (fraction)						
Other Constituents						
pH	7.1		8.3		8.0	
Suspended solids (mg/L)	47		34		39	
Turbidity (NTU)	18		7		25	
Particle Size						
10% larger (by vol.) than:	55		46		82	
25	52		25		55	
50	49		20		26	
75	44		17		16	
85	41		16		15	
90	39		16		14	
95	35		14		13	
99	29		13		11	
Base Neutrals Detected (μg/L)						
Pesticides Detected						
Chlordane	1					
Heavy Metals Detected						
Aluminum	810	18	590	<5	930	<5
Cadmium	2.4	0.56	1.2	0.48	0.73	0.28
Chromium	2.4		8.9		40	
Copper	15	15	20		30	2.6
Lead	60		80		25	2.3
Nickel	4.2	1.3	8.1		7.8	
Zinc	79	62	31	4	<1	

Table C-6. Vehicle Service Area Runoff Sheetflow Quality Observations

	C-Gas Station		5-Car Service		8-Car Wash		45-Auto Serv. Stor.	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	0	0	32	40	10	14	5	0
I35 (% light decrease)	0	0	49	46	16	20	9	3
EC50 (fraction)								
Other Constituents								
pH	7.8		7.3		7.3		8.1	
Suspended solids (mg/L)	22		17		38		22	
Turbidity (NTU)	11		12		2.6		4.8	
Particle Size								
10% larger (by vol.) than:	84		47		64		31	
25	59		42		48		17	
50	46		37		30		12	
75	23		33		22		10	
85	20		29		18		10	
90	18		27		17		10	
95	17		25		16		9	
99	15		22		13		8	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether					45	23		
1,3-Dichlorobenzene	6	4.9	72		65	47		
Bis(chloroisopropyl) ether			161		74			
Hexachloroethane					57	53		
Naphthalene			37		104	82		
Acenaphylene								
Fluorene	0.8							
Phenanthrene					11			
Anthracene					44	11		
Benzyl butyl phthalate					47	16		
Fluoranthene			53		25	6.8		
Pyrene			38		51	7.4		
Benzo(a) anthracene			39		31			
Chrysene			25					
Benzo(b) fluoranthene			107		90			
Benzo(k) fluoranthene			15		103			
Benzo(a) pyrene			60		120			
Pesticides Detected								
Chlordane			0.8					
Heavy Metals Detected								
Aluminum	1340	n/a	1370	410	230	200	490	63
Cadmium	30	0.2	1.7		10		2.1	0.34
Chromium	320		30		2.4		8.1	
Copper	6.6	6.3	580	1.1	1.5		10	2.1
Lead	90		110		60		30	1.4
Nickel	60		10		70		7.9	
Zinc	83	83	130	13	50	23	30	11

Table C-6. Vehicle Service Area Runoff Sheetflow Quality Observations (Continued)

	S4-Car Service	
	Non-filtered	**Filtered**
Microtox Toxicity		
I10 (% light decrease)	44	45
I35 (% light decrease)	49	50
EC50 (fraction)		
Other Constituents		
pH	5.3	
Suspended solids (mg/L)	20	
Turbidity (NTU)	21	
Particle Size		
10% larger (by vol.) than:	66	
25	63	
50	60	
75	57	
85	55	
90	54	
95	52	
99	47	
Base Neutrals Detected (mg/L)		
Bis(2-chloroethyl) ether		
1,3-Dichlorobenzene		
Bis(chloroisopropyl) ether		
Hexachloroethane		
Naphthalene		
Acenaphylene		
Fluorene		
Phenanthrene		
Anthracene		
Benzyl butyl phthalate		
Fluoranthene		
Pyrene		
Benzo(a) anthracene		
Chrysene		
Benzo(b) fluoranthene		
Benzo(k) fluoranthene		
Benzo(a) pyrene		
Pesticides Detected		
Chlordane		
Methoxychlor	0.3	
Heavy Metals Detected		
Aluminum	93	<5
Cadmium	2.4	0.50
Chromium	11	2.5
Copper	76	24
Lead	27	3.4
Nickel	62	31
Zinc	234	234

Table C-7. Landscaped Area Runoff Sheetflow Quality Observations

	E-Park		41-Resid. Lawn		17-Inst. Grass		28-Inst. Grass	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	8	4	18	39	0	0	0	6
I35 (% light decrease)	10	11	23	47	0	0	12	21
EC50 (fraction)								
Other Constituents								
pH	6.4		6.4		7.2		7	
Suspended solids (mg/L)	12		10		11		81	
Turbidity (NTU)	62		13		6		64	
Particle Size								
10% larger (by vol.) than:	50		50		49		37	
25	37		35		44		36	
50	33		30		39		33	
75	28		25		36		29	
85	26		24		31		27	
90	25		23		28		25	
95	23		20		25		24	
99	21		17		22		22	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether					56			
1,3-Dichlorobenzene	4.5				54			
Bis(chloroisopropyl) ether					85			
Bis(2-chloroethoxyl) methane					12			
Naphthalene					49			
Phenanthrene					28			
Anthracene					20			
Benzyl butyl phthalate					128			
Fluoranthene	0.7				38			
Pyrene					8.2			
Benzo(a) anthracene					54			
Benzo(b) fluoranthene					30			
Benzo(k) fluoranthene					61			
Benzo(a) pyrene					54			
Pesticides Detected								
Heavy Metals Detected								
Aluminum	2920	1860	180	120	2090	810	1770	1650
Cadmium			1.0	1.0	0.04		0.32	
Chromium	2.2	1.5	110	1.6	100		10	1.4
Copper	50	1.7	4	0.94	110	3.6	10	2.0
Lead	70		1.7	1.7	1.4		9.4	
Nickel			30		130		30	
Zinc	83	83	32	32	24	24	18	18

Table C-7. Landscaped Area Runoff Sheetflow Quality Observations (Continued)

	B-Indus. Grass		S5-Indus. Sidewalk	
	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity				
I10 (% light decrease)	25	75	7	6
I35 (% light decrease)	74	80	10	9
EC50 (fraction)	0.5	0.4		
Other Constituents				
pH	6.2		7.0	
Suspended solids (mg/L)	74		8	
Turbidity (NTU)	130		0.5	
Particle Size				
10% larger (by vol.) than:	13		71	
25	12		59	
50	11		31	
75	10		16	
85	9		13	
90	9		11	
95	9		10	
99	8		8	
Base Neutrals Detected (mg/L)				
Bis(2-chloroethyl) ether				
1,3-Dichlorobenzene	>7.5	7.5		
Bis(chloroisopropyl) ether				
Bis(2-chloroethoxyl) methane	>6	6		
Naphthalene				
Phenanthrene				
Anthracene				
Benzyl butyl phthalate				
Fluoranthene	1.3	1.3		
Pyrene	2.3			
Benzo(a) anthracene				
Benzo(b) fluoranthene				
Benzo(k) fluoranthene				
Benzo(a) pyrene				
Pesticides Detected				
Heavy Metals Detected				
Aluminum	4610	1590	<5	<5
Cadmium			>0.11	0.11
Chromium	250	4.1	3.2	1.5
Copper	300	8.3	17	8.8
Lead	60		3.5	<1
Nickel			21	2.1
Zinc	1160	669	32	32

Table C-8. Dry Weather Urban Creek Water Quality Observations

	35-Det. Pond Influent		**33-Det. Pond Influent**		**12-Det. Pond Influent**		**4-Det. Pond Influent**	
	Non-filtered	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**
Microtox Toxicity								
I10 (% light decrease)	5	9	0	23	20	27	30	33
I35 (% light decrease)	5	17	0	26	20	61	36	42
EC50 (fraction)						0.7		
Other Constituents								
pH	7.0		6.8		7.2		7.1	
Suspended solids (mg/L)	135		126		5		30	
Turbidity (NTU)	59		30		7.9		7.7	
Particle Size								
10% larger (by vol.) than:	41		54		83		56	
25	39		50		45		50	
50	35		44		29		45	
75	30		38		23		39	
85	27		34		21		36	
90	25		32		19		34	
95	24		29		17		32	
99	22		25		16		28	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether					204			
1,3-Dichlorobenzene					120		65	
Bis(chloroisopropyl) ether					78		40	
Hexachloroethane					38		25	
Bis(2-chloroethoxyl) methane					21			
Naphthalene					297	6.7		
Acenaphylene								
Fluorene								
Di-n-butyl phthalate								
Phenanthrene					69			
Anthracene					40			
Benzyl butyl phthalate					59			
Fluoranthene					128			
Bis(2-ethyl hexyl) phthalate								
Pyrene					102			
Benzo(a) anthracene					61			
Chrysene					237			
Benzo(b) fluoranthene					64		8	
Benzo(k) fluoranthene					78		31	
Benzo(a) pyrene					126		19	
Benzo(g,h,i) perylene								
Pesticides Detected								
Alpha BHC								
Delta BHC								
Aldrin								
DDT								
Endrin								
Chlordane								
Heavy Metals Detected								
Aluminum	3250	500	2310	350	103	43	920	120
Cadmium	10		0.33		0.76		30	

Chromium	10		3.7		2.4		30	
Copper	6.2	1.3	6.4	1.5	310		440	1.2
Lead	60		16		100		2.8	
Nickel	30		10	3.6	70			
Zinc	32	17	20	20	23	23	25	16

Table C-8. Dry Weather Urban Creek Water Quality Observations (Continued)

	59-Linda Dr. Creek		61-Shades Plaza Creek		62-Patton Cr. at Hwy 31		63-Patton CR. at P.C. Rd.	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	17	0	0	12	0	1	0	0
I35 (% light decrease)	17	2	0	20	0	7	0	0
EC50 (fraction)								
Other Constituents								
pH	6.9		7.6		8.1		8.2	
Suspended solids (mg/L)	23		8		12		5	
Turbidity (NTU)	5.4		1.2		0.7		0.5	
Particle Size								
10% larger (by vol.) than:	73		52		84		51	
25	62		37		72		33	
50	49		25		45		17	
75	37		19		20		12	
85	32		17		16		10	
90	29		17		14		9	
95	25		16		11		8	
99	22		14		9		7	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene								
Bis(chloroisopropyl) ether								
Hexachloroethane								
Bis(2-chloroethoxyl) methane								
Naphthalene								
Acenaphylene								
Fluorene								
Di-n-butyl phthalate								
Phenanthrene								
Anthracene								
Benzyl butyl phthalate								
Fluoranthene								
Bis(2-ethyl hexyl) phthalate								
Pyrene								
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene								
Benzo(k) fluoranthene								
Benzo(a) pyrene								
Benzo(g,h,i) perylene								
Pesticides Detected								
Alpha BHC								
Delta BHC								
Aldrin								
DDT								
Endrin								
Chlordane								
Heavy Metals								
Aluminum	353	321	251	251	251	251	>303	303
Cadmium	>0.31	0.31	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Chromium	52	3.1	30	<0.1	14	<0.1	<0.1	<0.1
Copper	10	1.6	10	<1	4.8	<1	4.7	<1
Lead	23	<1	23	1.5	2.9	<1	1.5	<1
Nickel	1.7	<1	>2.1	2.1	<1	<1	2.1	<1
Zinc	11	10	5	3	10	<1	3	<1

Table C-8. Dry Weather Urban Creek Water Quality Observations (Continued)

	69-Shades Cr. at Irondale		70-Shades Ck. at Mt. Brook		71-Shades Cr. at Brookwood		76-Shades Cr. at Oxmoor	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	5	5	11	9	6	2	0	11
I35 (% light decrease)	7	6	15	13	13	2	7	11
EC50 (fraction)								
Other Constituents								
pH	8.2		8.6		8.2		7.7	
Suspended solids (mg/L)	5		5		30		27	
Turbidity (NTU)	0.4		0.6		0.4		23	
Particle Size								
10% larger (by vol.) than:	23		85		63		52	
25	17		63		36		50	
50	16		26		25		46	
75	14		16		20		43	
85	13		12		17		40	
90	12		10		17		38	
95	11		9		16		35	
99	10		7		14		29	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene								
Bis(chloroisopropyl) ether								
Hexachloroethane								
Bis(2-chloroethoxyl) methane								
Naphthalene								
Acenaphylene								
Fluorene								
Di-n-butyl phthalate								
Phenanthrene								
Anthracene								
Benzyl butyl phthalate								
Fluoranthene								
Bis(2-ethyl hexyl) phthalate								
Pyrene								
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene								
Benzo(k) fluoranthene								
Benzo(a) pyrene								
Benzo(g,h,i) perylene								
Pesticides Detected								
Alpha BHC								
Delta BHC								
Aldrin								
DDT								
Endrin								
Chlordane								
Heavy Metals								
Aluminum	53	<5	94	93	284	92	1180	64

Cadmium	<0.1	<0.1	<0.1	<0.1	<1	<0.1	<0.1	<0.1
Chromium	>38	3.8	22	1.7	>0.72	0.72	2.6	0.26
Copper	2.9	<1	3.0	<1	4.8	1.2	11	<1
Lead	1.4	<1	21	1.6	13	<1	13	<1
Nickel	13	1.9	<1	<1	22	<1	24	1.7
Zinc	4	4	<1	<1	4	1	9	5

Table C-8. Dry Weather Urban Creek Water Quality Observations (Continued)

	74-Little Cahaba at Moody		73-Little Cahaba at Leeds		72-Little Cahaba at Bailey Rd.		75-Little Cahaba below Dam	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	6	12	0	13	4	6	4	5
I35 (% light decrease)	7	14	0	13	4	11	9	6
EC50 (fraction)								
Other Constituents								
pH	7.7		7.7		8.0		7.8	
Suspended solids (mg/L)	20		8		7		7	
Turbidity (NTU)	1.4		2.5		1.7		5.7	
Particle Size								
10% larger (by vol.) than:	42		47		27		50	
25	38		37		17		40	
50	33		26		15		32	
75	29		20		12		26	
85	27		18		11		24	
90	25		17		10		23	
95	23		16		10		21	
99	22		15		9		18	
Base Neutrals Detected (mg/L)		n/a[1]		n/a[1]				n/a[1]
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene								
Bis(chloroisopropyl) ether								
Hexachloroethane								
Bis(2-chloroethoxyl) methane								
Naphthalene								
Acenaphylene								
Fluorene								
Di-n-butyl phthalate								
Phenanthrene								
Anthracene								
Benzyl butyl phthalate								
Fluoranthene								
Bis(2-ethyl hexyl) phthalate								
Pyrene								
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene								
Benzo(k) fluoranthene								
Benzo(a) pyrene								
Benzo(g,h,i) perylene								
Pesticides Detected								
Alpha BHC								
Delta BHC								
Aldrin								
DDT								
Endrin								
Chlordane								
Heavy Metals								
Aluminum	252	<5	180	43	84	84	24	<5

Cadmium	<0.1	<0.1	0.14	<0.1	<1	<1	<0.1	<0.1
Chromium	>5.7	5.7	3.8	0.19	26	0.49	17	0.83
Copper	3.0	<1	2.2	<1	2.3	<1	14	<1
Lead	1.9	<1	1.6	<1	30	<1	2.1	1.4
Nickel	<1	<1	63	<1	74	<1	30	<1
Zinc	4	4	1	<1	2	<1	4	4

[1] sample bottle for filterable BNA analyses broke for these samples.

Table C-8. Dry Weather Urban Creek Water Quality Observations (Continued)

	70(2)-Shades Cr. at Mt. Brook		71(2)-Shades Cr. at Brookwood		72(2)-Little Cahaba at Bailey Rd.	
	Non-filtered	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**
Microtox Toxicity						
I10 (% light decrease)	15	21	0	0	0	7
I35 (% light decrease)	9.4	17	0	7.3	0	21
EC50 (fraction)						
Other Constituents						
pH	8.4		7.9		7.9	
Suspended solids (mg/L)	10		7		30	
Turbidity (NTU)	0.2		0.2		0.8	
Particle Size						
10% larger (by vol.) than:	60		51		60	
25	32		32		54	
50	17		16		48	
75	12		8		41	
85	11		7		39	
90	10		6		37	
95	9		6		34	
99	8		5		30	
Base Neutrals Detected (mg/L)						
Bis(2-chloroethyl) ether						
1,3-Dichlorobenzene						
Bis(chloroisopropyl) ether						
Hexachloroethane						
Bis(2-chloroethoxyl) methane						
Naphthalene						
Acenaphylene						
Fluorene						
Di-n-butyl phthalate						
Phenanthrene						
Anthracene						
Benzyl butyl phthalate						
Fluoranthene						
Bis(2-ethyl hexyl) phthalate						
Pyrene						
Benzo(a) anthracene						
Chrysene						
Benzo(b) fluoranthene						
Benzo(k) fluoranthene						
Benzo(a) pyrene						
Benzo(g,h,i) perylene						
Pesticides Detected						
Alpha BHC						
Delta BHC						
Aldrin						
DDT						
Endrin						
Chlordane						
Heavy Metals						

Aluminum	<5	<5	<5	<5	692	<5
Cadmium	<0.1	<0.1	0.18	0.18	<0.1	<0.1
Chromium	>1.4	1.4	>4.3	4.3	3.9	1.2
Copper	21	1.7	42	1.2	<1	<1
Lead	16	1.5	11	1.4	44	1.1
Nickel	<1	<1	35	<1	1.8	<1
Zinc	11	11	6	6	9	9

Table C-9. Dry Weather Urban Detention Pond Water Quality Observations

	3-Hoover Pond		11-Georgetown		32-Georgetoen Lake		36-Hoover Pond	
	Non-filtered	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**
Microtox Toxicity								
I10 (% light decrease)	5	0	16	0	9	4	16	20
I35 (% light decrease)	12	15	16	0	13	9	16	20
EC50 (fraction)								
Other Constituents								
pH	7.0		7.1		6.9		7.6	
Suspended solids (mg/L)	6		5		33		12	
Turbidity (NTU)	4		4.5		28		8.5	
Particle Size								
10% larger (by vol.) than:	76		87		55		85	
25	65		72		49		77	
50	45		39		44		58	
75	17		26		37		34	
85	15		23		34		24	
90	14		21		32		20	
95	12		18		29		17	
99	10		16		24		15	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether			15					
1,3-Dichlorobenzene			27	21				
Bis(chloroisopropyl) ether								
Hexachloroethane			53					
Bis(2-chloroethoxyl) methane								
Naphthalene	18	6.6	68	17				
Acenaphylene								
Fluorene								
Di-n-butyl phthalate								
Phenanthrene			10					
Anthracene			5.8					
Benzyl butyl phthalate			13					
Fluoranthene	6.6	6.6	14					
Bis(2-ethyl hexyl) phthalate								
Pyrene	6	5.8	57					
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene								
Benzo(k) fluoranthene								
Benzo(a) pyrene								
Benzo(g,h,i) perylene								
Pesticides Detected								
Alpha BHC								
Delta BHC								
Aldrin								
DDT								
Endrin								
Chlordane								
Heavy Metals Detected								
Aluminum	230	210	860	51	1350	330	190	190

Cadmium	0.20	0.04	0.12		0.28		1	
Chromium	230		1		10			
Copper	210		70		23		22	
Lead	1.5		1		8.8		2.2	
Nickel	70				30		10	
Zinc	22	22	25	25	22	22	10	10

Table C-9. Dry Weather Urban Detention Pond Water Quality Observations (Continued)

	60-Mt. Lake		64-Star Lake		65-Georgetown L		66-Hoover Pond	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	8	7	25	0	2	5	11	16
I35 (% light decrease)	9	12	25	0	2	6	11	17
EC50 (fraction)								
Other Constituents								
pH	7.2		7.2		7.0		7.6	
Suspended solids (mg/L)	7		60		13		7	
Turbidity (NTU)	4.5		13.7		2.7		2.5	
Particle Size								
10% larger (by vol.) than:	52		62		59		52	
25	48		57		42		35	
50	42		50		35		26	
75	37		44		31		23	
85	34		40		28		21	
90	32		37		27		19	
95	30		34		25		18	
99	27		29		22		16	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene								
Bis(chloroisopropyl) ether								
Hexachloroethane								
Bis(2-chloroethoxyl) methane								
Naphthalene								
Acenaphylene								
Fluorene								
Di-n-butyl phthalate								
Phenanthrene								
Anthracene								
Benzyl butyl phthalate								
Fluoranthene								
Bis(2-ethyl hexyl) phthalate								
Pyrene								
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene								
Benzo(k) fluoranthene								
Benzo(a) pyrene								
Benzo(g,h,i) perylene								
Pesticides Detected								
Alpha BHC								
Delta BHC								
Aldrin								
DDT								
Endrin								
Chlordane								
Heavy Metals								
Aluminum	>362	362	1480	<5	334	<5	141	121

Cadmium	11	0.2	0.13	0.10	<0.1	<0.1	<0.1	<0.1
Chromium	15	<0.1	<0.1	<0.1	33	<0.1	<0.1	<0.1
Copper	19	<1	0.2	<1	11	<1	10	<1
Lead	4.5	<1	55	<1	31	<1	43	<1
Nickel	<1	<1	1.2	<1	37	2.2	<1.6	1.6
Zinc	<1	<1	10	8	>12	12	3	3

Table C-9. Dry Weather Urban Detention Pond Water Quality Observations (Continued)

	67-Meadowbrook		**68-Brook Highlands**		**66(2)-Hoover Pond**		**67(2)-Meadowbrook**	
	Non-filtered	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**
Microtox Toxicity								
I10 (% light decrease)	41	7	0	17	10	3.7	0	6.7
I35 (% light decrease)	65	8	0	17	19	14	8.4	16
EC50 (fraction)	n/a							
Other Constituents								
pH	8.0		8.5		7.7		8.6	
Suspended solids (mg/L)	20		3		13		28	
Turbidity (NTU)	1.2		0.5		0.7		1.6	
Particle Size								
10% larger (by vol.) than:	52		34		50		63	
25	49		27		36		60	
50	45		21		29		57	
75	39		17		24		53	
85	37		16		23		50	
90	35		16		22		50	
95	33		15		19		52	
99	29		14		17		43	
Base Neutrals Detected (mg/L)								
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene								
Bis(chloroisopropyl) ether								
Hexachloroethane								
Bis(2-chloroethoxyl) methane								
Naphthalene								
Acenaphylene								
Fluorene								
Di-n-butyl phthalate								
Phenanthrene								
Anthracene								
Benzyl butyl phthalate								
Fluoranthene								
Bis(2-ethyl hexyl) phthalate								
Pyrene								
Benzo(a) anthracene								
Chrysene								
Benzo(b) fluoranthene								
Benzo(k) fluoranthene								
Benzo(a) pyrene								
Benzo(g,h,i) perylene								
Pesticides Detected								
Alpha BHC								
Delta BHC								
Aldrin								
DDT								
Endrin								
Chlordane								
Heavy Metals Detected								
Aluminum	1570	<5	<5	<5	430	211	8.3	<5

Cadmium	<0.1	<0.1	<0.1	<0.1	>0.7	0.69	<0.1	<0.1
Chromium	1.2	<0.1	<0.1	<0.1	1.6	1.3	1.6	2.6
Copper	37	<1	13	<1	>35	35	11	4.8
Lead	>1.4	1.4	18	1.4	24	<1	25	<1
Nickel	15	2.5	>1.5	1.5	6.3	6.3	24	<1
Zinc	7	7	3	<1	<1	<1	<1	<1

Table C-10. New York City Combined Sewer Overflow Water Quality Observations

	Reg 46-49		TI-10A		TI-13		BB-L-22	
	Non-filtered	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**
Microtox Toxicity								
I10 (% light decrease)	9	23	43	37	23	13	59	54
I35 (% light decrease)	14	32	47	43	26	48	61	59
EC50 (fraction)							0.1	0.8
Other Constituents								
pH	7.2		7.1		7.1		7.3	
Suspended solids (mg/L)	36		48		31		34	
Turbidity (NTU)	25		10		5.4		11	
Particle Size								
10% larger (by vol.) than:	81		80		70		74	
25	71		69		55		65	
50	59		58		43		59	
75	48		48		36		51	
85	43		43		33		47	
90	39		40		31		44	
95	35		37		28		41	
99	29		32		23		36	
Base Neutrals Detected (mg/L)						n/a[1]		
Nitrobenzene								
Isophorone								
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene								
Naphthalene								
Diethyl phthalate								
Fluorene								
Di-n-butyl phthalate	17		17					
Phenanthrene								
Benzyl butyl phthalate								
Fluoranthene								
Bis(2-ethyl hexyl) phthalate								
Pyrene								
Di-n-octyl phthalate								
Benzo(a) anthracene								
Chrysene								
Pesticides Detected						n/a[1]		
BHC								
DDD	1.2							
Chlordane								
Heavy Metals Detected								
Aluminum	410	120	2510	30	1450	161	23030	164
Cadmium	1.4	0.43	1.0	0.16	0.65	0.22	1.9	0.72
Chromium	30	1.0					30	
Copper	50	8.8	50	4.2	60	11	160	9.3
Lead	50		120		50		40	
Nickel	5.6	3.0	3.2	1.3	9.1	9.1	16	7.08
Zinc	41	19	31	6	19	9	225	64

[1] insufficient sample for filtered BNA and filtered pesticide analyses.

Table C-10. New York City Combined Sewer Overflow Water Quality Observations (Continued)

	BB-U4		BB-U2		TI-reg 46-49(2)		BB-U-2(2)	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	54	47	58	57	48	42	71	69
I35 (% light decrease)	54	52	63	64	54	49	76	75
EC50 (fraction)	0.1	0.4	<0.1	0.1	0.85		0.01	0.05
Other Constituents								
pH	7.1		7.1		6.7		6.5	
Suspended solids (mg/L)	61		56		44		447	
Turbidity (NTU)	13		13		25		107	
Particle Size								
10% larger (by vol.) than:	61		69		69		17	
25	56		62		60		15	
50	51		55		52		14	
75	44		49		45		12	
85	40		45		41		11	
90	37		42		39		10	
95	33		38		35		9	
99	28		33		32		8	
Base Neutrals Detected (mg/L)								
Nitrobenzene								
Isophorone							10	
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene							22	
Naphthalene							7.7	
Diethyl phthalate								
Fluorene							9.3	
Di-n-butyl phthalate	61						38	
Phenanthrene							33	
Benzyl butyl phthalate							82	
Fluoranthene							6.6	
Bis(2-ethyl hexyl) phthalate							56000[1]	
Pyrene							15	
Di-n-octyl phthalate							43	
Benzo(a) anthracene							11	
Chrysene							8.2	
Pesticides Detected								
BHC								
DDD								
Chlordane								
Heavy Metals Detected								
Aluminum	1610	253	710	<5	720	20	>161	161
Cadmium	1.1	0.19	2.0	0.25	1.6	0.88	1.2	0.74
Chromium	9.6		30		40		8.8	
Copper	100	4.4	90	5.7	50		64	
Lead	60		70		19	1.6	1.7	1.5
Nickel	10	4.2	20	5.1	30	3.5	30	15
Zinc	53	8	55	13	120	48	220	6

[1] likely contamination.

Table C-10. New York City Combined Sewer Overflow Water Quality Observations (Continued)

	TI-10A (2)		BB-L-22 (2)		BB-U4 (2)		TI-13 (2)	
	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered	Non-filtered	Filtered
Microtox Toxicity								
I10 (% light decrease)	60	54	72	66	54	54	54	62
I35 (% light decrease)	65	68	74	72	60	62	60	67
EC50 (fraction)	0.24	0.28	0.14	0.14	0.54	0.45	0.93	0.26
Other Constituents								
pH	6.6		6.6		6.6		6.6	
Suspended solids (mg/L)	140		184		129		52	
Turbidity (NTU)	17		29		21		8.3	
Particle Size								
10% larger (by vol.) than:	62		33		67		77	
25	57		28		61		64	
50	48		24		53		50	
75	40		20		46		40	
85	36		18		42		36	
90	34		17		39		33	
95	31		16		35		30	
99	26		15		29		25	
Base Neutrals Detected (mg/L)								
Nitrobenzene								
Isophorone								
Bis(2-chloroethyl) ether					15.5			
1,3-Dichlorobenzene								
Naphthalene								
Diethyl phthalate					103			
Fluorene								
Di-n-butyl phthalate								
Phenanthrene								
Benzyl butyl phthalate								
Fluoranthene								
Bis(2-ethyl hexyl) phthalate	541		836		115		142	
Pyrene								
Di-n-octyl phthalate								
Benzo(a) anthracene								
Chrysene								
Pesticides Detected								
BHC								
DDD								
Chlordane	0.5							
Heavy Metals Detected								
Aluminum	49	<5	1780	<5	810	<5	740	<5
Cadmium	1.9	0.87	10	0.93	1.6	0.81	0.86	0.67
Chromium	8.3	<1	130	<1	7.5	<1	20	<1
Copper	70	8.3	190	6.9	130	5.0	340	5.7
Lead	9.3	1.7	110	2.2	14	1.5	10	1.8
Nickel	9.7	8.7	29	5.8	16	2.3	9.5	
Zinc	100	18	390	31	210	20	120	35

Table C-10. New York City Combined Sewer Overflow Water Quality Observations (Continued)

	N 16		N 18		N 23		M 36	
	Non-filtered	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**
Microtox Toxicity								
I10 (% light decrease)	68	70	67	68	40	33	64	66
I35 (% light decrease)	72	76	71	77	49	46	70	72
EC50 (fraction)	0.03	0.23	0.15	0.03			0.10	0.14
Other Constituents								
pH	6.7		6.8		6.8		6.7	
Suspended solids (mg/L)	44		11		62		10	
Turbidity (NTU)	12		9.5		31		10	
Particle Size								
10% larger (by vol.) than:	65		75		61		76	
25	59		66		53		68	
50	53		58		44		62	
75	45		49		36		55	
85	42		44		32		51	
90	39		41		29		48	
95	36		38		26		43	
99	32		33		20		37	
Base Neutrals Detected (mg/L)								
Nitrobenzene	27							
Isophorone								
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene								
Naphthalene								
Diethyl phthalate								
Fluorene								
Di-n-butyl phthalate								
Phenanthrene								
Benzyl butyl phthalate								
Fluoranthene								
Bis(2-ethyl hexyl) phthalate								
Pyrene								
Di-n-octyl phthalate								
Benzo(a) anthracene								
Chrysene								
Pesticides Detected								
BHC								
DDD								
Chlordane								
Heavy Metals Detected								
Aluminum	800	423	330	174	500	144	>543	543
Cadmium	2.0		1.7		8.9	0.17	1.1	
Chromium	3.8	<1	3.9	3.6	16	14	>3.9	3.9
Copper	110	22	110	26	30	23	30	23
Lead	40	3.9	15	2.9	14	7.5	4.2	4.2
Nickel	48	48	13	13	6.1	6.1	7.6	5.7
Zinc	91	49	100	80	75	62	63	63

Table C-10. New York City Combined Sewer Overflow Water Quality Observations (Continued)

	M 13		M 36 (2)		M 2 (2)		N 23 (2)	
	Non-filtered	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**	**Non-filtered**	**Filtered**
Microtox Toxicity								
I10 (% light decrease)	59	54	78	61	30	37	77	66
I35 (% light decrease)	60	58	82	65	43	46	79	68
EC50 (fraction)	0.34	0.83	0.09	0.55			0.01	0.19
Other Constituents								
pH	6.6		7.1		7.0		6.5	
Suspended solids (mg/L)	169		93		101		122	
Turbidity (NTU)	28		31		26		11	
Particle Size								
10% larger (by vol.) than:	75		56		51		57	
25	65		50		45		54	
50	58		44		38		49	
75	50		36		31		43	
85	47		33		28		39	
90	44		30		25		37	
95	42		27		23		34	
99	37		22		18		28	
Base Neutrals Detected (mg/L)								
Nitrobenzene								
Isophorone								
Bis(2-chloroethyl) ether								
1,3-Dichlorobenzene								
Naphthalene								
Diethyl phthalate								
Fluorene								
Di-n-butyl phthalate								
Phenanthrene								
Benzyl butyl phthalate								
Fluoranthene								
Bis(2-ethyl hexyl) phthalate								
Pyrene								
Di-n-octyl phthalate								
Benzo(a) anthracene								
Chrysene								
Pesticides Detected								
BHC							0.3	
DDD								
Chlordane								
Heavy Metals Detected								
Aluminum	570	203	1290	283	n/a	174	140	<5
Cadmium	5.1	5.1	10		0.97		0.86	
Chromium	40		29		19		3.5	
Copper	70	25	110	17	27	27	30	12
Lead	90	6.6	90	3.8	92	6.6	6.0	3.2
Nickel	5.4	5.4	15	5.5	9.8	5.5	14	14
Zinc	130	53	200	44	49	49	32	32

Table C-11. Sampling Site Descriptions – Rainfall Conditions During Source Area Sampling

Sample #	Sample Date	Sample Time	Rain depth before sample was collected (in.)	Peak rain intensity before sample was collected (in./h)
A	3/30/89	6:05 AM	1.73 (large)	0.37 (heavy)
B	3/30/89	6:10	1.73	0.37
C	3/30/89	6:25	1.73	0.37
D	3/30/89	6:40	1.73	0.37
E	3/30/89	6:50	1.73	0.37
1	5/14/89	2:40 PM	0.41 (small)	0.20 (light)
2	5/14/89	2:50	0.45	0.20
3	5/14/89	3:00	0.50	0.20
4	5/14/89	3:30	0.53	0.20
5	5/14/89	3:35	0.53	0.20
6	5/14/89	3:50	0.53	0.20
7	5/14/89	4:00	0.53	0.20
8	5/14/89	4:05	0.54	0.20
9	5/14/89	4:15	0.54	0.20
10	5/14/89	4:25	0.54	0.20
11	5/14/89	4:45	0.54	0.20
12	5/14/89	4:50	0.55	0.20
13	5/14/89	5:30	0.55	0.20
14	5/14/89	5:30	0.55	0.20
15	5/14/89	5:40	0.55	0.20
16	5/14/89	5:40	0.55	0.20
17	5/14/89	6:04	0.55	0.20
23	6/4/90	10:45 AM	0.19 (small)	0.18 (light)
24	6/4/90	11:00	0.19	0.18
25	6/4/90	11:05	0.20	0.18
26	6/4/90	11:10	0.22	0.18
27	6/4/90	11:35	0.24	0.18
28	6/4/90	11:45	0.27	0.18
29	6/4/90	11:55	0.29	0.18
31	6/4/90	12:20	0.29	0.18
31	6/4/90	12:25	0.29	0.18
32	6/4/90	12:35	0.29	0.18
33	6/4/90	12:45	0.29	0.18
34	6/4/90	12:55	0.29	0.18
35	6/4/90	1:00 PM	0.29	0.18
36	6/4/90	1:10	0.29	0.18
37	6/4/90	1:30	0.29	0.18
38	6/4/90	1:35	0.29	0.18
39	6/4/90	1:40	0.29	0.18
40	6/4/90	1:45	0.29	0.18
41	7/2/89	7:00 AM	2.06 (large)	0.99 (heavy)

Continued

Table C-11. Sampling Site Descriptions – Rainfall Conditions During Source Area Sampling (Continued)

Sample #	Sample Date	Sample Time	Rain depth before sample was collected (in.)	Peak rain intensity before sample was collected (in./h)
42	7/2/89	7:10	2.15	0.99
43	7/2/89	7:20	2.20	0.99
44	7/2/89	7:30	2.28	0.99
45	7/2/89	7:45	2.38	0.99
46	7/2/89	7:45	2.38	0.99
47	7/2/89	8:10	2.48	0.99
48	7/2/89	8:15	2.48	0.99
49	7/2/89	8:15	2.48	0.99
50	7/2/89	8:30	2.48	0.99
51	7/2/89	8:30	2.48	0.99
52	7/2/89	8:45	2.48	0.99
53	7/2/89	8:55	2.48	0.99
54	7/2/89	9:00	2.48	0.99
55	7/2/89	9:05	2.48	0.99
56	7/2/89	9:20	2.49	0.99
57	7/2/89	9:30	2.49	0.99
58	7/2/89	9:45	2.50	0.99
71(2)	8/30/89	3:10 PM	0.05 (small)	0.09 (light)
70(2)	8/30/89	3:30	0.09	0.09
67(2)	8/30/89	4:10	0.09	0.09
72(2)	8/30/89	4:30	0.10	0.09
66(2)	8/30/89	5:30	0.11	0.09

Note: the rain depths and rain intensities shown are the approximate amounts for these events, up until the time shown for sample collection. The rain values were obtained from the meteorological station in Birmingham (in Homewood) and are only approximate for the sampling locations. These values were used to approximate the rain category (light or heavy rain intensity, and small or large rain amount). The rain history was also used to approximate the antecedent dry period before the event. Samples 59 – 76 were collected during dry weather from local streams. The following list shows the approximate antecedent rain periods for these rains:

3/30/89: 3 days since previous rain to total 1”, or more (short period)
5/14/89: 9 days since previous rains to total 1”, or more (long period)
6/4/89: 13 days since previous rains to total 1”, or more (long period)
7/2/89: <1 day since previous rains to total 1”, or more (short period)
8/30/89: 28 days since previous rains to total 1”, or more (long period)

Table C-12. Sampling Location Descriptions

Table C-12. Sampling Location Descriptions (Continued)

Table C-12. Sampling Location Descriptions (Continued)

Table C-12. Sampling Location Descriptions (Continued)

Table C-12. Sampling Location Descriptions (Continued)

Appendix D
Receiving Water Impacts

The main purpose of treating stormwater is to reduce its adverse impacts on receiving water beneficial uses. Therefore, it is important in any urban stormwater runoff study to assess the detrimental effects that runoff is actually having on a receiving water. Urban receiving waters may have many beneficial use goals, including:

- stormwater conveyance (flood prevention)
- biological uses (warm water fishery, biological integrity, etc.)
- non-contact recreation (linear parks, aesthetics, boating, etc.)
- contact recreation (swimming)
- water supply

With full development in an urban watershed and with no stormwater controls, it is unlikely that any of these uses can be obtained. With less development and with the application of stormwater controls, some uses may be possible. It is important that unreasonable expectations not be placed on urban waters, as the cost to obtain these uses may be prohibitive. With full-scale development and lack of adequate stormwater controls, severely degraded streams will be common. However, stormwater conveyance and aesthetics should be the basic beneficial use goals for all urban waters. Biological integrity should also be a goal, but with the realization that the natural stream ecosystem will be severely modified with urbanization. Certain basic controls, installed at the time of development, plus protection of stream habitat, may enable partial use of some of these basic goals in urbanized watersheds. Careful planning and optimal utilization of stormwater controls are necessary to obtain these basic goals in most watersheds. Water contact recreation, consumptive fisheries, and water supplies are not appropriate goals for most urbanized watersheds. These higher uses may be possible in urban areas where the receiving waters are large and drain mostly undeveloped areas.

In general, monitoring of urban stormwater runoff has indicated that the biological beneficial uses of urban receiving waters are most likely affected by habitat destruction and long-term pollutant exposures (especially to macroinvertebrates via contaminated sediment), while documented effects associated from acute exposures of toxicants in the water column are rare (Field and Pitt 1990; Pitt 1994; Pitt 1995). Receiving water pollutant concentrations resulting from runoff events and typical laboratory bioassay test results have not indicated many significant short-term receiving water problems. As an example, Lee and Jones-Lee (1993) state that exceedences of numeric criteria by short-term discharges do not necessarily imply that a beneficial use impairment exists. Many toxicologists and water quality expects have concluded that the relatively short periods of exposures to the toxicant concentrations in stormwater are not sufficient to produce the receiving water effects that are evident in urban receiving waters, especially considering the relatively large portion of the toxicants that are associated with particulates (Lee and Jones-Lee 1995). Lee and Jones-Lee (1995) conclude that the biological problems evident in urban receiving waters are mostly associated with illegal discharges and that the sediment bound toxicants are of little risk. Mancini and Plummer (1986) have long been advocates of numeric water quality standards for stormwater that reflect the partitioning of the toxicants and the short periods of exposure during rains. Unfortunately, this approach attempts to isolate individual runoff events and does not consider the accumulative adverse effects caused by the frequent exposures of receiving water organisms to stormwater (Davies 1995; Herricks, *et al*. 1996a and 1996b). Recent investigations have identified acute toxicity problems associated with short-term (about 10 to 20 day) exposures to adverse toxicant concentrations in urban receiving streams (Crunkilton, *et al*.

1996). However, the most severe receiving water problems are likely associated with chronic exposures to contaminated sediment and to habitat destruction. The following is a summary of recent work describing the toxicological and ecological effects of stormwater.

Toxicological Effects of Stormwater

The need for endpoints for toxicological assessments using multiple stressors was discussed by Marcy and Gerritsen (1996). They used five watershed-level ecological risk assessments to develop appropriate endpoints based on specific project objectives. Dyer and White (1996) also examined the problem of multiple stressors affecting toxicity assessments. They felt that field surveys rarely can be used to verify simple single parameter laboratory experiments. They developed a watershed approach integrating numerous databases in conjunction with *in-situ* biological observations to help examine the effects of many possible causative factors. Toxic effect endpoints are additive for compounds having the same "mode of toxic action", enabling predictions of complex chemical mixtures in water, as reported by *Environmental Science & Technology* (1996a). According to EPA researchers at the Environmental Research Laboratory in Duluth, MN, there are about five or six major action groups that contain almost all of the compounds of interest in the aquatic environment. Much work still needs to be done, but these new developing tools may enable the in-stream toxic effects of stormwater to be better predicted.

Ireland, *et al*. (1996) found that exposure to UV radiation (natural sunlight) increased the toxicity of PAH contaminated urban sediments to *C. dubia*. The toxicity was removed when the UV wavelengths did not penetrate the water column to the exposed organisms. Toxicity was also reduced significantly in the presence of UV when the organic fraction of the stormwater was removed. Photo-induced toxicity occurred frequently during low flow conditions and wet weather runoff and was reduced during turbid conditions.

Johnson, *et al*. (1996) and Herricks, *et al*. (1996a and 1996b) describe a structured tier testing protocol to assess both short-term and long-term wet weather discharge toxicity that they developed and tested. The protocol recognizes that the test systems must be appropriate to the time-scale of exposure during the discharge. Therefore, three time-scale protocols were developed, for intra-event, event, and long-term exposures. The use of standard whole effluent toxicity (WET) tests were found to over-estimate the potential toxicity of stormwater discharges.

The effects of stormwater on Lincoln Creek, near Milwaukee, WI, were described by Crunkilton, *et al*. (1996). Lincoln Creek drains a heavily urbanized watershed of 19 mi^2 that is about nine miles long. On-site toxicity testing was conducted with side-stream flow-through aquaria using fathead minnows, plus in-stream biological assessments, along with water and sediment chemical measurements. In the basic tests, Lincoln Creek water was continuously pumped through the test tanks, reflecting the natural changes in water quality during both dry and wet weather conditions. The continuous flow-through mortality tests indicated no toxicity until after about 14 d of exposure, with more than 80% mortality after about 25 d, indicating that short-term toxicity tests likely underestimate stormwater toxicity. The biological and physical habitat assessments supported a definitive relationship between degraded stream ecology and urban runoff.

Rainbow (1996) presented a detailed overview of heavy metals in aquatic invertebrates. He concluded that the presence of a metal in an organism cannot tell us directly whether that metal is poisoning the organism. However, if compared to concentrations in a suite of well-researched biomonitors, it is possible to determine if the accumulated concentrations are atypically high, with a possibility that toxic effects may be present. Allen (1996) also presented an overview of metal contaminated aquatic sediments. This book presents many topics that would enable the user to better interpret measured heavy metal concentrations in urban stream sediments.

Ecological Effects of Stormwater

A number of comprehensive and long-term studies of biological beneficial uses in areas not affected by conventional point source discharges have typically shown impairments caused by urban runoff. The following paragraphs briefly describe a variety of such studies.

Klein (1979) studied 27 small watersheds having similar physical characteristics, but having varying land uses, in the Piedmont region of Maryland. During an initial phase of the study, they found definite relationships between water quality and land use. Subsequent study phases examined aquatic life relationships in the watersheds. The principal finding was that stream aquatic life problems were first identified with watersheds having imperviousness areas comprising at least 12 percent of the watershed. Severe problems were noted after the imperviousness quantities reached 30 percent.

Receiving water impact studies were also conducted in North Carolina (Lenet, *et al*. 1979; Lenet and Eagleson 1981; Lenat, *et al*. 1981). The benthic fauna occurred mainly on rocks. As sedimentation increased, the amount of exposed rocks decreased, with a decreasing density of benthic macroinvertebrates. Data from 1978 and 1979 in five cities showed that urban streams were grossly polluted by a combination of toxicants and sediment. Chemical analyses, without biological analyses, would have underestimated the severity of the problems because the water column quality varied rapidly, while the major problems were associated with sediment quality and effects on macroinvertebrates. Macroinvertebrate diversities were severely reduced in the urban streams, compared to the control streams. The biotic indices indicated very poor conditions for all urban streams. Occasionally, high populations of pollutant tolerant organisms were found in the urban streams, but would abruptly disappear before subsequent sampling efforts. This was probably caused by intermittent discharges of spills or illegal dumpings of toxicants. Although the cities studied were located in different geographic areas of North Carolina, the results were remarkably uniform.

During the Coyote Creek, San Jose, California, receiving water study, 41 stations were sampled in both urban and nonurban perennial flow stretches of the creek over three years. Short and long-term sampling techniques were used to evaluate the effects of urban runoff on water quality, sediment properties, fish, macroinvertebrates, attached algae, and rooted aquatic vegetation (Pitt and Bozeman 1982). These investigations found distinct differences in the taxonomic composition and relative abundance of the aquatic biota present. The non-urban sections of the creek supported a comparatively diverse assemblage of aquatic organisms including an abundance of native fishes and numerous benthic macroinvertebrate taxa. In contrast, however, the urban portions of the creek (less than 5% urbanized), affected only by urban runoff discharges and not industrial or municipal discharges, had an aquatic community generally lacking in diversity and was dominated by pollution-tolerant organisms such as mosquitofish and tubificid worms.

A major nonpoint runoff receiving water impact research program was conducted in Georgia (Cook, *et al*. 1983). Several groups of researchers examined streams in major areas of the state. Benke, *et al*. (1981) studied 21 stream ecosystems near Atlanta having watersheds of one to three square miles each and land uses ranging from 0 to 98 percent urbanization. They measured stream water quality but found little relationship between water quality and degree of urbanization. The water quality parameters also did not identify a major degree of pollution. In contrast, there were major correlations between urbanization and the number of species found. They had problems applying diversity indices to their study because the individual organisms varied greatly in size (biomass). CTA (1983) also examined receiving water aquatic biota impacts associated with urban runoff sources in Georgia. They studied habitat composition, water quality, macroinvertebrates, periphyton, fish, and toxicant concentrations in the water, sediment, and fish. They found that the impacts of land use were the greatest in the urban basins. Beneficial uses were impaired or denied in all three urban basins studied. Fish were absent in two of the basins and severely restricted in the third. The native macroinvertebrates were replaced with pollution tolerant organisms. The periphyton in the urban streams were very different from those found in the control streams and were dominated by species known to create taste and odor problems.

Pratt, *et al*. (1981) used basket artificial substrates to compare benthic population trends along urban and nonurban areas of the Green River in Massachusetts. The benthic community became increasing disrupted as urbanization increased. The problems were not only associated with times of heavy rain, but seemed to be affected at all times. The stress was greatest during summer low flow periods and was probably localized near the stream bed. They concluded that the high degree of correspondence between the known sources of urban runoff and the observed effects on the benthic community was a forceful argument that urban runoff was the causal agent of the disruption observed.

Cedar swamps in the New Jersey Pine Barrens were studied by Ehrenfeld and Schneider (1983). They examined nineteen wetlands subjected to varying amounts of urbanization. Typical plant species were lost and replaced by weeds and exotic plants in urban runoff affected wetlands. Increased uptakes of phosphorus and lead in the plants were found. It was concluded that the presence of stormwater runoff to the cedar swamps caused marked changes in community structure, vegetation dynamics, and plant tissue element concentrations.

Medeiros and Coler (1982) and Medeiros, *et al*. (1984) used a combination of laboratory and field studies to investigate the effects of urban runoff on fathead minnows. Hatchability, survival, and growth were assessed in the laboratory in flow-through and static bioassay tests. Growth was reduced to one half of the control growth rates at 60 percent dilutions of urban runoff. The observed effects were believed to be associated with a combination of toxicants.

The University of Washington (Pederson 1981; Richey, *et al*. 1981; Perkins 1982; Richey 1982; Scott, *et al*. 1982; Ebbert, *et al*. 1983; Pitt and Bissonnette 1984; and Prych and Ebbert undated) conducted a series of studies to contrast the biological and chemical conditions in urban Kelsey Creek with rural Bear Creek in Bellevue, Washington. The urban creek was significantly degraded when compared to the rural creek, but still supported a productive, but limited and unhealthy salmonid fishery. Many of the fish in the urban creek, however, had respiratory anomalies. The urban creek was not grossly polluted, but flooding from urban developments had increased dramatically in recent years. These increased flows dramatically changed the urban stream's channel, by causing unstable conditions with increased stream bed movement, and by altering the availability of food for the aquatic organisms. The aquatic organisms were very dependent on the few relatively undisturbed reaches. Dissolved oxygen concentrations in the sediments depressed embryo salmon survival in the urban creek. Various organic and metallic priority pollutants were discharged to the urban creek, but most of them were apparently carried through the creek system by the high storm flows to Lake Washington. The urbanized Kelsey Creek also had higher water temperatures (probably due to reduced shading) than Bear Creek. This probably caused the faster fish growth in Kelsey Creek.

The fish population in the urbanized Kelsey Creek had adapted to its degrading environment by shifting the species composition from coho salmon to less sensitive cutthroat trout and by making extensive use of less disturbed refuge areas. Studies of damaged gills found that up to three-fourths of the fish in Kelsey Creek were affected with respiratory anomalies, while no cutthroat trout and only two of the coho salmon sampled in the forested Bear Creek had damaged gills. Massive fish kills in Kelsey Creek and its tributaries were also observed on several occasions during the project due to the dumping of toxic materials down the storm drains.

There were also significant differences in the numbers and types of benthic organisms found in urban and forested creeks during the Bellevue research. Mayflies, stoneflies, caddisflies, and beetles were rarely observed in the urban Kelsey Creek, but were quite abundant in the forested Bear Creek. These organisms are commonly regarded as sensitive indicators of environmental degradation. One example of degraded conditions in Kelsey Creek was shown by a specie of clams (*Unionidae*) that was not found in Kelsey Creek, but was commonly found in Bear Creek. These clams are very sensitive to heavy siltation and unstable sediments. Empty clam shells, however, were found buried in the Kelsey Creek sediments indicating their previous presence in the creek and their inability to adjust to the changing conditions. The benthic organism composition in Kelsey Creek varied radically with time and place while the organisms were much more stable in Bear Creek.

Urban runoff impact studies were conducted in the Hillsborough River near Tampa Bay, Florida, as part of the U.S. EPA’s Nationwide Urban Runoff Program (NURP) (Mote Marine Laboratory 1984). Plants, animals, sediment, and water quality were all studied in the field and supplemented by laboratory bioassay tests. Effects of salt water intrusion and urban runoff were both measured because of the estuarine environment. During wet weather, freshwater species were found closer to the Bay than during dry weather. In coastal areas, these additional natural factors made it even more difficult to identify the cause and effect relationships for aquatic life problems. During another NURP project, Striegl (1985) found that the effects of accumulated pollutants in Lake Ellyn (Glen Ellyn, Ill.) inhibited desirable benthic invertebrates and fish and increased undesirable phyotoplankton blooms.

The number of benthic organism taxa in Shabakunk Creek in Mercer County, New Jersey, declined from 13 in relatively undeveloped areas to four below heavily urbanized areas (Garie and McIntosh 1986 and 1990). Periphyton samples were also analyzed for heavy metals with significantly higher metal concentrations found below the heavily urbanized area than above.

Many of the above noted biological effects associated with urban runoff are likely caused by polluted sediments and benthic organism impacts. Examples of heavy metal and nutrient accumulations in sediments are numerous. In addition to the studies noted above, DePinto, *et al*. (1980) found that the cadmium content of river sediments can be more than 1,000 times greater than the overlying water concentrations and the accumulation factors in sediments are closely correlated with sediment organic content. Another comprehensive study on polluted sediment was conducted by Wilber and Hunter (1980) along the Saddle River in New Jersey where they found significant increases in sediment contamination with increasing urbanization.

The effects of urban runoff on receiving water aquatic organisms or other beneficial uses is very site specific. Different land development practices create substantially different runoff flow characteristics. Different rain patterns cause different particulate washoff, transport and dilution conditions. Local attitudes also define specific beneficial uses and, therefore, current problems. There is also a wide variety of water types receiving urban runoff, and these waters all have watersheds that are urbanized to various degrees. Therefore, it is not surprising that urban runoff effects, though generally dramatic, are also quite variable and site specific. Claytor (1996a) summarized the approach developed by the Center for Watershed Protection as part of their EPA sponsored research on stormwater indicators (Claytor and Brown 1996). The 26 stormwater indicators used for assessing receiving water conditions were divided into six broad categories: water quality, physical/hydrological, biological, social, programmatic, and site. These were presented as tools to measure stress (impacting receiving waters), to assess the resource itself, and to indicate stormwater control program implementation effectiveness. The biological communities in Delaware's Piedmont streams have been severely impacted by stormwater, after the extent of imperviousness in the watersheds exceeds about 8 to 15%, according to a review article by Claytor (1996c). If just conventional water quality measures are used, almost all (87%) of the state's non-tidal streams supported their designated biological uses. However, when biological assessments are included, only 13% of the streams were satisfactory.

Changes in physical stream channel characteristics can have a significant effect on the biological health of the stream. Schueler (1996) stated that channel geometry stability can be a good indicator of the effectiveness of stormwater control practices. He also found that once a watershed area has more than about 10 to 15% effective impervious cover, noticeable changes in channel morphology occur, along with quantifiable impacts on water quality, and biological conditions. Stephenson (1996) studied changes in streamflow volumes in South Africa during urbanization. He found increased stormwater runoff, decreases in the groundwater table, and dramatically decreased times of concentration. The peak flow rates increased by about two-fold, about half caused by increased pavement (in an area having only about 5% effective impervious cover), with the remainder caused by decreased times of concentration.

Fates of Stormwater Pollutants in Surface Waters

Many processes may affect urban runoff pollutants after discharge. Sedimentation in the receiving water is the most common fate mechanism because many of the pollutants investigated are mostly associated with settleable particulate matter and have relatively low filterable concentration components. Exceptions include zinc and 1,3-dichlorobenzene which are mostly associated with the filtered sample portions. Particulate reduction can occur in many stormwater runoff and combined sewer overflow (SCSO) control facilities, including (but not limited to) catchbasins, swirl concentrators, fine mesh screens, sand or other filters, drainage systems, and detention ponds. These control facilities (with the possible exception of drainage systems) allow reduction of the accumulated polluted sediment for final disposal in an appropriate manner. Uncontrolled sedimentation will occur in relatively quiescent receiving waters, such as lakes, reservoirs, or slow moving rivers or streams. In these cases, the wide dispersal of the contaminated sediment is difficult to remove and can cause significant detrimental effects on biological processes.

Biological or chemical degradation of the sediment toxicants may occur in the typically anaerobic environment of the sediment, but the degradation is quite slow for many of the pollutants. Degradation by photochemical reaction and volatilization (evaporation) of the soluble pollutants may also occur, especially when these pollutants are near the surface of aerated waters (Callahan, *et al*. 1979; Parmer 1993). Increased turbulence and aeration encourages these degradation processes, which in turn may significantly reduce toxicant concentrations. In contrast, quiescent waters would encourage sedimentation that would also reduce water column toxicant concentrations, but increase sediment toxicant concentrations. Metal precipitation and sorption of pollutants onto suspended solids increases the sedimentation and/or floatation potential of the pollutants and also encourages more efficient bonding of the pollutants to soil particles, preventing their leaching to surrounding waters.

Receiving waters have a natural capacity to treat and/or assimilate polluted discharges. This capacity will be exceeded sooner (assuming equal inputs), resulting in more degradation, in smaller urban creeks and streams, than in larger receiving waters. Larger receiving waters may still have ecosystem problems from the long-term build up of toxicants in the sediment and repeated exposures to high flowrates, but these problems will be harder to identify using chemical analyses of the water alone, because of increased dilution (Pitt and Bissonnette 1984).

In-stream receiving water investigations of urban runoff effects need a mult-tiered monitoring approach, including habitat evaluations, water and sediment quality monitoring, flow monitoring, and biological investigations, conducted over long periods of time (Pitt 1991). In-stream taxonomic (biological community structure) investigations are needed to help identify actual toxicity problems. Laboratory bioassay tests can be useful to determine the major sources of toxicants and to investigate toxicity reduction through treatment, but they are not a substitute for actual in-stream investigations of receiving water effects. In order to identify the sources and treatability of the problem pollutants, detailed watershed investigations are needed, including both dry and wet weather urban drainage monitoring and source area monitoring.

An estimate of the actual pollutant loads (calculated from the runoff volumes and pollutant concentrations) from different watershed areas is needed for the selection and design of most treatment devices. Several characteristics of a source area are significant influences on the pollutant concentrations and stormwater runoff volumes. The washoff of debris, soil, and pollutants depends on the intensity of the rain, the properties of the material removed, and the surface characteristics where the material resides. The potential mass of pollutants available to be washed off will be directly related to the time interval between runoff events during which the pollutants can accumulate.

Human Health Effects of Stormwater

Water Environment & Technology (1996b) reported on an epidemiology study conducted at Santa Monica Bay, CA, that found that swimmers who swam in front of stormwater outfalls were 50% more likely to develop a variety of symptoms than those who swam 400 m from the same outfalls (Haile, *et al*. 1996). This was a follow-up study after previous investigations found that human fecal waste was present in the stormwater collection systems. *Environmental Science & Technology* (1996b) also reported on this Santa Monica Bay study. They reported that more than 1% of the swimmers who swam in front of the outfalls were affected by fevers, chills, ear discharges, vomiting and coughing, based on surveys of more than 15,000 swimmers. The health effects were also more common for swimmers who were exposed on days when viruses were found in the outfall water samples.

Water Environment & Technology (1996a) reported that the fecal coliform counts decreased from about 500 counts/100 mL to about 150 counts/100 mL in the Mississippi River after the sewer separation program in the Minneapolis and St. Paul area of Minnesota. Combined sewers in 8,500 ha were separated during this 10-year, $332 million program.

Groundwater Impacts from Stormwater Infiltration

Prior to urbanization, groundwater recharge resulted from infiltration of precipitation through pervious surfaces, including grasslands and woods. This infiltrating water was relatively uncontaminated. With urbanization, the permeable soil surface area through which recharge by infiltration could occur was reduced. This resulted in much less groundwater recharge and greatly increased surface runoff. In addition, the waters available for recharge generally carried increased quantities of pollutants. With urbanization, new sources of groundwater recharge also occurred, including recharge from domestic septic tanks, percolation basins and industrial waste injection wells, and from agricultural and residential irrigation. The following paragraphs (from Pitt, *et al*. 1994 and 1996) describe the stormwater pollutants that have the greatest potential of adversely affecting groundwater quality during inadvertent or intentional stormwater infiltration, along with suggestions on how to minimize these potential problems.

Constituents of Concern

Nutrients

Nitrates are one of the most frequently encountered contaminants in groundwater. Groundwater contamination of phosphorus has not been as widespread, or as severe, as for nitrogen compounds. Whenever nitrogen-containing compounds come into contact with soil, a potential for nitrate leaching into groundwater exists, especially in rapid-infiltration wastewater basins, stormwater infiltration devices, and in agricultural areas. Nitrate has leached from fertilizers and affected groundwaters under various turf grasses in urban areas, including golf courses, parks and home lawns. Significant leaching of nitrates occurs during the cool, wet seasons. Cool temperatures reduce denitrification and ammonia volatilization, and limit microbial nitrogen immobilization and plant uptake. The use of slow-release fertilizers is recommended in areas having potential groundwater nitrate problems. The slow-release fertilizers include urea formaldehyde (UF), methylene urea, isobutylidene diurea (IBDU), and sulfur-coated urea. Residual nitrate concentrations are highly variable in soil due to soil texture, mineralization, rainfall and irrigation patterns, organic matter content, crop yield, nitrogen fertilizer/sludge rate, denitrification, and soil compaction. Nitrate is highly soluble (>1 kg/L) and will stay in solution in the percolation water, after leaving the root zone, until it reaches the groundwater.

Pesticides

Urban pesticide contamination of groundwater can result from municipal and homeowner use of pesticides for pest control and their subsequent collection in stormwater runoff. Pesticides that have been found in urban groundwaters include: 2,4-D, 2,4,5-T, atrazine, chlordane, diazinon, ethion, malathion, methyl trithion, silvex, and simazine. Heavy repetitive use of mobile pesticides on irrigated and sandy soils likely contaminates groundwater. Fungicides and nematocides must be mobile in order to reach the target pest and hence, they generally have the highest contamination potential. Pesticide leaching depends on patterns of use, soil texture, total organic carbon content of the soil, pesticide persistence, and depth to the water table.

The greatest pesticide mobility occurs in areas with coarse-grained or sandy soils without a hardpan layer, having low clay and organic matter content and high permeability. Structural voids, which are generally found in the surface layer of finer-textured soils rich in clay, can transmit pesticides rapidly when the voids are filled with water and the adsorbing surfaces of the soil matrix are bypassed. In general, pesticides with low water solubilities, high octanol-water partitioning coefficients, and high carbon partitioning coefficients are less mobile. The slower moving pesticides have been recommended in areas of groundwater contamination concern. These include the fungicides iprodione and triadimefon, the insecticides isofenphos and chlorpyrifos and the herbicide glyphosate. The most mobile pesticides include: 2,4-D, acenaphthylene, alachlor, atrazine, cyanazine, dacthal, diazinon, dicamba, malathion, and metolachlor.

Pesticides decompose in soil and water, but the total decomposition time can range from days to years. Literature half-lives for pesticides generally apply to surface soils and do not account for the reduced microbial activity found deep in the vadose zone. Pesticides with a thirty-day half life can show considerable leaching. An order-of-magnitude difference in half-life results in a five- to ten-fold difference in percolation loss. Organophosphate pesticides are less persistent than organochlorine pesticides, but they also are not strongly adsorbed by the sediment and are likely to leach into the vadose zone, and the groundwater.

Other Organics

The most commonly occurring organic compounds that have been found in urban groundwaters include phthalate esters (especially bis(2-ethylhexyl)phthalate) and phenolic compounds. Other organics more rarely found, possibly due to losses during sample collection, have included the volatiles: benzene, chloroform, methylene chloride, trichloroethylene, tetrachloroethylene, toluene, and xylene. PAHs (especially benzo(a)anthracene, chrysene, anthracene and benzo(b)fluoroanthenene) have also been found in groundwaters near industrial sites.

Groundwater contamination from organics, like from other pollutants, occurs more readily in areas with sandy soils and where the water table is near the land surface. Removal of organics from the soil and recharge water can occur by one of three methods: volatilization, sorption, and degradation. Volatilization can significantly reduce the concentrations of the most volatile compounds in groundwater, but the rate of gas transfer from the soil to the air is usually limited by the presence of soil water. Hydrophobic sorption onto soil organic matter limits the mobility of less soluble base/neutral and acid extractable compounds through organic soils and the vadose zone. Sorption is not always a permanent removal mechanism, however. Organic re-solubilization can occur during wet periods following dry periods. Many organics can be at least partially degraded by microorganisms, but others cannot. Temperature, pH, moisture content, ion exchange capacity of soil, and air availability may limit the microbial degradation potential for even the most degradable organic.

Pathogenic Microorganisms

Viruses have been detected in groundwater where stormwater recharge basins were located short distances above the aquifer. Enteric viruses are more resistant to environmental factors than enteric bacteria and they exhibit longer survival times in natural waters. They can occur in potable and marine waters in the absence of fecal coliforms. Enteroviruses are also more resistant to commonly used disinfectants than are indicator bacteria, and can occur in groundwater in the absence of indicator bacteria.

The factors that affect the survival of enteric bacteria and viruses in the soil include pH, antagonism from soil microflora, moisture content, temperature, sunlight, and organic matter. The two most important attributes of viruses that permit their long-term survival in the environment are their structure and very small size. These characteristics permit virus occlusion and protection within colloid-size particles. Viral adsorption is promoted by increasing cation concentration, decreasing pH and decreasing soluble organics. Since the movement of viruses through soil to groundwater occurs in the liquid phase and involves water movement and associated suspended virus particles, the distribution of viruses between the adsorbed and liquid phases determines the viral mass available for movement. Once the virus reaches the groundwater, it can travel laterally through the aquifer until it is either adsorbed or inactivated.

The major bacterial removal mechanisms in soil are straining at the soil surface and at intergrain contacts, sedimentation, sorption by soil particles, and inactivation. Because of their larger size than for viruses, most bacteria are therefore retained near the soil surface due to this straining effect. In general, enteric bacteria survive in soil between two and three months, although survival times up to five years have been documented.

Heavy Metals and Other Inorganic Compounds

Heavy metals and other inorganic compounds in stormwater of most environmental concern, from a groundwater pollution standpoint, are aluminum, arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, and zinc. However, the majority of these compounds, with the consistent exception of zinc, are mostly found associated with the particulate solids in stormwaters and are thus relatively easily removed through sedimentation practices. Filterable forms of the metals may also be removed by either sediment adsorption or are organically complexed with other particulates.

In general, studies of recharge basins receiving large metal loads found that most of the heavy metals are removed either in the basin sediment or in the vadose zone. Dissolved metal ions are removed from stormwater during infiltration mostly by adsorption onto the near-surface particles in the vadose zone, while the particulate metals are filtered out at the soil surface. Studies at recharge basins found that lead, zinc, cadmium, and copper accumulated at the soil surface with little downward movement over many years. However, nickel, chromium, and zinc concentrations have exceeded regulatory limits in the soils below a recharge area at a commercial site. Elevated groundwater heavy metal concentrations of aluminum, cadmium, copper, chromium, lead, and zinc have been found below stormwater infiltration devices where the groundwater pH has been acidic. Allowing percolation ponds to go dry between storms can be counterproductive to the removal of lead from the water during recharge. Apparently, the adsorption bonds between the sediment and the metals can be weakened during the drying period.

Similarities in water quality between runoff water and groundwater has shown that there is significant downward movement of copper and iron in sandy and loamy soils. However, arsenic, nickel, and lead did not significantly move downward through the soil to the groundwater. The exception to this was some downward movement of lead with the percolation water in sandy soils beneath stormwater recharge basins. Zinc, which is more soluble than iron, has been found in higher concentrations in groundwater than iron. The order of attenuation in the vadose zone from infiltrating stormwater is: zinc (most mobile) > lead > cadmium > manganese > copper > iron > chromium > nickel > aluminum (least mobile).

Salts

Salt applications for winter traffic safety is a common practice in many northern areas and the sodium and chloride, which are collected in the snowmelt, travel down through the vadose zone to the groundwater with little attenuation. Soil is not very effective at removing salts. Salts that are still in the percolation water after it travels through the vadose zone will contaminate the groundwater. Infiltration of stormwater has led to increases in sodium and chloride concentrations above background concentrations. Fertilizer and pesticide salts also accumulate in urban areas and can leach through the soil to the groundwater.

Studies of depth of pollutant penetration in soil have shown that sulfate and potassium concentrations decrease with depth, while sodium, calcium, bicarbonate, and chloride concentrations increase with depth. Once contamination with salts begin, the movement of salts into the groundwater can be rapid. The salt concentration may not decrease until the source of the salts is removed.

Recommendations to Protect Groundwater During Stormwater Infiltration

Table D-1 is a summary of the pollutants found in stormwater that may cause groundwater contamination problems for various reasons. This table does not consider the risk associated with using groundwater contaminated with these pollutants. Causes of concern include high mobility (low sorption potential) in the vadose zone, high abundance (high concentrations and high detection frequencies) in stormwater, and high soluble fractions (small fraction associated with particulates which would have little removal potential using conventional stormwater sedimentation controls) in the stormwater. The contamination potential is the lowest rating of the influencing factors. As an example, if no pretreatment was to be used before percolation through surface soils, the mobility and abundance criteria are most important. If a compound was mobile, but was in low abundance (such as for VOCs), then the groundwater contamination potential would be low. However, if the compound was mobile and was also in high abundance (such as for sodium chloride, in certain conditions), then the groundwater contamination would be high. If sedimentation pretreatment was to be used before infiltration, then much of the pollutants will likely be removed before infiltration. In this case, all three influencing factors (mobility, abundance in stormwater, and soluble fraction) would be considered important. As an example, chlordane would have a low contamination potential with sedimentation pretreatment, while it would have a moderate contamination potential if no pretreatment was used. In addition, if subsurface infiltration/injection was used instead of surface percolation, the compounds would most likely be more mobile, making the abundance criteria the most important, with some regard given to the filterable fraction information for operational considerations.

This table is only appropriate for initial estimates of contamination potential because of the simplifying assumptions made, such as the likely worst case mobility measures for sandy soils having low organic content. If the soil was clayey and had a high organic content, then most of the organic compounds would be less mobile than shown on this table. The abundance and filterable fraction information is generally

Table D-1. Groundwater Contamination Potential for Stormwater Pollutants (Source: Pitt, *et al.* 1996)

	Compounds	Mobility (sandy/low organic soils)	Abundance in stormwater	Fraction filterable	Contamination potential for surface infilt. and no pretreatment	Contamination potential for surface infilt. with sedimentation	Contamination potential for sub-surface inj. with minimal pretreatment
Nutrients	nitrates	mobile	low/moderate	high	low/moderate	low/moderate	low/moderate
Pesticides	2,4-D	mobile	low	likely low	low	low	low
	γ-BHC (lindane)	intermediate	moderate	likely low	moderate	low	moderate
	malathion	mobile	low	likely low	low	low	low
	atrazine	mobile	low	likely low	low	low	low
	chlordane	intermediate	moderate	very low	moderate	low	moderate
	diazinon	mobile	low	likely low	low	low	low
Other organics	VOCs	mobile	low	very high	low	low	low
	1,3-dichlorobenzene	low	high	high	low	low	high
	anthracene	intermediate	low	moderate	low	low	low
	benzo(a) anthracene	intermediate	moderate	very low	moderate	low	moderate
	bis (2-ethylhexyl) phthalate	intermediate	moderate	likely low	moderate	low?	moderate
	butyl benzyl phthalate	low	low/moderate	moderate	low	low	low/moderate
	fluoranthene	intermediate	high	high	moderate	moderate	high
	fluorene	intermediate	low	likely low	low	low	low
	naphthalene	low/inter.	low	moderate	low	low	low
	pentachlorophenol	intermediate	moderate	likely low	moderate	low?	moderate
	phenanthrene	intermediate	moderate	very low	moderate	low	moderate
	pyrene	intermediate	high	high	moderate	moderate	high
Pathogens	enteroviruses	mobile	likely present	high	high	high	high
	Shigella	low/inter.	likely present	moderate	low/moderate	low/moderate	high
	Pseudomonas aeruginosa	low/inter.	very high	moderate	low/moderate	low/moderate	high
	protozoa	low/inter.	likely present	moderate	low/moderate	low/moderate	high
Heavy metals	nickel	low	high	low	low	low	high
	cadmium	low	low	moderate	low	low	low
	chromium	inter./very low	moderate	very low	low/moderate	low	moderate
	lead	very low	moderate	very low	low	low	moderate
	zinc	low/very low	high	high	low	low	high
Salts	chloride	mobile	seasonally high	high	high	high	high

applicable for warm weather stormwater runoff at residential and commercial area outfalls. The concentrations and detection frequencies would likely be greater for critical source areas (especially vehicle service areas) and critical land uses (especially manufacturing industrial areas).

The stormwater pollutants of most concern (those that may have the greatest adverse impacts on groundwaters) include:

- nutrients: nitrate has a low to moderate groundwater contamination potential for both surface percolation and subsurface infiltration/injection practices because of its relatively low concentrations found in most stormwaters. However, if the stormwater nitrate concentration was high, then the groundwater contamination potential would also likely be high.

- pesticides: lindane and chlordane have moderate groundwater contamination potentials for surface percolation practices (with no pretreatment) and for subsurface injection (with minimal pretreatment). The groundwater contamination potentials for both of these compounds would likely be substantially reduced with adequate sedimentation pretreatment. Pesticides have been mostly found in urban runoff from residential areas, especially in dry-weather flows associated with landscaping irrigation runoff.

- other organics: 1,3-dichlorobenzene may have a high groundwater contamination potential for subsurface infiltration/injection (with minimal pretreatment). However, it would likely have a lower groundwater contamination potential for most surface percolation practices because of its relatively strong sorption to vadose zone soils. Both pyrene and fluoranthene would also likely have high groundwater contamination potentials for subsurface infiltration/injection practices, but lower contamination potentials for surface percolation practices because of their more limited mobility through the unsaturated zone (vadose zone). Others (including benzo(a)anthracene, bis (2-ethylhexyl) phthalate, pentachlorophenol, and phenanthrene) may also have moderate groundwater contamination potentials, if surface percolation with no pretreatment, or subsurface injection/infiltration is used. These compounds would have low groundwater contamination potentials if surface infiltration was used with sedimentation pretreatment. Volatile organic compounds (VOCs) may also have high groundwater contamination potentials if present in the stormwater (likely for some industrial and commercial facilities and vehicle service establishments). The other organics, especially the volatiles, are mostly found in industrial areas. The phthalates are found in all areas. The PAHs are also found in runoff from all areas, but they are in higher concentrations and occur more frequently in industrial areas.

- pathogens: enteroviruses likely have a high groundwater contamination potential for all percolation practices and subsurface infiltration/injection practices, depending on their presence in stormwater (likely if contaminated with sanitary sewage). Other pathogens, including *Shigella*, *Pseudomonas aeruginosa*, and various protozoa, would also have high groundwater contamination potentials if subsurface infiltration/injection practices are used without disinfection. If disinfection (especially by chlorine or ozone) is used, then disinfection byproducts (such as trihalomethanes or ozonated bromides) would have high groundwater contamination potentials. Pathogens are most likely associated with sanitary sewage contamination of storm drainage systems, but several bacterial pathogens are commonly found in surface runoff in residential areas.

- heavy metals: nickel and zinc would likely have high groundwater contamination potentials if subsurface infiltration/injection was used. Chromium and lead would have moderate groundwater contamination potentials for subsurface infiltration/injection practices. All metals would likely have low groundwater contamination potentials if surface infiltration was used with sedimentation pretreatment. Zinc is mostly found in roof runoff and other areas where galvanized metal comes into contact with rainwater.

- salts: chloride would likely have a high groundwater contamination potential in northern areas where road salts are used for traffic safety, irrespective of the pretreatment, infiltration or percolation practice used. Salts are at their greatest concentrations in snowmelt and early spring runoff in northern areas.

It has been suggested that, with a reasonable degree of site-specific design considerations to compensate for soil characteristics, infiltration can be very effective in controlling both urban runoff quality and quantity problems (EPA 1983a). This strategy encourages infiltration of urban runoff to replace the natural infiltration capacity lost through urbanization and to use the natural filtering and sorption capacity of soils to remove pollutants. However, potential groundwater contamination through infiltration of some types of urban runoff requires some restrictions. Infiltration of urban runoff having potentially high concentrations of pollutants that may pollute groundwater requires adequate pretreatment, or the diversion of these waters away from infiltration devices. The following general guidelines for the infiltration of stormwater and other storm drainage effluent are recommended in the absence of comprehensive site-specific evaluations:

- Dry-weather storm drainage effluent should be diverted from infiltration devices because of their probable high concentrations of soluble heavy metals, pesticides, and pathogenic microorganisms.

- Combined sewage overflows should be diverted from infiltration devices because of their poor water quality, especially high pathogenic microorganism concentrations, and high clogging potential.

- Snowmelt runoff should also be diverted from infiltration devices because of its potential for having high concentrations of soluble salts.

- Runoff from manufacturing industrial areas should also be diverted from infiltration devices because of its potential for having high concentrations of soluble toxicants.

- Construction site runoff must be diverted from stormwater infiltration devices (especially subsurface devices) because of its high SS concentrations which would quickly clog infiltration devices.

- Runoff from other critical source areas, such as vehicle service facilities and large parking areas, should at least receive adequate pretreatment to eliminate their groundwater contamination potential before infiltration.

- Runoff from residential areas (the largest component of urban runoff from most cities) is generally the least polluted urban runoff flow and should be considered for infiltration. Very little treatment of residential area stormwater runoff should be needed before infiltration, especially if surface infiltration is through the use of grass swales. If subsurface infiltration (French drains, infiltration trenches, dry wells, etc.) is used, then some pretreatment may be needed, such as by using grass filter strips, or other surface filtration devices.

All other runoff should include pretreatment using sedimentation processes before infiltration, to both minimize groundwater contamination and to prolong the life of the infiltration device (if needed). This pretreatment can take the form of grass filters, sediment sumps, wet detention ponds, etc., depending on the runoff volume to be treated and other site specific factors. Pollution prevention can also play an important role in minimizing groundwater contamination problems, including reducing the use of galvanized metals, pesticides, and fertilizers in critical areas. The use of specialized treatment devices can also play an important role in treating runoff from critical source areas before these more contaminated flows commingle with cleaner runoff from other areas. Sophisticated treatment schemes, especially the use of chemical processes or disinfection, may not be warranted, except in special cases, especially considering the potential of forming harmful treatment by-products (such as THMs and soluble aluminum).

Most past stormwater quality monitoring has not been adequate to completely evaluate groundwater contamination potential. The following list shows the parameters that are recommended to be monitored if stormwater contamination potential needs to be considered, or infiltration devices are to be used. Other analyses are appropriate for additional monitoring objectives (such as evaluating surface water problems). In addition, all phases of urban runoff should be sampled, including stormwater runoff, dry-weather flows, and snowmelt.

- Contamination potential:
    - Nutrients (especially nitrates)

  - Salts (especially chloride)
  - VOCs (if expected in the runoff, such as from manufacturing industrial or vehicle service areas, could screen for VOCs with purgable organic carbon, POC, analyses)
  - Pathogens (especially enteroviruses, if possible, along with other pathogens such as *Pseudomonas aeruginosa*, Shigella, and pathogenic protozoa)
  - Bromide and total organic carbon, TOC (to estimate disinfection by-product generation potential, if disinfection by either chlorination or ozone is being considered)
  - Pesticides, in both filterable and total sample components (especially lindane and chlordane)
  - Other organics, in both filterable and total sample components (especially 1,3 dichlorobenzene, pyrene, fluoranthene, benzo (a) anthracene, bis (2-ethylhexyl) phthalate, pentachlorophenol, and phenanthrene)
  - Heavy metals, in both filterable and total sample components (especially chromium, lead, nickel, and zinc)
- Operational considerations:
  - Sodium, calcium, and magnesium (in order to calculate the sodium adsorption ratio to predict clogging of clay soils)
  - Suspended solids (to determine the need for sedimentation pretreatment to prevent clogging)

The Technical University of Denmark (Mikkelsen, *et al*. 1996a and 1996b) has been involved in a series of tests to examine the effects of stormwater infiltration on soil and groundwater quality. They found that heavy metals and PAHs present little groundwater contamination threat, if surface infiltration systems are used. However, they express concern about pesticides which are much more mobile. Squillace, *et al*. (1996) along with Zogorski, *et al*. (1996) presented information concerning stormwater and its potential as a source of groundwater MTBE contamination. Mull (1996) stated that traffic areas are the third most important source of groundwater contamination in Germany (after abandoned industrial sites and leaky sewers). The most important contaminants are chlorinated hydrocarbons, sulfate, organic compounds, and nitrates. Heavy metals are generally not an important groundwater contaminant because of their affinity for soils. Trauth and Xanthopoulus (1996) examined the long-term trends in groundwater quality at Karlsruhe, Germany. They found that the urban landuse is having a long-term influence on the groundwater quality. The concentration of many pollutants have increased by about 30 to 40% over 20 years. Hütter and Remmler (1996) describe a groundwater monitoring plan, including monitoring wells that were established during the construction of an infiltration trench for stormwater disposal in Dortmund, Germany. The worst case problem expected is with zinc, if the infiltration water has a pH value of 4.

Appendix E
Laboratory Procedures Used For MCTT Pilot-Scale Evaluations

Contents

Quality Assurance Objectives

QA Objectives

A very important aspect of any research is the assurance that the samples collected represent the conditions to be tested and that the number of samples to be collected are sufficient to provide statistically relevant conclusions. Because this research is interested in comparing paired data sets, an experimental design process was used that estimates the number of needed sample pairs. The equation used to estimate the needed number of samples (Cameron, undated) is as follows:

$$n = 2\left[\frac{\left(Z_{1-a} + Z_{1-b}\right)}{(m_1 - m_2)}\right]^2 s^{2}$$

where α = false positive rate (1-α is the degree of confidence. A value of α of 0.05 is usually considered statistically significant, corresponding to a 1-α degree of confidence of 0.95, or 95%)

β = false negative rate (1-β is the power. If used, a value of β of 0.2 is common, but it is frequently ignored, corresponding to a β of 0.5)

$Z_{1-\alpha}$ = Z score (associated with area under normal curve) corresponding to 1-α

$Z_{1-\beta}$ = Z score corresponding to 1-β value

μ_1 = mean of data set one

μ_2 = mean of data set two

σ = standard deviation (same for both data sets, same units as μ. Both data sets are also assumed to be normally distributed)

This equation is only approximate, as it requires that the two data sets be normally distributed and have the same standard deviations. In most cases, stormwater constituent concentrations are more closely log-normally distributed. However, if the coefficient of variation (COV) values are low (less than about 0.4), then there is probably no significant difference in the predicted sampling effort. Stormwater samples are generally expected to have COV values of slightly greater values. Therefore, this equation is only appropriate as an approximation. The statistical procedures to be used to evaluate this data (as described in a following subsection) will calculate the exact degree of confidence of the pollutant reductions.

Figure 1 is a plot of this equation (normalized using COV and differences of sample means) showing the approximate number of sample pairs needed for an α of 0.05 (degree of confidence of 95%), and a β of 0.2 (power of 80%). This figure and the above equation demonstrate that 12 sample pairs will be sufficient to detect significant differences (with at least a 50% pollutant reduction) for constituents having coefficient of variations of no more than about 0.5.

Determining Sample Concentration Variations

Figure 2 (Pitt and Lalor 1997) can be used to estimate the COV value for a parameter by knowing the 10th and 90th percentile ratios (the "range ratio"), assuming a log-normal distribution. This is used to make initial estimates for COV that are needed to calculate the approximate number of samples that actually need to be sampled and analyzed. In many cases, the approximate range of likely concentrations can be estimated for a parameter of interest. The extreme values are not well known, but the approximate 10th and 90th percentile values can be estimated with better confidence. As an example, the likely 10th and 90th percentile values of fluoride in tap water can be estimated to be about 0.7 and 1.5 mg/L, respectively. The resulting range ratio is therefore 1.5/0.7 = 2.1 and the estimated COV value is 0.25, from Figure 2.

Also shown on Figure 2 is an indication of the location of the median value, compared to the 10^{th} percentile value and the range ratio. As the range ratio decreases, the median becomes close to the midpoint between the 10^{th} and 90^{th} percentile values. Therefore, at low COV values, the differences between normal distributions and log-normal distributions diminish. As the COV values increase, the mean values are located much closer to the 10th percentile value. In log-normal distributions, no negative concentration values are allowed, but very large positive "outliers" can occur. In the above example, the median location is about 0.4, for a range ratio of 2.1. The following calculation shows how the median value can be estimated using this "median location" value:

median location = 0.4 = $(X_{50}-X_{10})/(X_{90}-X_{10})$

therefore X_{50}-X_{10}= 0.4(X_{90}-X_{10}).

(X_{90}-X_{10}) = 1.5 mg/L - 0.7 mg/L = 0.8 mg/L.

Therefore X_{50}-X_{10} = 0.4 (0.8) = 0.32 mg/L,

and X_{10} = 0.7 mg/L, X_{50} = 0.32 mg/L + 0.7 mg/L = 1.0 mg/L.

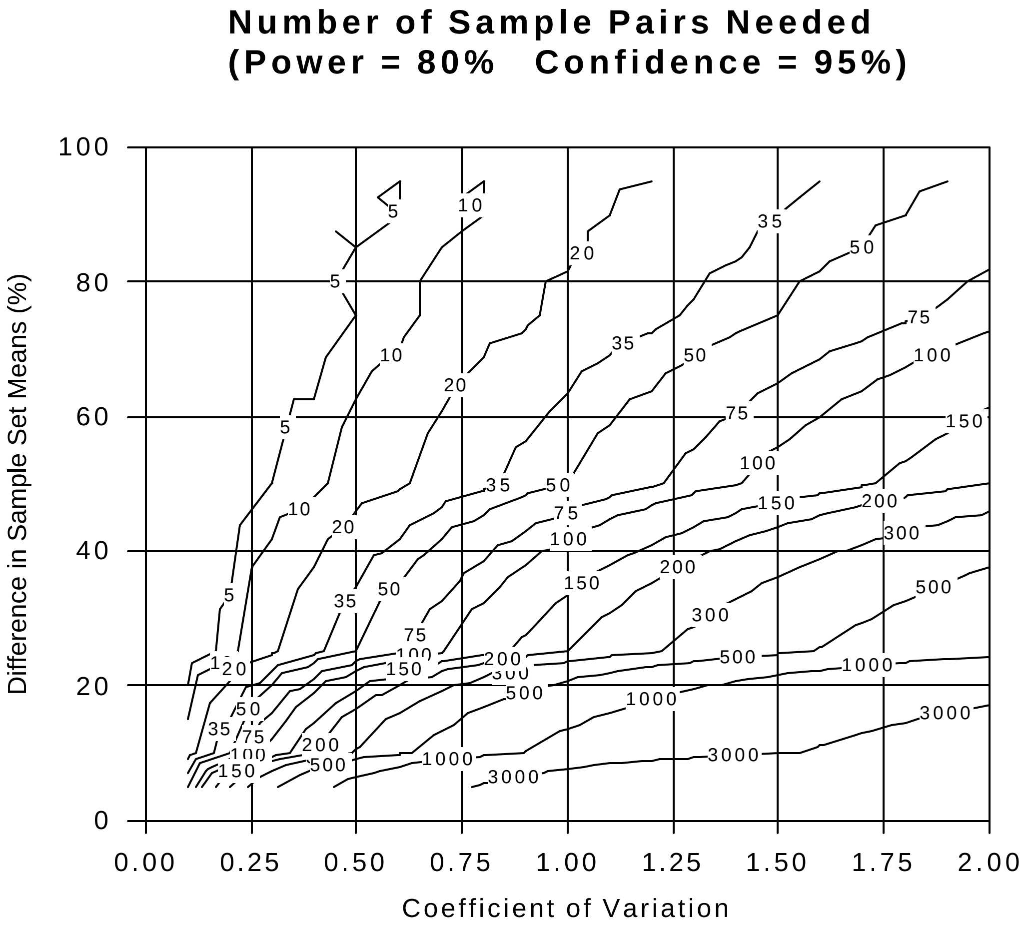

Figure 1. Sampling requirements for power of 80% and confidence of 95%

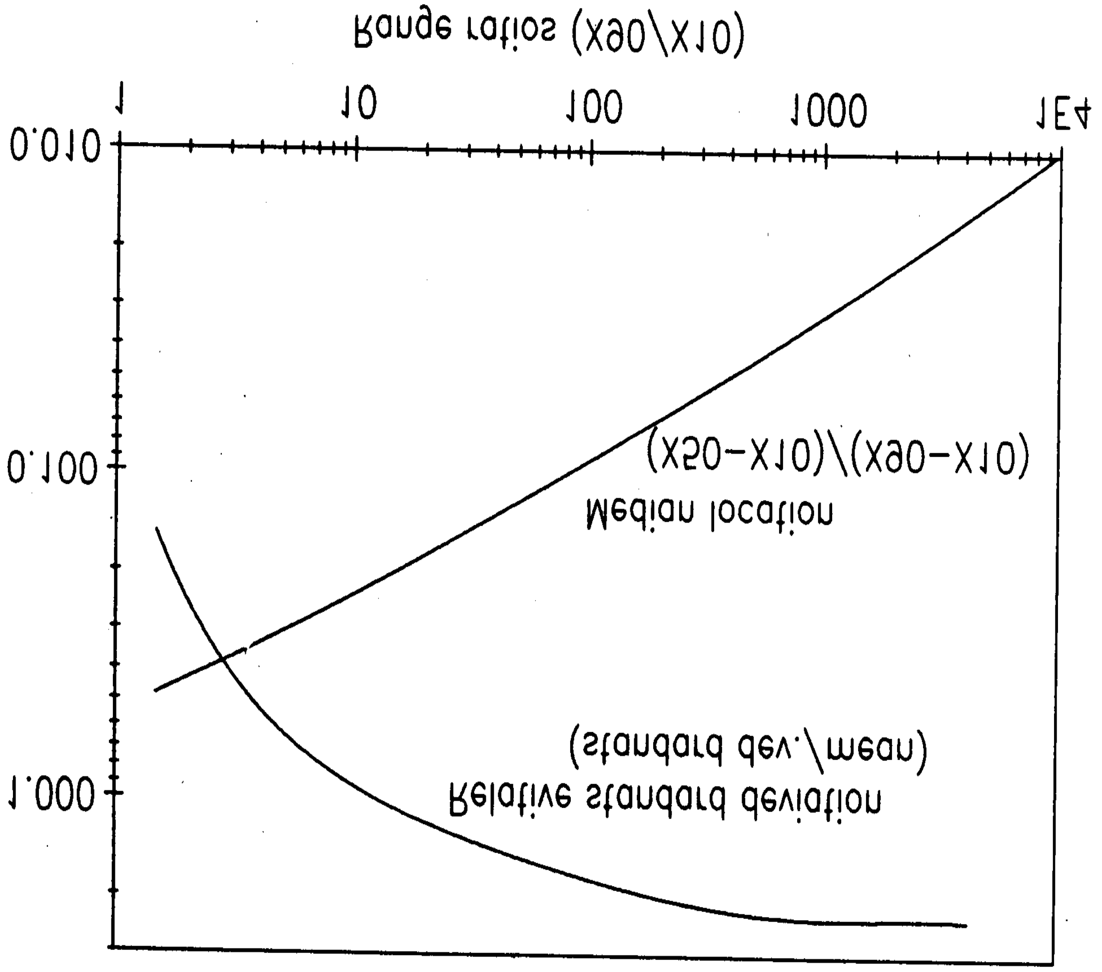

Figure 2. Relationship between data ranges and coefficient of variation

For comparison, the average of the 10th and 90th percentile values is 1.1 mg/L. Because these two values are quite close, the fluoride distribution is likely close to being normally distributed and the equation shown previously can be used to estimate the required number of samples needed. Pitt and Lalor (1997) show how log transformations of real-space data descriptors (COV and median) can be used in modifications of these equations.

Detection Limit Requirements

There are a number of different types of detection limits defined for laboratory use. Most instrument manufactures present a minimum readable value as the instrument detection limit (IDL) in their specifications for simple test kits. The usual definition of IDL, however, is a concentration that produces a signal to noise ratio of five. The method detection limit (MDL) is a more conservative value and is established for the complete preparation and analysis procedure. The practical quantification limit (PQL) is higher yet and is defined as a routinely achievable detection limit with a relatively good certainty that any reported value is reliable. *Standard Methods* (APHA, *et al.* 1989) estimates that the relationship between these detection limits is approximately: IDL:MDL:PQL = 1:4:20. Therefore, the detection limit shown in much of the manufacturer's literature is much less than what would be used by most analytical laboratories.

A quick (and conservative) estimate of the needed method detection limit (with at least a 90% confidence) can be made by knowing only the median concentration and the concentration variation of the contaminant, based on numerous Monte Carlo probability calculations presented by Pitt and Lalor (1997):

Table 1. Monte Carlo values for MDL calculations

COV value	Multiplier for MDL
< 0.5 (low)	0.8
0.5 to 1.25 medium	0.23
> 1.25 (high)	0.12

As an example, if the contaminant has a low COV (<0.5), then the estimated required MDL is about 0.8 times the estimated median contaminant concentration. This MDL value would result in most observations being in the “detectable” range.

Required Sample Analytical Precision

The precision (repeatability) of an analytical method is another important consideration in its selection. Precision, as defined in *Standard Methods* (APHA, *et al.* 1992), is a measure of the closeness with which multiple analyses of a given sample agree with each other. It is determined by repeated analyses of a stable standard, conducting replicate analyses on the samples, or by analyzing known standard additions to samples. Precision is expressed as the standard deviation of the multiple analysis results.

Figure 3 is a summary of probability plots prepared by Pitt and Lalor (1997) and indicates one approach that can be used to calculate the needed analytical precision for a specific research objective. This figure was prepared as an aid in resolving one percent contamination levels at a 90 percent confidence level. This figure was developed for COV values ranging from 0.16 to 1.67, and indicates the needed analytical precision (as a fraction of the uncontaminated flow’s low concentration) to resolve one percent contamination levels at a 90 percent confidence level. This figure was developed for contamination levels between zero and 15 percent. If the analytical precision is worse than these required values, then small contamination levels may not be detected. Therefore, even with adequate analytical detection limits, poor analytical precision may not allow adequate identification of low levels of contamination. As an example, if the median contaminant concentrations differ by a factor of 10 in two flow components, but have high concentration variations (high COV values), a precision of between 0.015 to 0.03 of the lower baseflow median contaminant concentration is needed, for each percent contamination that needs to be detected. If the median contaminant concentration in the cleaner baseflow is 0.15 mg/L (with a corresponding contaminant median concentration of 10 times this amount, or 1.5 mg/L, in the contaminating source flow), then the required analytical precision is about 0.015 X 0.15 = 0.002 mg/L to 0.03 X 0.15 = 0.005 mg/L per one percent contamination detection. If at least five percent contamination is needed to be detected, then the minimum precision can be increased to 5 X 0.002 = 0.01 mg/L.

The method noted previously can be used to estimate the detection limit requirements for the above example:

low COV in the cleaner baseflow: 0.8 X 0.15 mg/L = 0.12 mg/L medium COV in the cleaner baseflow: 0.23 X 0.15 mg/L = 0.035 mg/L

high COV in the cleaner baseflow: 0.12 X 0.15 mg/L = 0.018 mg/L.

The required analytical precision would therefore be about one-half of the lowest detection limit needed, and about 1/12 of the largest estimated required detection limit. In most cases, the required minimum precision (expressed as a COV) should be in the range of about 0.1 to 1, with the most restrictive precision needed for constituents having low COV values (in order to have the additional variability associated with analytical methods kept to an insignificant portion of the total variability of the results).

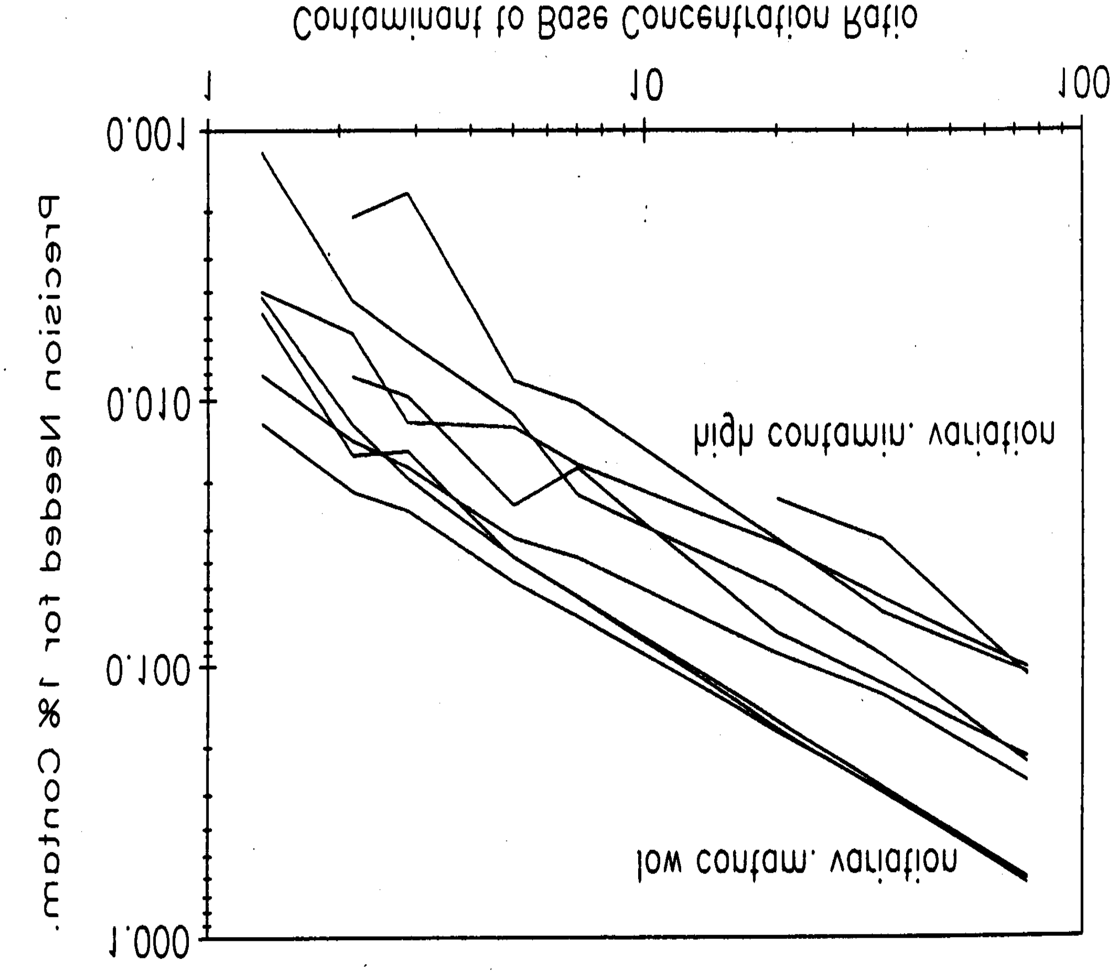

Figure 3. Analysis precision needed for detection of one percent contamination at 90% confidence

EPA-Approved or Other Validated Standard Methods

This section describes physical and chemical measurements utilized in this project. Sample preparation and cleanup procedures are included in the attachments which contain the method descriptions or SOPs. There are 14 methods that were utilized in this project. The methods or SOPs are presented in attachments listed in the tables below.

Table 2. Critical compound analytical methods

Class	Compound	Method	Attachment
Physical	color	EPA 110.3	6
	conductance	EPA 120.1	7
	chemical oxygen demand	EPA 410.4	14
	hardness	EPA 130.2	8
	particle size	UAB EEL[1]	5
	pH	EPA 150.1	9
	turbidity	EPA 180.1	11
	alkalinity	EPA 310.1	13
	suspended solids	EPA 160.3	10
Pesticides	Lindane	Modified EPA 608	2
	Chlordane	Modified EPA 608	2
SVOC	1,3-dichlorobenzene	Modified EPA 625	3
	benzo(a) anthracene	Modified EPA 625	3
	bis(2-ethylhexyl) phthalate	Modified EPA 625	3
	fluoranthene	Modified EPA 625	3
	pentachlorophenol	Modified EPA 625	3
	phenanthrene	Modified EPA 625	3
	butyl benzyl phthalate	Modified EPA 625	3
	pyrene	Modified EPA 625	3
Metals	copper	EPA 200.9	12
	chromium	EPA 200.9	12
	lead	EPA 200.9	12
	zinc	EPA 200.9	12
	nickel	EPA 200.9	12
Cations	sodium	Modified EPA 300	1
	calcium	Modified EPA 300	1
	magnesium	Modified EPA 300	1
	potassium	Modified EPA 300	1
Anions	chloride	Modified EPA 300	1
	nitrate	Modified EPA 300	1
	sulfate	Modified EPA 300	1
Toxicity	variable	UAB EEL[1]	4

[1] UAB Environmental Engineering Laboratory Method

Table 3. Non-critical compound analytical methods

Class	Compound	Method	Attachment
Physical	dissolved solids	EPA 160.1	10
	total solids	EPA 160.3	10
	volatile solids	EPA 160.4	10
Pesticides	modified method 608 chlorinated pesticides	Modified EPA 608	2
SVOC	modified method 625 semi-volatile compounds	Modified EPA 625	3
Metals	cadmium	EPA 200.9	12
Cations	ammonium	Modified EPA 300	1
	lithium	Modified EPA 300	1
Anions	fluoride	Modified EPA 300	1
	nitrite	Modified EPA 300	1
	phosphate	Modified EPA 300	1

Nonstandard or Modified Methods

EPA method 300 is modified as follows:

For anions:

2.0 Summary of Method

2.5 Samples are filtered through C18 and cation exchange columns prior to analysis to remove interferences

For cations:

1.0 Scope and Application

1.1 This method covers the determination of the following inorganic cations:

lithium, sodium, potassium, calcium, ammonium, magnesium,

2.0 Summary of Method

2.5 Samples are filtered through C18 and anion exchange columns prior to analysis to remove

interferences.

6.0 Equipment and Supplies

6.2.2.1 Cation analytical column utilized is a Dionex Cation exchange column

EPA method 608 and 625 are modified as follows:

10. Sample Extraction

1. Samples are extracted using a separatory funnel technique. If emulsions prevent achieving acceptable solvent recovery with separatory funnel extraction, continuous extraction is used. The separatory funnel extraction scheme described below assumes a sample volume of 250 mL. The serial

extraction of the base/neutrals uses 10 mL and 10 mL volumes of methylene chloride as does the serial extraction of the acids. Prior to the extraction, all glassware is oven baked at 300°C.

2. A sample volume of 250 mL is collected in a 400 mL beaker and poured into a 500 mL separation funnel. For every twelve samples extracted, an additional four samples are extracted for quality control and assurance. These include three 250 mL composite samples made of equal amounts of the twelve samples and one 250 mL sample of reverse osmosis water. Standard solution additions consisting of 25 μL of 1000 μg/mL base/neutral spiking solution, 25 μL of 1000 μg/mL base/neutral surrogates, 12.5 μL of 2000 μg /mL acid spiking solution , and 12.5 μL of 2000 μg /mL acid surrogates are made to the separation funnels of two of the three composite samples and mixed well. Sample pH is measured with wide range pH paper and adjusted to pH > 11 with sodium hydroxide solution.

3. A 10 mL volume of methylene chloride is added to the separatory funnel and sealed by capping. The separatory funnel is gently shaken by hand for 15 s and vented to release pressure. The cap is removed from the separatory funnel and replaced with a vented snorkel stopper. The separatory funnel is then placed on a mechanical shaker and shaken for 2 min. After returning the separatory funnel to its stand and replacing the snorkel stopper with cap, the organic layer is allowed to separate from the water phase for a minimum of 10 minutes, longer if an emulsion develops. The extract and any emulsion present is then collected into a 125 mL Erlenmeyer flask.

4. A second 10 mL volume of methylene chloride is added to the separatory funnel and the extraction method is repeated, combining the extract with the previous in the Erlenmeyer flask. For persistent emulsions, those with emulsion interface between layers more than one-third the volume of the solvent layer, the extract including the emulsion is poured into a 50 mL centrifuge vial, capped, and centrifuged at 2000 rpm for 2 min. to break the emulsion. Water phase separated in by centrifuge is collected from the vial and returned to the separatory funnel using a disposable pipette. The centrifuge vial with the extract is recapped before performing the extraction of the acid portion.

5. The pH of the remaining sample in the separatory funnel is adjusted to pH < 2 using sulfuric acid. The acidified aqueous phase is serially extracted two times with 10 mL aliquots of methylene chloride as done in the previous base/neutral extraction procedure. Extract and any emulsions are again collected in the 125 mL Erlenmeyer flask.

6. The base/neutral extract is poured from the centrifuge vial though a drying column of at least 10 cm of anhydrous sodium sulfate and is collected in a 50 mL beaker. The Erlenmeyer flask is rinsed with 5 mL of methylene chloride which is then used to rinse the centrifuge vial and then for rinsing the drying column and completing the quantitative transfer.

7. The base/neutral extract is transferred into 50 mL concentration vials and is placed in an automatic vacuum/centrifuge concentrator (Vacuum concentration is used in place of the Kuderna-Danish method). Extract is concentrated to approximately 0.5 mL.

8. The acid extract collected in the 125 mL Erlenmeyer flask is placed in the 50 mL centrifuge vial. Again, if persistent emulsions persist, the extract is centrifuged at 2000 rpm for 2 min. Water is drawn from the extract and discarded. Extract is poured through the 10 cm anhydrous sodium sulfate drying column and collected in the 50 mL beaker as before. The Erlenmeyer flask is then rinsed with 5 mL of methylene chloride which is then poured into the centrifuge vial and finally through the drying column.

9. The acid extract is then poured into the 50 mL concentration vial combining it with the evaporated base/neutral extract. The combined extract is then concentrated to approximately 0.5 mL in the automatic vacuum/centrifuge concentrator.

10. Using a disposable pipette, extract is transferred to a graduated Kuderna-Danish concentrator. Approximately 1.5 mL of methylene chloride is placed in the concentration vial for rinsing. This rinse solvent is then used to adjust the volume of extract to 2.0 mL. Extract is then poured into a labeled Teflon-sealed screw-cap vial and freezer stored until analysis.

Notes for method 608:

Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Florisil cleanup is not utilized unless sample matrix creates excessive background interference.

Calibration Procedures and Frequency

Calibration procedures for all methods are described in standard methods or the particular UAB Environmental Engineering Laboratory method. All QA criteria for calibrations are met or are upgraded, e.g., 5 point calibrations versus single point or 3 point calibrations.

Approach to QA/QC

CALCULATION OF RESULTS

Statistical Approach for Reducing Data

MCTT Data Observations. Comparison tests will be made of inlet and outlet conditions in the MCTT to determine the level of pollutant removal and the statistical significance of the concentration differences. Tests of significance will rely mostly on the nonparametric Wilcoxon Signed Rank Test for paired data. The 12 sets of observations for each test parameter will be used for the following six test groups:

1) inlet vs. grit chamber outlet

2) inlet vs. main settling chamber outlet

3) inlet vs. final effluent

4) grit chamber outlet vs. main settling chamber outlet

5) grit chamber outlet vs. final effluent

6) main settling chamber outlet vs. final effluent

The Wilcoxon signed rank test is a nonparametric test that doesn’t require assumptions concerning the distribution of the data or residuals (Lehmann 1975). StatXact-Turbo (CYTEL, Cambridge, MA) is a microcomputer program that computes exact nonparametric levels of significance, without resorting to normal approximations. This is especially important for the relatively small data sets that will be evaluated during this research. The significance test results (the α value) will indicate the level of confidence that the two sets of observations are the same. In most cases, an α level of less than 0.05 is used to signify significant differences between two set of paired observations.

Even if the α level is significant (less than 0.05), the pollutant reduction may not be very important. Therefore, a calculation to determine the level of pollutant reduction will also be made using the microcomputer spreadsheet program Excel (Microsoft Corp.). Excel is the basic data base system used in our laboratory. The pollutant reduction will be calculated using the following conventional formula:

% reduction = 100 X (inlet-outlet)/inlet

The importance of the level of pollutant reductions will also be graphically presented using grouped box plots indicating the range and variations of the concentrations at each of the four sampling locations in the MCTT. These plots will be prepared using SigmaPlot (Jandel, San Rafael, CA). Overlaying line graphs, showing all 12 sets of observations may also be prepared using Excel.

Determination of Outliers

Analytical results less than the PQL or the MDL will be flagged, but the result (greater than the IDL) will still be used in most of the statistical calculations. Results less than the IDL will be treated as less than detectable values (LDV) and will be treated according to Berthouex and Brown (1994). Generally, the statistical procedures will be used twice, once with the LDV equal to zero, and again with the LDV equal to the IDL. This procedure will determine if a significant difference in conclusions would occur with handling the data in a specific manner.

Unusually high values will be critically examined to identify any possible errors. In most cases, the sample will also be re-evaluated, as described earlier. It is difficult to reject stormwater constituent observations solely because they are unusually high, as stormwater can easily have wide ranging constituent observations.

INTERNAL QC CHECKS

Several quality control activities occur as specified in standard methods, however, standard methods for EPA 625 do not list several QC parameters. These parameters are listed in Table 4.

Table 4. Internal quality control checks

Tuning	
Requirement	50 ng DFTPP
Frequency	per extraction batch
Criteria	per method
Surrogates	
	Phenol-d5
	2-Fluorophenol
	2,4,6-Tribromophenol
	Nitrobenzene-d5
	2-Fluorobiphenyl
	p-Terphenyl
	2-Chlorophenol-d4
	1,2-Dichlorobenzene-d4
Internal Standards	
	1,4-Dichlorobenzene-d4
	Naphthalene-d8
	Acenaphthene-d10
	Phenanthrene-d10
	Chrysene-d12
	Perylene-d12
Spike	Matrix Spike
Frequency	5% samples or greater
Concentration	1 - 5x sample level for QA monitoring (25-50 ug/L)
Criteria	Method % rec. limits
Duplicate	Matrix spike duplicate
Frequency	5% samples or 1 per extraction batch (16)
Criteria	Method % rec and RPD
Sample Analysis	
Qualitative ID	RRT within +/-0.06 RRT units of standard RRT Ions >10% in std. present in sample within +/-20% of ion abundance in std.
IS Area	-50 to +100% of cal. area
IS RRT	+/- 30 sec of Cal. RT
Surrogate Criteria	Method % rec. limits
Quantitative	Within calibration range
QC Check Sample	Performance Evaluation
Frequency	Each study
Criteria	EPA QC limits
Surrogate Recoveries	
Nitrobenzene-d5	34 - 114 %
2-Fluorobiphenyl	43 - 116 %
p-Terphenyl-d14	33 - 141 %
Phenol-d6	10 - 110 %

Tuning	
2-Fluorophenol	21 - 110 %
2,4,6-Tribromophenol	10 - 123 %
1,2-Dichlorobenzene-d4	16 - 110 %
2-Chlorophenol-d4	33 - 110 %

Calculation of data quality indicators

Precision

precision, when calculated from duplicate measurements:

$$RPD = \frac{(C_1 - C_2) \times 100\%}{(C_1 + C_2)/2}$$

RPD = relative percent difference

C_1 = larger of the two observed values

C_2 = smaller of the two observed values

if calculated from three or more replicates, use relative standard deviation (RSD) rather than RPD:

$$RSD = \left(s/\bar{y} \right) \times 100\%$$

RSD = relative standard deviation

s = standard deviation

$\bar{y}$ = mean of replicate analyses

Accuracy

For measurements where matrix spikes are used:

$$\%R = 100\% \times \left(\frac{S - U}{C_{sa}} \right)$$

%R = percent recovery

S = measured concentration in spiked aliquot

U = measured concentration in unspiked aliquot

C_{sa} = actual concentration of spike added

For situations where a standard reference material (srm) is used instead of or in addition to a matrix spike:

$$\%R = 100\% \times \left(\frac{C_m}{C_{srm}} \right)$$

%R = percent recovery

C_m = measured concentration of srm

C_{srm} = actual concentration of srm

Method Detection Limit

$$MDL = t_{(n-1,1-a=0.99)} \times s$$

MDL = method detection limit

s = standard deviation of replicate analyses

$t_{(n-1,1-a=0.99)} \times s$ = Student's t-value appropriate to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

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Attachment 1

DETERMINATION OF INORGANIC IONS BY ION CHROMATOGRAPHY

UAB METHOD 300.0

SCOPE AND APPLICATION

1.1 This method covers the determination of the following inorganic ions:

PART A. anions

fluoride, chloride, nitrate-N, nitrite-N, ortho-phosphate-P, sulfate

PART B. cations

lithium, sodium, potassium, ammonium, magnesium, calcium

1.2 The matrices applicable to this method are drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 11.7), and leachates (when no acetic acid is used).

1.3 The single analyst Method Detection Limit (MDL defined in Sect. 3.2) for the above analytes is listed in Tables 2 and 3. The MDL for a specific matrix or analyst may differ from those listed, depending upon the nature of the sample and care utilized during analysis.

1.4 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.5 When this method is used to analyze unfamiliar samples for any of the above ions, ion identification should be supported by the use of a fortified sample matrix covering the anions of interest. The fortification procedure is described in Sect. 11.6.

1.6 Users of the method data should state the data quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results with this method, using the procedures described in Sect. 9.0.

SUMMARY OF METHOD

2.1 A small volume of sample, typically 2 to 3 mL, is introduced into an ion chromatograph. The ions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

2.2 The main differences between Parts A and B are the separator columns, guard columns, and sample preparation procedures. Sections 6.0 and 7.0 elicit the differences.

2.3 An extraction procedure must be performed to use this method for solids (See 11.7).

2.4 Limited performance-based method modifications may be acceptable provided they are fully documented and meet or exceed requirements expressed in Sect. 9.0, Quality Control.

DEFINITIONS

3.1 CALIBRATION BLANK (CB)-- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.

3.2 CALIBRATION STANDARD (CAL)-- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 FIELD DUPLICATES (FD)-- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.4 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC)-- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.5 LABORATORY FORTIFIED BLANK (LFB)-- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6 LABORATORY FORTIFIED SAMPLE MATRIX (LFM)-- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.7 LABORATORY REAGENT BLANK (LRB)-- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.8 LINEAR CALIBRATION RANGE (LCR)-- The concentration range over which the instrument response is linear.

3.9 MATERIAL SAFETY DATA SHEET (MSDS)-- Written information provided by vendors concerning a chemical 's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.10 METHOD DETECTION LIMIT (MDL)-- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.11 PERFORMANCE EVALUATION SAMPLE (PE)-- A solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL- Cincinnati), U.S. Environmental Protection Agency, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by

QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.12 QUALITY CONTROL SAMPLE (QCS)-- A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.13 STOCK STANDARD SOLUTION (SSS)-- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

INTERFERENCES

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the ion of interest. Large amounts of an ion can interfere with the peak resolution of an adjacent ion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 lOOX) to 100 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.5 Any ion that is not retained by the column or only slightly retained will elute in the area of fluoride or lithium and interfere. Known co-elution is caused by carbonate and other small organic ions. At concentrations of fluoride and lithium above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment or extraction.

4.7 The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate etc .) which are conductive and co-elute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

4.8 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample purge the sample with an inert gas (argon or nitrogen) for about five minutes or until no chlorine dioxide remains.

SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in the chemical analysis.

5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1 Sulfuric acid (7.4)

Equipment and Supplies

6.1 Balance-- Analytical, capable of accurately weighing to the nearest 0.0001gm.

6.2 Sample preparation equipment consisting of vacuum apparatus to reproducibly perform solid phase clean up with various columns: C18 to remove non-polar interferences, silica to remove polar interferences, anion exchange to remove anion interferences, cation exchange to remove cation interferences.

6.3 Ion chromatograph-- Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.

6.3.1 Guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with a substrate the same as that in the separator column.

6.3.2 Analytical column: This column produces the separation shown in Figures 1 and 2.

6.3.3 Anion analytical column (Method A): Dionex ASA column (P/N 37041). An optional column may be used if comparable resolution of peaks is obtained, and the requirements of Sect. 9.2 can be met.

6.3.4 Cation analytical column (Method B): Dionex column (P/N 37041). An optional column may be used if comparable resolution of peaks is obtained, and the requirements of Sect. 9.2 can be met.

6.3.5 Suppressor device: The data presented in this method were generated using a Dionex anion or cation micro membrane suppressor (P/N 37106).

6.3.6 Detector-- Conductivity cell: approximately 1.25 @L internal volume, (Dionex, or equivalent) capable of providing data as required in Sect. 9.2.

6.3.7 The Dionex AI-450 Data Chromatography Software was used to generate all the data in the attached tables. Systems using a strip-chart recorder and integrator or other computer based data system may achieve approximately the same MDL's but the user should demonstrate this by the procedure outlined in Sect. 9. 2.

Reaqents and Standards

7.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of anions of interest.

1.2 Reagent water: Distilled or de-ionized water, free of the ions of interest. Water should contain particles no larger than 0.20 microns.

7.3 Eluent solution (Method A and Method B): Sodium bicarbonate (CASRN 144-55-8) 1.7 mM, sodium carbonate (CASRN 497-19-8) 1.8 mM. Dissolve 0.2856 gm sodium bicarbonate ($NaHCO_3$) and 0.3816 gm of sodium carbonate (Na_2CO_3) in reagent water (7.2) and dilute to 2 L.

7.4 Regeneration solution, if necessary.

7.5 Stock standard solutions: Stock standard solutions are purchased as certified solutions from Dionex Corportaion.

NOTE: Stability of standards: Stock standards (7.5) are stable for at least 1 month when stored at 4°C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

Sample Collection, Preservation and Storage

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

8.2 Sample preservation and holding times for the ions that can be determined by this method are as follows:

Ion preservation and holding times

Analyte	Preservation	Holding Time
Fluoride	None required	28 days
Chloride	None required	28 days
Nitrate- N	Cool to 4°C	48 hours
Combined (Nitrate/Nitrite)	conc. H_2SO_4 to a pH < 2	28 days
Nitrite-N	Cool to 4°C	48 hours
O-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days
Lithium	Cool to 4°C	28 days
Sodium	Cool to 4°C	28 days
Ammonium	Cool to 4°C	48 hours
Potassium	Cool to 4°C	28 days
Magnesium	Cool to 4°C	28 days
Calcium	Cool to 4°C	28 days

NOTE: If the determined value for the combined nitrate/nitrite exceeds 0.5 mg/L as N, a re-sample must be analyzed for the individual concentrations of nitrate and nitrite.

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the ions of interest. In a given sample, the ion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. It is recommended that all samples be cooled to 4°C and held for no longer than 28 days.

QUALITY CONTROL

9.1 Each analyst using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of analyst capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The analyst is required to maintain performance records that define the quality of the data that are generated.

INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 Linear Calibration Range (LCR)-- The LCR must be determined initially and verified every 6 months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.2.3 Quality Control Sample (QCS)-- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within ±10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4 Method Detection Limit (MDL)-- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

MDL= (t) x (S)

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t =3.14 for seven replicates].

S = standard deviation of the replicate analyses.

MDLs should be determined every 6 months, when a new operator begins work or whenever there is a significant change in the background or instrument response.

9.3 ASSESSING ANALYST PERFORMANCE

9.3.1 Laboratory Reagent Blank (LRB)-- The analyst must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

9.3.2 Laboratory Fortified Blank (LFB)-- The analyst must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery (Sect. 9.4.2). If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The analyst must use LFB analyses data to assess performance against the required control limits of 90-110%. When sufficient internal performance data become available (usually a minimum of 20- 30 analyses), optional control limits can be developed from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT =x + 3S

LOWER CONTROL LIMIT $= x - 3S$

The optional control limits must be equal to or better than the required control limits of 90-110%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument Performance Check Solution (IPC)-- For all determinations the laboratory must analyze the IPC (a midrange check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within ±10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within ±10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9.4.1 Laboratory Fortified Sample Matrix (LFM)-- The analyst must add a known amount of analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.4.1.1 If the concentration of fortification is less than 25% of the background concentration of the matrix the matrix recovery should not be calculated.

9.4.2 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110%. Percent recovery may be calculated using the following equation:

$$R = (C_s - C)/s\ (100)$$

where, R = percent recovery, C_s = fortified sample concentration, C = sample background concentration, s = concentration equivalent of analyte added to sample.

9. 4. 3 Until sufficient data becomes available (usually a minimum of 20 to 30 analyses), assess laboratory performance against recovery limits of 80 to 120%. When sufficient internal performance data becomes available develop control limits from percent mean recovery and the standard deviation of the mean recovery.

9.4.4 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (Sect. 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

9. 4. 5 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

9.4.6 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Sect. 9.2.

9.4.7 It is recommended that the analyst adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirming techniques such as sample dilution and fortification, must be used. Whenever possible, the analyst should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

9.4.8 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

Calibration and Standardization

10.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1.

10.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (7.5) to a volumetric flask and diluting to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

10.3 Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

10.4 The calibration curve must be verified on each working day, or whenever the ion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than ±10%, the test must be repeated, using fresh calibration standards. If the results are still more than ±10%, a new calibration curve must be prepared for that analyte.

10.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). The response of the detector to the sample when diluted 1:1, and when not diluted, should be compared. If the calculated responses are the same, samples of this total ionic concentration need not be diluted.

Procedure

11.1 Tables 2 and 3 summarize the recommended operating conditions for the ion chromatograph. Included in these tables are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.2 are met.

11.2 Check system calibration daily and, if required, re-calibrate as described in Sect. 10.

11.3 Load and inject a fixed amount of wel1 mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.6 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific ions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

NOTE: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all ions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

11.7 The following extraction should be used for solid materials. Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed for ten minutes using a magnetic stirring device. Filter the resulting slurry before injecting using a 0.45 µ membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the user's matrix through the use of fortified samples.

11.8 Should more complete resolution be needed between peaks the eluent (7.3) can be diluted. This will spread out the run but will also cause the later eluting ions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

DATA ANALYSIS AND CALCULATIONS

12.1 Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

12.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3 Report results in mg/L.

12.4 Report NO_2^- as N, NO_3^- as N, HPO_4^- as P.

METHOD PERFORMANCE

13.1 The following tables give the single laboratory MDL for each ion included in the method under the conditions listed.

Anion chromatographic conditions and detection limits in water

Analyte	Peak #	Retention Time (min)	MDL (mg/L)
fluoride	1	1.2	0.027
chloride	2	1.7	0.08
nitrite -N	3	2.0	0.111
nitrate-N	4	3.2	0.040
o-phosphate-P	5	5.4	0.084
sulfate	6	7.0	0.083

Standard Conditions:
Column, detector, and eluent as specified, pump rate 2.0 mL/min, sample loop 25 µL.

Cation chromatographic conditions and detection limits in water

Analyte	Peak #	Retention Time (min)	MDL (mg/L)
lithium	1	1.3	0.0138
sodium	2	2.0	0.454
ammonium	3	3.2	0.123
potassium	4	4.8	0.081
magnesium	5	5.7	0.055
calcium	6	7.9	0.318

Standard Conditions:
Column, detector, and eluent as specified, pump rate 1.0 mL/min, sample loop 25 µL.

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Attachment 2

ORGANOCHLORINE PESTICIDES AND PCBs

UAB METHOD 608

Scope and Application

1.1 This method covers the determination of certain organochlorine pesticides. The following parameters can be determined by this method:

Parameter	Method detection limit (µg/L)
α-BHC	0.0081
δ-BHC	0.0034
heptachlor	0.0067
β-BHC	0.0016
δ-BHC	0.0086
aldrin	0.0475
heptachlor epoxide	0.0106
endosulfan I	0.0145
gamma chlordane	0.0027
alpha chlordane	0.0030
4,4'-dde	0.0259
dieldrin	0.0122
endrin	0.0078
4,4'-ddd	0.0065
endosulfan II	0.0046
4,4'-ddt	0.0314
endrin aldehyde	0.0465
endosulfan sulfate	0.0075
methoxychlor	0.0387
endrin ketone	0.0065

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in stormwater discharges. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. UAB Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL defined in Section 14.1)[1] for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix, and experience of the analyst performing the procedure.

1.4 The sample extraction and concentration steps in this method are essentially the same as in UAB Method 625. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate cleanup procedures. The analyst is allowed the latitude, under Section 12, to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

Summary of Method

2.1 A measured volume of sample, approximately 250 mL, is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried to a volume of 1 mL or less, then volumetrically increased to 2.0 mL. The extract is separated by gas chromatography and the parameters are then measured with an electron capture detector.[2]

2.2. The method provides a Florisil column cleanup procedure and an elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.[3] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. **Volumetric ware should not be heated in a muffle furnace**. After drying and cooling glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as large late eluting peaks, especially in the 15 and 50% fractions from Florisil. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.[4,5] The interferences from phthalate esters can be avoided by using a microcoulometric or electrolytic conductivity detector.

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[6,8] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian an carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle--500 mL amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.5.1.2 Automatic sampler (optional)--The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4°C and protected from light during composting. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsing with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5-2 Glassware:

5.2.1 Separatory funnel--500 mL, with Teflon stopcock.

5.2.2 Drying column--Chromatographic column, approximately 400 mm long x 19 mm ID, with coarse frit filter disc.

5.2.3 Chromatographic column--400 mm long x 22 mm ID, with Teflon stopcock and coarse frit filter disc

5.2.4 Concentrator tube, Kuderna-Danish--2.0-mL, graduated. Calibration must be checked at the volumes employed in the test. Teflon-lined screwcap is used to prevent evaporation of extracts.

5.2.5 Evaporative flask,

5.2.6 Vials--4-mL, amber glass, with Teflon-lined screw cap.

5.3. Balance--Analytical, capable of accurately weighing 0.0001 g.

5.4. Gas chromatograph--An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended-mended for measuring peak areas.

5.4.1 Column 1 - Supelco SPB-1701, 30 m length, 0.25µ i.d.,

5.4.2 Column 2 - Supelco PTE-5, 30 m length, 0.25µ i.d.,

5.4.3 Detector--Electron capture detector. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), [*sic*] and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1.

5.5 Savant Vacuum Centrifuge for controlled evaporation of extraction solvent

Reagents

6.1 Reagent water--Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)-- Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate--(ACS) Granular.

6.4 Sulfuric acid (1+1)--Slowly, add 50 mL to H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, hexane, isooctane, [and] methylene chloride--Pesticide quality or equivalent.

6.6 Ethyl ether--Nanograde, re-distilled in glass if necessary-

6.6.1 Ethyl ether must be shown to be free of peroxides before it is used as indicated by EM Laboratories Quant test strips. (Available from Scientific Products Co., Cat. No. P1126-8, and other suppliers.)

6.6.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

6.7 Sodium sulfate--(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.8 Florisil--PR grade (60/100 mesh). Purchase activated at 1250°F and store in the dark in glass containers with ground glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 h at 130 °C in a foil-covered glass container and allow to cool.

6.9 Mercury--Triple distilled.

6.10 Copper powder--Activated.

6.11 Stock standard solutions (1.00 μg/μL)--Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in methylene chloride and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.11.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.11.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.12 Quality control check sample concentrate--See Section 8.2.1.

6.13 Methylene chloride

Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those given in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methylene chloride. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 μL, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure--To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with methylene chloride. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (µg/L).

C_s = Concentration of the parameter to be measured (µg/L).

If the RF value over the working range is a constant (< 10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±15%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.5 The cleanup procedure in Section 11 utilizes Florisil column chromatography. Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value[9] is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount or Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g.

7.6 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

Quality Control

8.1 Each analyst that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The analyst must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.4, 11.1, and 12.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The analyst must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The analyst must, on an ongoing basis, demonstrate through the analyses of quality control check standard that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check stand-standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The analyst must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each single-component parameter of interest at the following concentrations in acetone or methylene chloride: 4,4'-DDD, 10 µg/mL; 4,4'-DDT, 10 µg/ mL; endosulfan II, 10 µg/mL; endosulfan sulfate, 10 µg/mL; endrin, 10 µg/mL; any other single-component pesticide, 2 µg/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxpahene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 50 µg/mL in acetone or methylene chloride. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipette, prepare QC check samples at the mid-point of the calibration range by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery (X) in μg/mL; and the standard deviation of the recovery (s) in μg/mL, for each parameter using the four results.

8.2.5 For each parameter compare s and X with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 3 of EPA Method 608. If s and X for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, the system performance is unacceptable for that parameter.

NOTE: The large number of parameters in Table 3 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure. however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The analyst must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For analysts analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 8.2.2 or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 8.2.2.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as 100(A-B)%/T, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 3 of EPA Method 608. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.[10] If spiking was performed at a concentration lower than the test concentration in Section 8.2.2, the analyst must use either the QC acceptance criteria in Table 3 EPA Method 608, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy (X') using the equation in Table 4 EPA Method 608, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 4 EPA Method 608, substituting X' for X; (3) calculate the range for recovery at the spike concentration as (100 X'/T)±2.44(100 S'/T)%.[10]

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of parameters in Table 1 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Section 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standards to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 3. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the analyst performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for compliance purposes.

8.5 As part of the QC program for the analyst, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (P) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P-2s_p$ to $P+2s_p$. If $P=90\%$ and $s_p=10\%$, for example. the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the analyst adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirming techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the analyst should analyze standard reference materials and participate in relevant performance evaluation studies.

Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[11] should be followed, except that the bottle must not be pre-rinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction. If the samples will not be extracted within 72 h of collection, the sample should be adjusted to a pH range of 5.0 to 9.0 with sodium hydroxide solution or sulfuric acid. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.[12] Field test kits are available for this purpose.

9.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.[2]

Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 0.5-L separatory funnel.

10.2 Add 10 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min. with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 125-mL Erlenmeyer flask.

10.3 Add a second 10-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 5 to 10 mL of methylene chloride to complete the quantitative transfer.

10.5 Transfer the extract to a pear shaped vacuum centrifuge flask. Place the flask in the SAVANT vacuum centrifuge and run the solvent evaporation program on the SAVANT vacuum centrifuge.

10.6 After the SAVANT run, remove the flask and rinse the flask and its lower joint into the concentrator tube with 1 mL of methylene chloride. A disposable glass pippette is recommended for this operation. Fill the concentrator tube to the 2 mL mark with methylene chloride. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use either procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure. The Florisil column allows for a select fractionation of the compounds and will eliminate polar interferences. Elemental sulfur, which interferes with the electron capture gas chromatography of certain pesticides, can be removed by the technique described in Section 11.3.

11.2 Florisil column cleanup:

11.2.1 Place a weight of Florisil (nominally 1.0 g) predetermined by calibration (Section 7.5), into a pesticide chromatographic column with stopcock. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

11.2.2 Add 10.0 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate layer to the air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

11.2.3 Transfer the sample extract volume from the K-D concentrator tube onto the column. Rinse the tube twice with 1 to 2 mL of hexane, adding each rinse to the column.

11.2.4 Place a pear shaped SAVANT flask and under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 20.0 mL of 6% ethyl ether in hexane (V/V) (Fraction 1) at a rate of about 5 mL/min. Remove the SAVANT flask and set it aside for later concentration. Elute the column again, using 20.0 mL of 15% ethyl ether in hexane (V/V) (Fraction 2), into a second SAVANT flask. Perform a third elution using 20.0 mL of 50% ethyl ether in hexane (V/V) (Fraction 3).

11.2.5 Concentrate the fractions as in Section 10.5, and adjust the volume of each fraction to 2.0 mL with methylene chloride and analyze by gas chromatography (Section 12).

11.3 Elemental sulfur will usually elute entirely in Fraction 1 of the Florisil column cleanup. To remove sulfur interference from this fraction or the original extract, pipet 1.00 mL of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add one to three drops of mercury and seal.[13] Agitate the contents of the vial for 15 to 30 s. Prolonged shaking (2 h) may be required. If so, this may be accomplished with a reciprocal shaker. Alternatively, activated copper powder may be used for sulfur removal.[14] Analyze by gas chromatography.

Gas Chromatography

12.1 Table 1 summarizes the MDL's that can be achieved under these conditions. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the gas chromatograph.

12.4 Inject 2 to 5 µL of the sample extract or standard into the gas chromatograph using splitless or solvent-flush technique.[15] Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume to the nearest 0.05 µL, the total extract volume, and the resulting peak size in area or peak height units.

12.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the stand-standard deviation of a retention time for a compound-pound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from the equation below:

$$Concentration\left({}^{mg}\!/_{L} \right) = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (µg/.L).

V_t = Volume of total extract (µg/.L).

V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

$$Concentration\left({}^{mg}\!/\!{}_{L}\right) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract (µg).

V_o = Volume of water extracted (L).

13.2 When it is apparent that two or more PCB (Aroclor) mixtures are present, the Webb and McCall procedure[16] may be used to identify and quantify the Aroclors.

13.3 For multi-component mixtures (chlordane, toxaphene, and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

13.4 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[1] The MDL concentrations listed in Table 1 were obtained using reagent water.[17] Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity, matrix effects, and analyst experience.

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Attachment 3

Base/Neutral and Acid Semi-volatile Compounds

UAB method 625

Scope and Application

1.1 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2 Benzidine can be subject to oxidative losses during solvent concentration. Under the alkaline conditions of extraction, α-BHC, γ–BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethlyamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

1.3 This is a gas chromatographic/mass spectrometry (GC/MS) method[2, 14] applicable to the determination of compounds listed in Table 1 in municipal and industrial discharges

1.4 Due to routine and gross improvements in the method, the method detection limit (MDL, defined in section 16.1)[1] for each parameter is determined on a project specific basis. The MDL for a specific wastewater may differ, depending on the nature of interferences in the sample matrix.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

Summary of Method

2.1 A measured volume of sample, approximately 0.25-L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuos extractor.[2] The methylene chloride extract is dried, concentrated to a volume of 2 mL, and analyzed by the GC/MS. Qualitative identification of the parameters in the extract is performed using the SCAN mode of acquisition, retention time, and matching of acquired mass spectra to standard mass spectral reference libraries. Quantitative analysis is performed using the SIM mode of acquisition, internal standard techniques, and relative abundance of characteristic m/z.

Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 The base/neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets is also available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[4, 6] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidene, 3,3'-dichlorobenzidene, benzo(a)pyrene, α-BHC, β-BHC, δ-BHC, γ–BHC, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls (PCBs). Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

Apparatus and Materials

5.1 Sampling equipment for discrete or composite sampling.

5.1.1 Grab sample bottle--1-L or 1-gt[*sic*], amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon is the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)--The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4°C and protected from light during composite procedures. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. before [*sic*] use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinses with distilled water to minimize the potential for contamination of the sample. An integrated flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—0.5-L, with Teflon stopcock.

5.2.2 Drying column--Chromatographic column, 19 mm ID, with coarse frit filter disc or glass wool.

5.2.3 SAVANT Vacuum Centrifuge programmed to evaporate 45 mL extract to 2 mL utilizing only vacuum, cold trap, and sample compartment controlled temperature not to exceed 40° C.

5.2.4 Evaporative flask, pear-shaped , to fit centrifuge

5.2.5 Vials - 4 mL, amber glass, with Teflon-lined screw cap.

5.2.6 Continuos liquid-liquid extractor--Equipped with Teflon or glass connection joints and stopcocks requiring no lubrication.

5.3 Boiling chips--Approximately 10/40 mesh. Heat to 400°C for 30 min of Soxhlet extract with methylene chloride.

5.4 Water bath or round-bottom heating mantle-- capable of temperature control (± 2°C). The bath should be used in a hood.

5.5 Balance--Analytical, capable of accurately weighing 0.0001g.

5.6 GC/MS system:

5.6.1 Gas Chromatograph--An analytical system complete with a temperature programmable gas Chromatograph and all required accessories [*sic*] including syringes, analytical columns, and gases. The injection port must be designed for splitless injection using capillary columns.

5.6.2 Capillary column for analysis of combined fraction of extract—HP-5, SP-5 or equivalent, 30 meter, WCOT type.

5.6.3 Capillary pre-column 1 meter length.

5.6.4 Capillary column connectors.

Reagents

6.1 Reagent water--reagent water is defined as a water in which an interference is not observed at the MDL of the parameters of interest.

6.2 Sodium Hydroxide solution (10 N)--Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium Thiosulfate--(ACS) Granular.

6.4 Sulfuric acid (1+1) Slowly add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Methanol, methylene chloride--pesticide quality or equivalent.

6.6 Sodium sulfate--(ACS) Granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray.

6.7 Stock standard solutions (1.00 µg/µL)--Standard solutions purchased as certified solutions.

6.7.1 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.2 Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

6.8 DFTPP standard--Prepare a 25 µg/mL solution of DFTPP in methylene chloride.

6.9 Quality control check sample concentrate--See Section 8.2.1.

Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated Table 1.

7.2 Internal standard calibration procedure--To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of internal standards is not affected by method or matrix interferences. Use the base peak of m/z as the primary m/z for quantification of standards. If interferences are noted, use one of the next two most intense m/z quantities for quantification.

7.2.1 Prepare calibration standards at a minimum of three concentrations for each parameter of interest by adding appropriate volumes of one or more standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and dilute to a volume with methylene chloride. One of the calibration standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.2.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 13 and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate the response factors for each compound using the following equation:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard (µg/L).

C_s = Concentration of the parameter to be measured (µg/L).

If the RF value over the working range is a constant (< 35% RSD), the RF can be assumed to be invariant and the average RF used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s / A_{is} vs. RF.

7.3 The working calibration curve or RF must be verified on each working day by the measure measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by ± 25 %, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

Quality Control

8.1 Each analyst that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The analyst must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial , one-time, demonstration of ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.6 and 13.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The analyst must on an ongoing basis, spike and analyze a minimum of 5% of all samples analyzed to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The analyst must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The analyst must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 μg/mL in methylene chloride. Multiple solutions may be required. PCBs and multi-component pesticides may be omitted from this test. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental

Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipette, prepare QC check samples at a concentration of 100 µg/mL by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10 or 11.

8.2.4 Calculate the average recovery (X) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and X with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6 of EPA Method 625. If s and X for all parameters meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual X falls outside the range of accuracy, the system performance is unacceptable for that parameter.

NOTE: The large number of parameters in Table 1 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The analyst must on an ongoing basis spike at least 5% of the samples form each sample site being monitored to assess accuracy. For analysts analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1[*sic*] If as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at least 100 µg/L or 1 to 5 times the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g. maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration of 100 µg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second ample aliquot with 1.0 mL of the QC check concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as 100 (A-B)%/T where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6 of EPA Method 625. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1.[7] If spiking was performed at a concentration lower than 100 µg/L, the analyst must use either the QC acceptance criteria in Table 6 (EPA Method 625), or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy (X') using the equation in Table 7 (EPA Method 625), substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting X' for X; (3) calculate the range for recovery at the spike concentration as (100 X'/T)±2.44(100 S'/T)%.[7]

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of sample matrix, and the performance of the analyst. If the entire list of single-component parameters in Table 6 must be measured in the sample in Section 8.3, the probability that the analysis of the QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of the QC check sample concentrate (Section 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs to only to contain the parameters that failed the criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate the percent recovery (P_s) as 100(A/T)% where T is the true value of the of the standard concentration..

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 6 (EPA Method 625),. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the analysis is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect.

8.5 As part of the QC program for the analyst, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (P) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent interval from P-2s_p to P+2s_p. If P=90% and s_p=10% for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 As a quality control check, the analyst must spike composite samples from an analytical batch with the surrogate standard spiking solution as described in Section 10.2, and calculate the percent recovery of each surrogate compound.

8.7 It is recommended that the analyst adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend on the needs of the analyst and the nature of the samples. Field duplicates may be analyzed to the assess the precision of the environmental measurements. Whenever possible, the analyst should analyze standard reference materials and participate in relevant performance evaluation studies.

Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[8] should be followed, except that the bottle must not be pre-rinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other sources of contamination.

9.2 All sampling must be iced or refrigerated at 4°C from the time of collection until extraction. Fill the sample bottles and if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurements of residual chlorine.[9] Field test kits are available for this purpose.

9.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

Separatory Funnel Extraction

10.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuos extraction (Section 11) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 0.25 L. When sample volumes of 0.25 L are to be extracted, use 3-10 mL volumes of methylene chloride for the serial extraction of the base/neutrals and 3-10 mL volumes of methylene chloride for the acids. If emulsions prevent achieving acceptable solvent recovery with separatory funnel extraction, continuous extraction is used.

10.2. A sample volume of 250 mL is collected in a 400 mL beaker and poured into a 500 mL separation funnel. For every twelve samples extracted, an additional four samples are extracted for quality control and assurance. These include three 250 mL composite samples made of equal amounts of the twelve samples and one 250 mL sample of reverse osmosis water. Standard solution additions consisting of 25 µL of 1000 µg/mL base/neutral matrix spiking solution, 25 µL of 1000 ug/mL base/neutral surrogates, 12.5 µL of 2000 µg /mL acid matrix spiking solution , and 12.5 µL of 2000 µg /mL acid surrogates are made to the separation funnels of two of the three composite samples and mixed well. Sample pH is measured with wide range pH paper and adjusted to pH > 11 with sodium hydroxide solution.

10.3. A 10 mL volume of methylene chloride is added to the separatory funnel and sealed by capping. The separatory funnel is gently shaken by hand for 15 s and vented to release pressure. The cap is removed from the separatory funnel and replaced with a vented snorkel stopper. The separatory funnel is then placed on a mechanical shaker and shaken for 2 min. After returning the separatory funnel to its stand and replacing the snorkel stopper with cap, the organic layer is allowed to separate from the water phase for a minimum of 10 minutes, longer if an emulsion develops. The extract and any emulsion present is then collected into a 125 mL Erlenmeyer flask.

10.4. A second and third 10 mL volume of methylene chloride is added to the separatory funnel and the extraction method is repeated, combining the extract with the previous in the Erlenmeyer flask. For persistent emulsions, those with emulsion interface between layers more than one-third the volume of the solvent layer, the extract including the emulsion is poured into a 50 mL centrifuge vial, capped, and centrifuged at 2000 rpm for 2 min. to break the emulsion. Water phase separated by centrifuge is collected from the vial and returned to the separatory funnel using a disposable pipette. The centrifuge vial with the extract is recapped before performing the extraction of the acid portion.

10.5. The pH of the remaining sample in the separatory funnel is adjusted to pH < 2 using sulfuric acid. The acidified aqueous phase is serially extracted three times with 10 mL aliquots of methylene chloride as done in the previous base/neutral extraction procedure. Extract and any emulsions are again collected in the 125 mL Erlenmeyer flask..

10.6. The base/neutral extract is poured from the centrifuge vial though a drying column of at least 10 cm of anhydrous sodium sulfate and is collected in a 50 mL beaker. The Erlenmeyer flask is rinsed with 5 mL of methylene chloride which is then used to rinse the centrifuge vial and then for rinsing the drying column and completing the quantitative transfer.

10.7. The base/neutral extract is transferred into 50 mL concentration vials and is placed in an automatic vacuum/centrifuge concentrator (Vacuum concentration is used in place of the Kuderna-Danish method). Extract is concentrated to approximately 0.5 mL.

10.8. The acid extract collected in the 125 mL Erlenmeyer flask is placed in the 50 mL centrifuge vial. Again, if persistent emulsions persist, the extract is centrifuged at 2000 rpm for 2 min. Water is drawn from the extract and discarded. Extract is poured through the 10 cm anhydrous sodium sulfate drying column and collected in the 50 mL beaker as before. The Erlenmeyer flask is then rinsed with 5 mL of methylene chloride which is then poured into the centrifuge vial and finally through the drying column.

10.9. The acid extract is then poured into the 50 mL concentration vial combining it with the evaporated base/neutral extract. The combined extract is then concentrated to approximately 0.5 mL in the automatic vacuum/centrifuge concentrator.

10. Using a disposable pipette, extract is transferred to a graduated vial. Approximately 1.5 mL of methylene chloride is placed in the extraction vial for rinsing. This rinse solvent is then used to adjust the volume of extract to 2.0 mL. Extract is then poured into a labeled Teflon-sealed screw-cap vial and freezer stored until analysis

Continuous Extraction

11.1 When experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel as in Section 10, a continuos extractor should be used.

11.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH>11 with sodium hydroxide solution. Transfer the sample to the continuous extractor and as in Section 10, add matrix and surrogate standard spiking solutions and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the extractor.

11.3 Repeat the sample bottle rinse with an additional 50 to 100 mL portion of methylene chloride and add the rinse to the extractor.

11.4 Add 200 to 500 mL of methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 h. Allow to cool, then detach the distilling flask. Dry, concentrate, and seal the extract as in Section 10.

11.5 Charge a clean distilling flask 500 mL of methylene chloride and attach it to the continuos extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 24 h. Dry, concentrate, and seal the extract as in Sections 10.

Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked out to see if acceptable performance criteria are performed for DFTPP.[10]

12.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 V (nominal)

Mass Range: 35 to 450 amu

Scan Time: To give at least 5 scans per peak but not to exceed 7 s per scan.

12.3 DFTPP performance test--At the beginning of each day, inject 2 µL (50 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 9 (EPA Method 625) are achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved before any sampling , blanks, or standards are analyzed. The tailing factor tests in Sections 12.4 and 12.5 may be performed simultaneously with the DFTPP test.

12.4 Column performance test. At the beginning of each day the tailing factor must be calculated. standard mixture containing Inject 50 ng of pentachlorophenol either separately or as part of a standard mix that may contain DFTPP and calculate the tailing factor. The tailing factor for pentachlorophenol must be less than 5. Replace the column, pre-column, or inlet, (as appropriate) if the tailing factor criterion cannot be achieved.

Gas Chromatograph/Mass Spectrometry

13.1 The following listing summarizes the recommended gas chromatographic operating conditions

GC/MS Operating Parameters for selected ion monitoring

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TOPLEVEL PARAMETERS
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Method Information For: C:\HPCHEM\1\METHODS\BNASIM.M

Method Sections To Run:

  ( ) Save Copy of Method With Data
  ( ) Pre-Run Cmd/Macro  =
  (X) Data Acquisition
  (X) Data Analysis
  ( ) Post-Run Cmd/Macro =

Method Comments:
  Semivolatile BNA compounds quantitative analysis method


                              END OF TOPLEVEL PARAMETERS
                              --------------------------


                             ACQUISITION PARAMETERS



General Information
------- -----------

Inlet             : GC
Tune File         : DFTPP.U
Acquisition Mode  : Sim


MS Information
-- -----------

Solvent Delay     : 3.00 min

EM Absolute       : False
EMV Offset        : 0.0
Resulting Voltage : 3000.0

[Sim Parameters]

GROUP 1
Group ID         : Group 1
Dwell Per Ion    : 150 msec.
Low Resolution   : No
Group Start Time : 3.00
Ions In Group    : 42.00   74.00   44.00

GROUP 2
Group ID         : Group 2
Dwell Per Ion    : 150 msec.
Low Resolution   : No
Group Start Time : 5.00
Ions In Group    :112.00   64.00   92.00

GROUP 3
Group ID         : Group 3
Dwell Per Ion    : 14 msec.
Low Resolution   : No
Group Start Time : 6.00
```

```
Ions In Group    : 94.00   71.00   70.00   66.00   65.00
                   93.00   63.00   95.00  128.00   64.00
                  130.00  146.00  148.00  113.00  150.00
                  152.00  115.00   99.00

GROUP 4
Group ID         : Group 4
Dwell Per Ion    : 14 msec.
Low Resolution   : No
Group Start Time : 7.00
Ions In Group    :146.00  148.00  113.00   45.00  121.00
                   77.00   43.00   70.00  130.00  117.00
                  201.00  199.00   82.00  128.00   70.00
                   77.00  123.00   65.00

GROUP 5
Group ID         : Group 5
Dwell Per Ion    : 10 msec.
Low Resolution   : No
Group Start Time : 7.60
Ions In Group    :136.00  137.00  108.00   82.00   39.00
                  138.00  139.00   65.00  109.00  107.00
                  122.00   77.00   93.00   63.00   95.00
                  162.00  164.00   63.00  180.00  182.00
                  145.00  128.00  102.00  129.00

GROUP 6
Group ID         : Group 6
Dwell Per Ion    : 150 msec.
Low Resolution   : No
Group Start Time : 8.30
Ions In Group    :225.00  190.00  260.00

GROUP 7
Group ID         : Group 7
Dwell Per Ion    : 150 msec.
Low Resolution   : No
Group Start Time : 8.70
Ions In Group    :107.00  142.00   77.00

GROUP 8
Group ID         : Group 8
Dwell Per Ion    : 28 msec.
Low Resolution   : No
Group Start Time : 9.10
Ions In Group    :237.00  239.00  235.00  196.00  198.00
                   97.00  172.00  171.00  170.00  162.00
                  127.00  164.00

GROUP 9
Group ID         : Group 10
Dwell Per Ion    : 41 msec.
Low Resolution   : No
Group Start Time : 10.00
Ions In Group    :163.00   77.00  194.00  165.00   63.00
                   89.00  152.00  151.00  153.00

GROUP 10
Group ID         : Group 11
Dwell Per Ion    : 22 msec.
Low Resolution   : No
```

```
Group Start Time : 10.50
Ions In Group    :164.00  162.00   80.00  153.00  154.00
                   76.00  184.00   63.00   53.00  139.00
                   65.00  109.00  165.00   89.00

GROUP 11
Group ID         : Group 12
Dwell Per Ion    : 14 msec.
Low Resolution   : No
Group Start Time : 11.25
Ions In Group    :149.00  177.00  150.00  166.00  165.00
                  167.00  204.00  141.00   77.00  198.00
                   51.00  105.00  169.00  168.00  182.00
                   62.00  141.00  330.00

GROUP 12
Group ID         : Group 13
Dwell Per Ion    : 69 msec.
Low Resolution   : No
Group Start Time : 12.25
Ions In Group    :250.00  248.00  141.00  284.00  142.00
                  249.00

GROUP 13
Group ID         : Group 14
Dwell Per Ion    : 42 msec.
Low Resolution   : No
Group Start Time : 12.90
Ions In Group    :188.00  189.00  186.00  266.00  268.00
                  264.00  178.00  176.00  179.00

GROUP 14
Group ID         : Group 15
Dwell Per Ion    : 150 msec.
Low Resolution   : No
Group Start Time : 13.60
Ions In Group    :167.00  139.00  165.00

GROUP 15
Group ID         : Group 16
Dwell Per Ion    : 150 msec.
Low Resolution   : No
Group Start Time : 14.50
Ions In Group    :149.00  150.00  104.00

GROUP 16
Group ID         : Group 17
Dwell Per Ion    : 69 msec.
Low Resolution   : No
Group Start Time : 15.20
Ions In Group    :202.00  198.00  101.00  244.00  245.00
                  122.00

GROUP 17
Group ID         : Group 18
Dwell Per Ion    : 150 msec.
Low Resolution   : No
Group Start Time : 17.20
Ions In Group    :149.00   91.00  206.00

GROUP 18
```

```
Group ID         : Group 19
Dwell Per Ion    : 28 msec.
Low Resolution   : No
Group Start Time : 18.20
Ions In Group    :228.00  226.00  229.00  240.00  241.00
                  238.00  228.00  226.00  229.00  149.00
                  167.00   57.00

GROUP 19
Group ID         : Group 20
Dwell Per Ion    : 69 msec.
Low Resolution   : No
Group Start Time : 19.50
Ions In Group    :149.00  150.00  279.00  252.00  253.00
                  250.00

GROUP 20
Group ID         : Group 21
Dwell Per Ion    : 69 msec.
Low Resolution   : No
Group Start Time : 21.50
Ions In Group    :264.00  265.00  132.00  252.00  250.00
                  253.00

GROUP 21
Group ID         : Group 22
Dwell Per Ion    : 150 msec.
Low Resolution   : No
Group Start Time : 23.00
Ions In Group    : 43.00  215.00  370.00

GROUP 22
Group ID         : Group 23
Dwell Per Ion    : 69 msec.
Low Resolution   : No
Group Start Time : 25.00
Ions In Group    :276.00  277.00  138.00  278.00  279.00
                  139.00

[Real Time Plot Parameters]

Time Window     : 27 min
Iconize Real Time Display : False
Plot 1 type     : Total ion
Scale minimum   : 0
Scale maximum   : 1000000
Plot 2 type     : No plot


GC Inlet Information
-- ----- -----------


[Inlet A Temperature Program Information]

Oven Track    : Off
Initial Temp. : 300 C
Initial Time  : 30.00 min

Level     Rate (C/min)    Final Temp. (C)   Final Time (min)
  1               0
```

```
Total Program Time: 30.00 min


[Inlet B Temperature Program Information]

Oven Track    : Off
Initial Temp. : 300 C
Initial Time  : 30.00 min

Level     Rate (C/min)    Final Temp. (C)   Final Time (min)
  1               0
Total Program Time: 30.00 min


[Inlet A Pressure Program Information]

Constant Flow : On 0 kPa  at 40 C
Pressure Units : kPa


[Inlet A Flow Settings]

Column length       : 30.00 m
Column diameter     : 0.250 mm
Gas                 : He
Vacuum compensation : Off
Pressure            : 0 kPa
Flow                : 0.0 ml/min
Linear velocity     : 0.0 cm/sec
Split flow          : 50 ml/min


[Inlet B Pressure Program Information]

Constant Flow : On 1 kPa  at 40 C
Pressure Units : kPa


[Inlet B Flow Settings]

Column length       : 30.00 m
Column diameter     : 0.250 mm
Gas                 : He
Vacuum compensation : On
Pressure            : 1 kPa
Flow                : 0.5 ml/min
Linear velocity     : 24.5 cm/sec


[Auxiliary Channel C Information]

Comment:

Pressure Program:
Initial Pres. : 0 kPa
Initial Time  : 480.00 min

Level     Rate(kPa/min)   Final Pres.(kPa)  Final Time (min)
  1               0
Total Program Time: 480.00 min
```

```
[Auxiliary Channel D Information]

Comment:

Pressure Program:
Initial Pres. : 0 kPa
Initial Time  : 480.00 min

Level     Rate(kPa/min)   Final Pres.(kPa)  Final Time (min)
  1               0
Total Program Time: 480.00 min



[Auxiliary Channel E Information]

Comment:

Pressure Program:
Initial Pres. : 0 kPa
Initial Time  : 480.00 min

Level     Rate(kPa/min)   Final Pres.(kPa)  Final Time (min)
  1               0
Total Program Time: 480.00 min



[Auxiliary Channel F Information]

Comment:

Pressure Program:
Initial Pres. : 0 kPa
Initial Time  : 480.00 min

Level     Rate(kPa/min)   Final Pres.(kPa)  Final Time (min)
  1               0
Total Program Time: 480.00 min





GC Temperature Information
-- ----------- -----------

[GC Zone Temperatures]

Inj. A : 300 C
Inj. B : 300 C
Det. A : 300 C
Det. B : 300 C
Aux.  : 280 C  Off

[Oven Parameters]

Oven Equib Time  : 0.50 min
Oven Max         : 300 C
```

```
Oven             : On
Cryo             : Off
Ambient          : 25 C
Cryo Blast       : Off

[Oven Program]

Initial Temp. : 40 C
Initial Time  : 4.00 min

Level     Rate (C/min)    Final Temp. (C)   Final Time (min)
  1           35.00             130            0.00
  2           12.00             280           10.93
  3            0.00
Next Run Time    : 30.00 min




Injector Information
-------- -----------

Injection Source   : Auto
Injection Location : Rear

Sample Washes     : 1
Sample Pumps      : 3
Sample Volume     : 2 stop(s)
Viscosity Delay   : 0 sec
Solvent A Washes  : 3
Solvent B Washes  : 3
On Column         : No




[Purge Information]

Purge A/B     Init. Value     On Time     Off Time
     A            On             0.00        0.00
     B            Off            1.00        0.00


                          END OF ACQUISITION PARAMETERS

                           DATA ANALYSIS PARAMETERS
                           ------------------------

Method Name: C:\HPCHEM\1\METHODS\BNASIM.M



Percent Report Settings
-----------------------

Sort By: Signal

Output Destination
    Screen:  No
    Printer: No
```

```
    File:    No

Integration Events: Meth Default

Generate Report During Run Method:  No

Signal Correlation Window: 0.020



Qualitative Report Settings
---------------------------

Peak Location of Unknown: Apex minus Start of Peak

Library to Search      Minimum Quality
kp625.l                 50
pripol.l                50
nbs49k.l

Integration Events: RTEINT.MAC

Report Type: Summary

Output Destination
    Screen:  No
    Printer: No
    File:    qual.txt

Generate Report During Run Method:  No



Quantitative Report Settings
----------------------------

Report Type: Detailed (text only)

Output Destination
    Screen:  No
    Printer: No
    File:    detail.xls

Generate Report During Run Method:  Yes



Semivolatile BNA Compounds


Reference Window: 5.00 Percent
Non-Reference Window: 5.00 Percent
Correlation Window: 0.03 minutes
Default Multiplier: 1.05
Default Sample Concentration: 0.00

Compound Information
--------------------

----------------------------------------------------------------------------
 1)  1,4-DICHLOROBENZENE D4                    (ISTD)
```

```
Ret. Time   6.86 min., Extract & Integrate from   6.36 to   7.36 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  150.00                                *** METH DEFAULT ***
Q1   152.00     56.60       20.0           *** METH DEFAULT ***
Q2   115.00     36.60       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON    ISTD conc:      100.000 uG/L
Curve Fit: Avg. RF
----------------------------------------------------------------------------

 2)  n-nitrosodimethylamine                    ( )

Ret. Time   3.37 min., Extract & Integrate from   2.87 to   3.87 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   42.00                                *** METH DEFAULT ***
Q1    74.00     17.30       20.0           *** METH DEFAULT ***
Q2    44.00      2.40       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

 3)  2-fluorophenol                            ( )

Ret. Time   5.63 min., Extract & Integrate from   5.13 to   6.13 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  112.00                                *** METH DEFAULT ***
Q1    64.00     43.70       20.0           *** METH DEFAULT ***
Q2    92.00     49.90       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

 4)  phenol d6                                 ( )

Ret. Time   6.63 min., Extract & Integrate from   6.13 to   7.13 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   99.00                                *** METH DEFAULT ***
Q1    71.00    104.90       20.0           *** METH DEFAULT ***
Q2    70.00     38.20       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

 5)  phenol                                    ( )

Ret. Time   6.65 min., Extract & Integrate from   6.15 to   7.15 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   94.00                                *** METH DEFAULT ***
Q1    66.00    120.40       20.0           *** METH DEFAULT ***
Q2    65.00     85.80       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

 6)  bis(2-chloroethyl)ether                   ( )
```

```
Ret. Time   6.66 min., Extract & Integrate from   6.16 to   7.16 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   93.00                                *** METH DEFAULT ***
Q1    63.00    138.60       20.0           *** METH DEFAULT ***
Q2    95.00     44.10       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

 7)  2-chlorophenol                            ( )

Ret. Time   6.71 min., Extract & Integrate from   6.21 to   7.21 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  128.00                                *** METH DEFAULT ***
Q1   130.00     35.00       20.0           *** METH DEFAULT ***
Q2    64.00     40.80       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

 8)  1,3-dichlorobenzene                       ( )

Ret. Time   6.87 min., Extract & Integrate from   6.37 to   7.37 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  146.00                                *** METH DEFAULT ***
Q1   148.00     65.10       20.0           *** METH DEFAULT ***
Q2   113.00     21.90       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

 9)  1,4-dichlorobenzene                       ( )

Ret. Time   6.87 min., Extract & Integrate from   6.37 to   7.37 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  146.00                                *** METH DEFAULT ***
Q1   148.00     65.10       20.0           *** METH DEFAULT ***
Q2   113.00     21.90       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

10)  1,2-dichlorobenzene                       ( )

Ret. Time   6.87 min., Extract & Integrate from   6.37 to   7.37 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  146.00                                *** METH DEFAULT ***
Q1   148.00     65.10       20.0           *** METH DEFAULT ***
Q2   113.00     21.90       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

11)  bis(2-chloroisopropyl)ether               ( )

Ret. Time   7.18 min., Extract & Integrate from   6.68 to   7.68 min.
```

```
Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   45.00                                *** METH DEFAULT ***
Q1   121.00     29.30       20.0           *** METH DEFAULT ***
Q2    77.00     41.60       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

12)  n-nitroso-di-n-propylamine                ( )

Ret. Time   7.32 min., Extract & Integrate from   6.82 to   7.82 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   43.00                                *** METH DEFAULT ***
Q1    70.00     83.20       20.0           *** METH DEFAULT ***
Q2   130.00     11.40       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

13)  hexachloroethane                          ( )

Ret. Time   7.35 min., Extract & Integrate from   6.85 to   7.85 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  117.00                                *** METH DEFAULT ***
Q1   201.00     76.10       20.0           *** METH DEFAULT ***
Q2   199.00     49.50       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

14)  nitrobenzene d5                           ( )

Ret. Time   7.43 min., Extract & Integrate from   6.93 to   7.93 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   82.00                                *** METH DEFAULT ***
Q1   128.00     39.60       20.0           *** METH DEFAULT ***
Q2    70.00     63.80       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

15)  nitrobenzene                              ( )

Ret. Time   7.44 min., Extract & Integrate from   6.94 to   7.94 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   77.00                                *** METH DEFAULT ***
Q1   123.00     19.30       20.0           *** METH DEFAULT ***
Q2    65.00     10.80       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

16)  NAPHTHALENE D8                            (ISTD)

Ret. Time   8.17 min., Extract & Integrate from   7.67 to   8.67 min.
```

```
Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  136.00                                *** METH DEFAULT ***
Q1   137.00     11.20       20.0           *** METH DEFAULT ***
Q2   108.00     20.40       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON    ISTD conc:      100.000 uG/L
Curve Fit: Avg. RF
----------------------------------------------------------------------------

17)  isophorone                                 ( )

Ret. Time   7.68 min., Extract & Integrate from   7.18 to   8.18 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   82.00                                *** METH DEFAULT ***
Q1    39.00     86.80       20.0           *** METH DEFAULT ***
Q2   138.00     19.40       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

18)  2-nitrophenol                              ( )

Ret. Time   7.79 min., Extract & Integrate from   7.29 to   8.29 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  139.00                                *** METH DEFAULT ***
Q1    65.00     67.50       20.0           *** METH DEFAULT ***
Q2   109.00     86.40       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

19)  2,4-dimethylphenol                         ( )

Ret. Time   7.85 min., Extract & Integrate from   7.35 to   8.35 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  107.00                                *** METH DEFAULT ***
Q1   122.00     56.00       20.0           *** METH DEFAULT ***
Q2    77.00     36.40       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

20)  bis(2-chloroethoxy)methane                 ( )

Ret. Time   7.94 min., Extract & Integrate from   7.44 to   8.44 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   93.00                                *** METH DEFAULT ***
Q1    63.00    221.20       20.0           *** METH DEFAULT ***
Q2    95.00     54.20       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

21)  2,4-dichlorophenol                         ( )

Ret. Time   8.06 min., Extract & Integrate from   7.56 to   8.56 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
```

```
Tgt  162.00                                *** METH DEFAULT ***
Q1   164.00     67.40       20.0           *** METH DEFAULT ***
Q2    63.00    150.20       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

22)  1,2,4-trichlorobenzene                    ( )

Ret. Time   8.13 min., Extract & Integrate from   7.63 to   8.63 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  182.00                                *** METH DEFAULT ***
Q1   180.00    102.70       20.0           *** METH DEFAULT ***
Q2   145.00     43.50       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

23)  naphthalene                               ( )

Ret. Time   8.19 min., Extract & Integrate from   7.69 to   8.69 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  128.00                                *** METH DEFAULT ***
Q1   102.00     27.70       20.0           *** METH DEFAULT ***
Q2   129.00     13.80       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

24)  hexachlorobutadiene                       ( )

Ret. Time   8.42 min., Extract & Integrate from   7.92 to   8.92 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  225.00                                *** METH DEFAULT ***
Q1   190.00     68.70       20.0           *** METH DEFAULT ***
Q2   260.00     36.10       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

25)  4-chloro-3-methylphenol                   ( )

Ret. Time   8.96 min., Extract & Integrate from   8.46 to   9.46 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  107.00                                *** METH DEFAULT ***
Q1   142.00     67.20       20.0           *** METH DEFAULT ***
Q2    77.00     90.00       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

26)  hexachlorocyclopentadiene                 ( )

Ret. Time   9.38 min., Extract & Integrate from   8.88 to   9.88 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  237.00                                *** METH DEFAULT ***
```

```
Q1   239.00     64.20       20.0           *** METH DEFAULT ***
Q2   235.00     69.60       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

27)  2,4,6-trichlorophenol                      ( )

Ret. Time   9.51 min., Extract & Integrate from   9.01 to  10.01 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  196.00                                *** METH DEFAULT ***
Q1   198.00     87.60       20.0           *** METH DEFAULT ***
Q2    97.00     72.90       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

28)  2-fluorobiphenyl                           ( )

Ret. Time   9.60 min., Extract & Integrate from   9.10 to  10.10 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  172.00                                *** METH DEFAULT ***
Q1   171.00     38.90       20.0           *** METH DEFAULT ***
Q2   170.00     32.90       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

29)  2-chloronaphthalene                        ( )

Ret. Time   9.74 min., Extract & Integrate from   9.24 to  10.24 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  162.00                                *** METH DEFAULT ***
Q1   127.00     42.60       20.0           *** METH DEFAULT ***
Q2   164.00     35.70       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

30)  ACENAPHTHENE D10                           (ISTD)

Ret. Time  10.63 min., Extract & Integrate from  10.13 to  11.13 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  164.00                                *** METH DEFAULT ***
Q1   162.00    106.40       20.0           *** METH DEFAULT ***
Q2    80.00      8.00       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON    ISTD conc:      100.000 uG/L
Curve Fit: Avg. RF
----------------------------------------------------------------------------

31)  dimethylphthalate                          ( )

Ret. Time  10.30 min., Extract & Integrate from   9.80 to  10.80 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  163.00                                *** METH DEFAULT ***
Q1    77.00     25.30       20.0           *** METH DEFAULT ***
```

```
Q2   194.00      9.30       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

32)  2,6-dinitrotoluene                        ( )

Ret. Time  10.39 min., Extract & Integrate from   9.89 to  10.89 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  165.00                                *** METH DEFAULT ***
Q1    63.00    134.10       20.0           *** METH DEFAULT ***
Q2    89.00     83.50       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

33)  acenaphthylene                            ( )

Ret. Time  10.38 min., Extract & Integrate from   9.88 to  10.88 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  152.00                                *** METH DEFAULT ***
Q1   151.00     25.50       20.0           *** METH DEFAULT ***
Q2   153.00     12.60       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

34)  acenaphthene                              ( )

Ret. Time  10.69 min., Extract & Integrate from  10.19 to  11.19 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  153.00                                *** METH DEFAULT ***
Q1   154.00     88.20       20.0           *** METH DEFAULT ***
Q2    76.00     11.00       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

35)  2,4-dinitrophenol                         ( )

Ret. Time  10.79 min., Extract & Integrate from  10.29 to  11.29 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  184.00                                *** METH DEFAULT ***
Q1    63.00     73.50       20.0           *** METH DEFAULT ***
Q2    53.00     88.10       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

36)  4-nitrophenol                             ( )

Ret. Time  10.69 min., Extract & Integrate from  10.19 to  11.19 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  139.00                                *** METH DEFAULT ***
Q1    65.00     70.90       20.0           *** METH DEFAULT ***
Q2   109.00     39.40       20.0           *** METH DEFAULT ***
```

```
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

37)  2,4-dinitrotoluene                         ( )

Ret. Time  11.05 min., Extract & Integrate from  10.55 to  11.55 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  165.00                                *** METH DEFAULT ***
Q1    89.00     92.10       20.0           *** METH DEFAULT ***
Q2    63.00    137.80       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

38)  PHENANTHRENE D10                           (ISTD TR)

Ret. Time  13.29 min., Extract & Integrate from  12.79 to  13.79 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  188.00                                *** METH DEFAULT ***
Q1   189.00     15.50       20.0           *** METH DEFAULT ***
Q2   186.00      8.50       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON    ISTD conc:      100.000 uG/L
Curve Fit: Linear
----------------------------------------------------------------------------

39)  diethylphthalate                           ( )

Ret. Time  11.52 min., Extract & Integrate from  11.02 to  12.02 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  149.00                                *** METH DEFAULT ***
Q1   177.00     14.00       20.0           *** METH DEFAULT ***
Q2   150.00     11.70       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

40)  fluorene                                   ( )

Ret. Time  11.56 min., Extract & Integrate from  11.06 to  12.06 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  166.00                                *** METH DEFAULT ***
Q1   165.00     88.10       20.0           *** METH DEFAULT ***
Q2   167.00     13.90       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

41)  4-chlorophenylphenylether                  ( )

Ret. Time  11.59 min., Extract & Integrate from  11.09 to  12.09 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  204.00                                *** METH DEFAULT ***
Q1   141.00    167.10       20.0           *** METH DEFAULT ***
Q2    77.00     36.90       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
```

```
Curve Fit: Avg. RF
----------------------------------------------------------------------------

42)  2-methyl-4,6-dinitrophenol                ( )

Ret. Time  11.76 min., Extract & Integrate from  11.26 to  12.26 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  198.00                                *** METH DEFAULT ***
Q1    51.00     83.70       20.0           *** METH DEFAULT ***
Q2   105.00     40.10       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

43)  n-nitrosodiphenylamine                    ( )

Ret. Time  11.82 min., Extract & Integrate from  11.32 to  12.32 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  169.00                                *** METH DEFAULT ***
Q1   168.00     66.00       20.0           *** METH DEFAULT ***
Q2   167.00     41.60       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

44)  azobenzene                                ( )

Ret. Time  11.87 min., Extract & Integrate from  11.37 to  12.37 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   77.00                                *** METH DEFAULT ***
Q1    51.00     98.30       20.0           *** METH DEFAULT ***
Q2   182.00     20.40       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

45)  2,4,6-tribromophenol                      ( )

Ret. Time  12.03 min., Extract & Integrate from  11.53 to  12.53 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   62.00                                *** METH DEFAULT ***
Q1   141.00    168.60       20.0           *** METH DEFAULT ***
Q2   330.00    104.70       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

46)  4-bromophenylphenylether                  ( )

Ret. Time  12.48 min., Extract & Integrate from  11.98 to  12.98 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  250.00                                *** METH DEFAULT ***
Q1   248.00    110.30       20.0           *** METH DEFAULT ***
Q2   141.00    115.90       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
```

```
----------------------------------------------------------------------------

47)  hexachlorobenzene                        ( )

Ret. Time  12.72 min., Extract & Integrate from  12.22 to  13.22 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  284.00                                *** METH DEFAULT ***
Q1   142.00     73.40       20.0           *** METH DEFAULT ***
Q2   249.00     46.10       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

48)  pentachlorophenol                        ( )

Ret. Time  13.10 min., Extract & Integrate from  12.60 to  13.60 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  266.00                                *** METH DEFAULT ***
Q1   268.00     72.70       20.0           *** METH DEFAULT ***
Q2   264.00     50.80       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

49)  phenanthrene                             ( )

Ret. Time  13.33 min., Extract & Integrate from  12.83 to  13.83 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  178.00                                *** METH DEFAULT ***
Q1   176.00     20.70       20.0           *** METH DEFAULT ***
Q2   179.00     14.60       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

50)  anthracene                               ( )

Ret. Time  13.33 min., Extract & Integrate from  12.83 to  13.83 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  178.00                                *** METH DEFAULT ***
Q1   179.00     14.60       20.0           *** METH DEFAULT ***
Q2   176.00     20.70       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

51)  carbazole                                ( )

Ret. Time  13.79 min., Extract & Integrate from  13.29 to  14.29 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  167.00                                *** METH DEFAULT ***
Q1   139.00     29.00       20.0           *** METH DEFAULT ***
Q2   165.00      2.40       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------
```

```
52)  di-n-butylphthalate                       ( )

Ret. Time  14.71 min., Extract & Integrate from  14.21 to  15.21 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  149.00                                *** METH DEFAULT ***
Q1   150.00     10.70       20.0           *** METH DEFAULT ***
Q2   104.00     10.70       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

53)  fluoranthene                              ( )

Ret. Time  15.70 min., Extract & Integrate from  15.20 to  16.20 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  202.00                                *** METH DEFAULT ***
Q1   101.00      2.10       20.0           *** METH DEFAULT ***
Q2   198.00      3.80       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

54)  pyrene                                    ( )

Ret. Time  16.13 min., Extract & Integrate from  15.63 to  16.63 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  202.00                                *** METH DEFAULT ***
Q1   198.00      4.20       20.0           *** METH DEFAULT ***
Q2   101.00      2.30       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

55)  4-terphenyl d14                           ( )

Ret. Time  16.58 min., Extract & Integrate from  16.08 to  17.08 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  244.00                                *** METH DEFAULT ***
Q1   245.00     18.90       20.0           *** METH DEFAULT ***
Q2   122.00     10.30       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

56)  CHRYSENE D12                              (ISTD)

Ret. Time  18.64 min., Extract & Integrate from  18.14 to  19.14 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  240.00                                *** METH DEFAULT ***
Q1   241.00     23.40       20.0           *** METH DEFAULT ***
Q2   238.00      8.60       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON    ISTD conc:      100.000 uG/L
Curve Fit: Linear
----------------------------------------------------------------------------
```

```
57)  benzylbutylphthalate                      ( )

Ret. Time  17.72 min., Extract & Integrate from  17.22 to  18.22 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  149.00                                *** METH DEFAULT ***
Q1    91.00     51.20       20.0           *** METH DEFAULT ***
Q2   206.00     10.10       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

58)  benzo(a)anthracene                        ( )

Ret. Time  18.59 min., Extract & Integrate from  18.09 to  19.09 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  228.00                                *** METH DEFAULT ***
Q1   226.00     28.60       20.0           *** METH DEFAULT ***
Q2   229.00     19.40       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

59)  chrysene                                  ( )

Ret. Time  18.67 min., Extract & Integrate from  18.17 to  19.17 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  228.00                                *** METH DEFAULT ***
Q1   226.00     31.60       20.0           *** METH DEFAULT ***
Q2   229.00     19.20       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

60)  bis(2-ethylhexyl)phthalate                ( )

Ret. Time  19.01 min., Extract & Integrate from  18.51 to  19.51 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  149.00                                *** METH DEFAULT ***
Q1   167.00     24.00       20.0           *** METH DEFAULT ***
Q2    57.00     24.10       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

61)  PERYLENE D12                              (ISTD)

Ret. Time  21.95 min., Extract & Integrate from  21.45 to  22.45 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  264.00                                *** METH DEFAULT ***
Q1   265.00     25.50       20.0           *** METH DEFAULT ***
Q2   132.00     10.60       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON    ISTD conc:      100.000 uG/L
Curve Fit: Avg. RF
----------------------------------------------------------------------------

62)  di-n-octylphthalate                       ( )
```

```
Ret. Time  20.33 min., Extract & Integrate from  19.83 to  20.83 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  149.00                                *** METH DEFAULT ***
Q1   150.00      9.30       20.0           *** METH DEFAULT ***
Q2   279.00      1.70       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

63)  benzo(b)fluoranthene                      ( )

Ret. Time  21.00 min., Extract & Integrate from  20.50 to  21.50 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  252.00                                *** METH DEFAULT ***
Q1   253.00     20.90       20.0           *** METH DEFAULT ***
Q2   250.00     21.80       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

64)  benzo(k)fluoranthene                      ( )

Ret. Time  21.00 min., Extract & Integrate from  20.50 to  21.50 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  252.00                                *** METH DEFAULT ***
Q1   250.00     21.80       20.0           *** METH DEFAULT ***
Q2   253.00     20.90       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

65)  benzo(a)pyrene                            ( )

Ret. Time  21.78 min., Extract & Integrate from  21.28 to  22.28 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  252.00                                *** METH DEFAULT ***
Q1   250.00     23.10       20.0           *** METH DEFAULT ***
Q2   253.00     21.20       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

66)  coprostanol                               ( )

Ret. Time  24.24 min., Extract & Integrate from  23.74 to  24.74 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt   43.00                                *** METH DEFAULT ***
Q1   215.00      0.00       20.0           *** METH DEFAULT ***
Q2   370.00      0.00       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Quadratic, forced through origin
----------------------------------------------------------------------------

67)  indeno(1,2,3-c,d)pyrene                   ( )
```

```
Ret. Time  25.76 min., Extract & Integrate from  25.26 to  26.26 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  276.00                                *** METH DEFAULT ***
Q1   277.00     16.10       20.0           *** METH DEFAULT ***
Q2   138.00      4.00       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

68)  dibenz(a,h)anthracene                         ( )

Ret. Time  25.93 min., Extract & Integrate from  25.43 to  26.43 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  278.00                                *** METH DEFAULT ***
Q1   279.00     24.20       20.0           *** METH DEFAULT ***
Q2   139.00      2.20       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

69)  benzo(g,h,i)perylene                          ( )

Ret. Time  26.83 min., Extract & Integrate from  26.33 to  27.33 min.

Signal       Rel Resp.  Pct. Unc.(rel)    Integration
Tgt  276.00                                *** METH DEFAULT ***
Q1   138.00      5.30       20.0           *** METH DEFAULT ***
Q2   277.00     22.20       20.0           *** METH DEFAULT ***
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
----------------------------------------------------------------------------

                   END OF DATA ANALYSIS PARAMETERS
                   -------------------------------
```

13.2 After conducting the GC/MS performance tests in Section 12, calibrate the system daily as described in Section 7.

13.3 The internal standard must be added to the sample extract and mixed thoroughly immediately before it is injected into the instrument. This procedure minimizes losses due to adsorption, chemical reaction, or evaporation.

13.4 Inject 2 to 5 µL of the sample extract or standard into the GC/MS system using the splitless or solvent flush technique.[12] Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL.

13.5 If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

13.6 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When the extracts are not being used for analyses, store them refrigerated at 4 °C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

Qualitative Identification

14.1 Selected ion monitoring (SIM) is utilized for quantitative determinations. For qualitative determinations, the GC/MS is operated in the Scan mode. Obtain EICPs for the primary m/z and the two other masses listed in Table 1. The following criteria must be met to make a qualitative identification:

14.1.1 The characteristic masses of each parameter of interest must maximize in the same or 1 scan from each other.

14.1.2 The retention time must fall with ±30 s of the retention time of the authentic compound.

14.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within ±20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

14.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between the authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to the valley height between the two isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

Calculations

15.1 When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/a in Tables 4 and 5. use the base peaks of the m/z for internal and surrogate standards if the sample introduces interferences for the primary m/z, use a secondary characteristic m/z to quantitate. Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and this equation:

$$Concentraion(mg/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

I_s = Amount of internal standard added to each extract (µg).

V_o = Volume of water extracted (L).

15.2 Report the results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

Method Performance

16.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured with 99% confidence that the value is above zero.[1] The MDL concentrations are obtained using reagent water.[13] The MDL actually achieved in a given analysis will vary depending on instrument sensitivity, matrix effects, and analyst experience.

16.2 The EPA 625 method has been tested using reagent water, drinking water, surface water, and industrial wastewaters spiked at different concentrations over the range 5 to 1300 μg/L.[14] Single operator precision, overall precision, and method accuracy were found to be directly related to the concentrations of the parameter and essentially independent of sample matrix. Linear equations to describe these relationships are presented in Table 7 of EPA Method 625. Attachment 1 to this method illustrates recovery & precision for the UAB method utilizing composites of reagent water, drinking water, surface water, and industrial wastewaters.

References

1. 40 CFR Part 136, Appendix B.

2. "Sampling and Analysis Procedures for Screening Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977. Available from Effluent Guidelines Division, Washington, DC 20460.

3. ASTM Annual Book of Standards, Part 31, D3694-78. "Standard Practices for Preparation of Sample Containers for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.

4. "Carcinogens--Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health. Publication No. 77-206, August 1977.

5. "OSHA Safety and Health Standards, General Industry," (29 CFR Part 1910), Occupational Health and Safety Administration, OSHA 2206 (Revised January 1976).

6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

7. Provost, L.P. and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, 15 58-63 (1983). (The value 2.44 used in equation in Section 8.3.3 is two times the value 1.22 derived in this report.)

8. ASTM Annual Book of Standards, Part 31, D3370-76. "Standard Practices for Sampling Water, " American Society for Testing and Materials, Philadelphia.

9. "Methods 330.4 (Titrametric, DPD-FAS) and 330.5 (Spectrophotometric , DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45628, March 1979.

10. Eichelberger, J.W., Harris, L.E., and Budde, W.L. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," *Analytical Chemistry*, 47, 995 (1975).

11. McNair, N.M. and Bonelli, E.J. “Basic Chromatography,” Consolidated Printing. Berkeley, California, p. 52, 1969.

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14. “EPA Method Study 30, Method 625, Base/Neutrals, Acids, and Pesticides,” EPA 600/4-84-053, National Technical Information Service, PB84-206572, Springfield, Virginia 22161, June 1984.

Standard Operating Procedure Supplement

1. *Solid Phase Extraction of Organic Compounds*

2. *Summary*

This SOP is for the extraction and concentration of semi-volatile compounds in the basic, acidic and neutral categories. The usable range of concentrations are from 1 to 250 ug per liter dependent on the individual compound. The matrix for samples prepared using this SOP is limited to stormwater samples with less than 4 g/L solids. Expected precision and accuracy are 25% precision (determined from replicate matrix spikes), and a range of accuracy (as recovery ranging from detection to 125%) dependent on the particular compound.

3. *Description of Item*

A Waters SepPak 3 mL syringe containing 500 mg C_{18} material bonded to a spherical silica support sandwiched between Teflon or glass mat filters comprises the absorbent material. A Vacuum Elution device (VacElut) holds the SepPak in place via a female luer adapter. An adapter attached to the top of the SepPak holds a 100 mL reservoir above the SepPak. The VacElut device also routes wastes and collects final elution volume in a glass tube for future analysis.

4. *Calibration Interval*

Although the procedure does not require calibration, spikes for recovery and precision determination are necessary every 30 samples. Since 12 samples can be extracted in one batch run, 3 batches will result in a total of 36 extraction samples. The following pattern of spikes are necessary:

Sample Position	Batch 1	Batch 2	Batch 3
1	RO water	sample	sample
2	composite	sample	sample
3	composite + semivolatile surrogates & matrix spikes	sample	sample
4	composite + semivolatile surrogates & matrix spikes	sample	sample
5	composite + pesticide surrogates & matrix spikes	sample	sample
6	composite + pesticide surrogates & matrix spikes	sample	sample
7	sample	sample	sample
8	sample	sample	sample
9	sample	sample	sample
10	sample	sample	sample
11	sample	sample	sample
12	sample	sample	sample

5. *Standards Needed*

a. Source - Surrogate and matrix spikes are available from various vendors. The surrogates and matrix spikes are listed in the UAB QA document which lists method descriptions - Quality Assurance Project Plan. Use spikes undiluted.

b. Preparation - Typically spiking solutions are 1000 to 2000 ug/mL. In order to obtain a 100 ug/L spike in a 250 mL sample from a 1000 ug/mL solution inject 25 uL of the standard below the surface of the sample. For a 2000 ug/mL solution inject 12.5 uL.

6. Procedure

1. Empty VacElut reservoir.
2. Setup 12 collection tubes in VacElut device.
3. Setup 12 clean SepPaks with adapter and reservoir on VacElut device. Insure the VacElut is in the waste position.
4. Turn on vacuum pump.
5. Wash the SepPaks with 5 mL HPLC grade methanol.
6. Wash the SepPaks with 5 mL RO water.
7. Load the samples into the reservoirs with vacuum on full. (*NOTE* - if vacuum exceeds 30 inches Hg, bleed system and shut down pump, contact Dr. Parmer)
8. After full volume of sample has been eluted through SepPak, allow to dry with vacuum on full for a minimum 20 minutes.
9. Switch VacElut to collect position and move to hood.
10. If there is any remaining water drops in sample container, add 1 gm sodium sulfate to sample container to absorb the water.
11. Move all sample containers and VacElut device to hood.
12. Insure all collection tubes on VacElut are in collection vials.
13. Introduce 3 mL methylene chloride into each sample container. Swirl methylene chloride to wash sample container walls and any sodium sulfate added.
14. Pour 3 mL methylene chloride wash into VacElut reservoir.

Note: This step should be accomplished using a maximum 5 inches Hg vacuum. If methylene chloride does not flow smoothly, the SepPak cartridge is still wet. Increase vacuum and proceed, but note in extraction log that the SepPak elution with methylene chloride was not smooth.

15. Transfer collected eluant to a labeled amber glass vial.
16. Store vial in freezer until analysis.

7 Calculations

Although there are no formal calculations associated with this procedure, have someone else in the lab check your calculations for spike additions. All spikes should be at the 100 ug/L level.

8. Report

There are no formal reporting procedures associated with this SOP other than recording samples extracted and composited in the extraction notebook.

9. References

To be added at a future date.

Attachment 4

MICROTOX Screening Test

Standard Operating Procedure

Scope

Parameters Measured

The parameter measured during the Microtox Screening Procedure is the reduction of light output by the sample at a specific time during the run, compared to a control sample.

Range

The Microtox Screening Procedure has a range of relative toxicities between 0 and 100% of light output reduction.

Matrix

Sample matrix is water. The freeze-dried reagent is bacteria contained within milk solids. The Reconstitution Solution, Diluent, and Osmotic Adjusting Solution are all sodium chloride in "pure" water.

Expected precision and accuracy

Extensive research has been performed to establish precision and accuracy for runoff samples. Please refer to A. Ayyoubi's Master's Thesis, "Physical Treatment of Urban Stormwater Runoff Toxicants".

Terminology

Toxicity: For this method, bacterial metabolic reduction.

Relative toxicity: Percentage that reflects the reduction in light output by the bacteria in a sample as compared to the light output by the bacteria in a control sample.

EC50 concentration: The fraction of sample, using the Microtox diluent as the dilution solution, that causes a light output from the sample that is 50% of the light output of the control. Also called the 50% effective concentration.

Summary of Method

The Microtox Screening Procedure uses a bioluminescent marine bacteria, *Photobacterium phosphoreum*, to measure the toxicity of a sample relative to a control sample at three times during the 25-minute run. At each of the three reading times, the light output of each sample and each control is measured on a chart recorder and is recorded as the height of the peak light output on a scale of 0 to 100.

Significance and Use

P. phosphoreum emit light as a byproduct of respiration. If a sample contains one or more components that interfere with respiration, then the bacteria's light output is reduced proportionally to the amount of interference with respiration, or toxicity. The light output reduction is proportional to the toxicity of the sample. The relative toxicity of a sample to the control can then be calculated. These relative toxicities can be compared to toxicity test results using standard reagents specified by this procedure.

Interferences

Samples having pH values outside the range of 6.3 to 7.8 may be toxic to the bacteria. Normally, the pH of the sample is not adjusted because pH may be the parameter causing toxicity in a natural environment. Color and turbidity will interfere with, and probably will reduce, the amount of emitted light leaving the cuvette and reaching the photomultiplier. Organic matter may provide a second food source for the bacteria and may result in a sample whose relative toxicity is calculated to be less than zero.

Sample storage containers must be clean and free of soap residues, and stoppers must not be made of cork. Detergents, cork and other materials may add chemicals to the sample and may add to the toxicity of the sample.

Tap water and distilled water are fatal to the bacteria. Sample storage containers must be rinsed with de-ionized or ultra-pure water prior to use, with ultra-pure water being preferable.

Apparatus

Microtox 2055 Analyzer

500 μL pipettor (with disposable tips)

10 μL pipettor (with disposable tips)

Glass Cuvettes (Disposable)

Reagents and Materials

Microtox Bacterial Reagent

4% Photobacterium phosphoreum

2% Sodium Chloride

94% Skim Milk Solids

Microtox Reconstitution Solution

100% Ultra Pure Water

Microtox Diluent

2% Sodium Chloride

98% Ultra Pure Water

Microtox Osmotic Adjusting Solution

22% Sodium Chloride

78% Ultra Pure Water

Sodium Chloride (solid) - Reagent Grade

Hazards and Precautions

None of the Reagents and Materials have OSHA PEL(s), AGGIH TLV(s), or other limits. Oral rat LD50 data has not been established for any of the reagents supplied by Microtox.

Sodium chloride, which is one of the reagents and is a component of most of the reagents supplied by Microtox, displays LD50 of 3000 mg/kg. The sodium chloride, either as a reagent or as a component of the other reagents, may cause eye irritation and ingestion of large quantities may cause vomiting, diarrhea and dehydration.

No special storage requirements are needed beyond keeping the freeze-dried bacteria culture in a freezer. Reagents are not considered to be a fire or explosion hazard (water may be used to extinguish if in a fire), and have no hazardous decomposition products. The reagents are stable under ordinary conditions of use and storage. Spilled reagent, whether reacted or not, may be cleaned up by adsorption with paper towels and excess fluid may be flushed down a regular sewer drain.

Sampling, Sample Preparation

Note: The Microtox instrument has space in its incubator for 15 cuvettes. For a normal run, three of the cuvettes (A1, B1, and C1) are reserved for the control solution. One of the remaining twelve cuvettes is reserved for the standard solution whose concentration is approximately the predetermined $ZnSO_4 \cdot 7H_2O$ EC50 concentration. The remaining eleven cuvettes contain the samples to be tested.

1) Rinse clean 40 mL sample vials, vial caps and teflon septa with ultrapure water.

2) Mix the sample by inverting the container several times.

3) Pour 10 mL of sample into the vial.

4) Add 0.2 g NaCl (Reagent Grade) to the vial.

5) Mix the sample and salt by inverting the vial until the salt is completely dissolved.

Preparation of Apparatus

1) Discard the cuvettes remaining in the Incubator and Pre-Cool slots.

2) Put new cuvettes into the fifteen slots in the Incubator and one in the Pre-Cool slot.

3) Pipette 1.0 mL of Diluent into the cuvettes in positions A1, B1, and C1.

4) Pipette 1.0 mL of Reconstitution Solution into a cuvette in the "Pre-Cool" position.

5) Pipette 1.0 mL of each sample into a cuvette in positions A2 through A5, B2 through B5, or C2 through C5.

6) Set the timer for 5 minutes to allow for temperature stabilization of the Reconstitution Solution.

7) Get a vial of the Microtox Reagent Bacteria out of the freezer. (Must be stored prior to use in a freezer at no warmer than -20^{o}C.

8) Tap the reagent vial on the countertop gently several times to break up the contents.

9) After the 5 minute temperature stabilization period has expired, open the vial.

10) Quickly, pour the Reconstitution Solution in the Pre-Cool slot into the reagent vial.

11) Swirl the contents to mix (all solid reagent should go into solution).

12) Pour the reagent solution back into the Pre-Cool cuvette.

13) Mix the reagent solution approximately 20 times with a 500 μL pipette.

14) Set the timer for 15 minutes.

Calibration and Standardization

The Microtox Analyzer is calibrated using solutions of either zinc sulfate or phenol. A standard solution of approximately 10 mg/L zinc sulfate or of approximately 50 mg/L phenol is made. Four dilutions of the standard solution, with three replicates of each dilution, are used in place of the twelve samples in the normal Microtox Screening Procedure. The four dilutions should bracket the expected EC50 concentration of the standard solution.

During each run, one of the twelve sample positions is occupied by the standard solution at the EC50 concentration. If the relative toxicity of the standard sample is outside the range of 45-55%, the run is rejected and repeated with freshly made standard solution. If the EC50 on the repeat agains falls outside the range of 45-55%, the calibration is repeated. If the calibrated EC50 is significantly higher than the previous calibrations on that box of reagent, then a new box of reagent is opened and the calibration Screening Procedure is performed on one of the reagents in that box.

Procedure

1) Pipette 10 μL of reagent solution into each cuvette in the following order: A1, B1, C1, A2 through A5, B2 through B5, and C2 through C5.

2) Gently mix each cuvette's contents 20 times with a 500 μL pipette. Mix the cuvettes in the same order in which reagent solution was added.

3) Push in the "HV" and "HV Check" buttons on the front of the Microtox analyzer. The panel on the front should read between -700 and -800.

4) Push in the "HV Check" button (so it toggles back out) and push in the "Sensitivity X10" and "Run" buttons.

5) Turn on the strip chart recorder.

6) Zero the chart recorder using the knob located on the right side of the machine.

7) Make sure the speed setting is for 1 inch per minute.

8) Make sure the pen is touching the recorder paper by putting the pen arm down.

9) Place the cuvette in A1 into the turret and close the turret to get a reading on A1.

10) After the reading is obtained, remove the cuvette from the turret.

11) "Read" the cuvettes in B1 and C1 also to determine which of the three has the largest reading. Place that cuvette back in the turret and close.

12) Adjust the chart reading to between 90 and 100 using the Scan knob on the front of the Analyzer. If display reads "1" (not "001"), change the sensitivity setting to "Sensitivity X1".

13) Open the turret and check the zero point again on the chart recorder. Adjust as necessary.

14) Close the turret.

15) Set the timer for 5 minutes.

16) When the timer rings, read the samples in the following order: A1, B1, C1, A1 through A5, B1 through B5, C1 through C5, A1, B1, and C1.

17) Place the control cuvette (A1, B1 or C1) which has the highest reading in the turret and close.

18) Set the timer for 10 minutes.

19) When the timer rings, read the samples in the following order: A1, B1, C1, A1 through A5, B1 through B5, C1 through C5, A1, B1 and C1.

20) Place the control cuvette(A1, B1, or C1) which has the highest reading in the turret and close.

21) Set the timer for 10 minutes.

22) When the timer rings, read the samples in the following order: A1, B1, C1, A1 through A5, B1through B5, C1 through C5, A1, B1 and C1.

23) Shut off the chart recorder and cap the pen.

24) Return the C1 cuvette to the Incubator and close the turret.

25) Push in the "HV" and "Turret" buttons on the front of the Analyzer (toggle them off).

Demonstration of Statistical Control

Please refer to A. Ayyoubi, “Physical Treatment of Urban Stormwater Runoff Toxicants”, pg. 11-23.

Calculations

At each of the three times that a sample is read, each of the three control samples is read three times. The results of these nine analyses are averaged and have a standard deviation and coefficient of variation calculated. If the coefficient of variation for the control samples at any time in the run is greater than 0.05, the run is rejected.

Relative toxicity is calculated as follows:

% Reduction [at time t] = (Control - Sample)/Control x 100
where: Control = average peak height of the control samples at t
Sample = peak height of sample at t

This completes a Microtox Analysis run. The spreadsheet that is used for data analysis is named "TOXDEMO.XLS".

Assignment of Uncertainty

to be developed

References

How to Run a Standard Microtox Test. Microbics Corporation, Carlsbad, CA. 1988.

Microtox 100% Screening Procedure (Handout). Microbics Corporation, Carlsbad, CA. 1990.

Ayyoubi, A. “Physical Treatment of Urban Stormwater Runoff Toxicants”, Master’s Thesis, University of Alabama at Birmingham, Birmingham, AL., 1993.

Attachment 5

Particle Size Analysis

Standard Operating Procedure

Scope

Parameters Measured

This method determines the number and size of particles suspended in a conductive liquid.

Range

This method is designed to provide accurate particle size distribution curves,within a 30:1 dynamic range by diameter, or a 27000:1 range by volume, from any one apeture. Size distributions from 0.4 µm to 1200 µm depending on the orifice tube apeture size (upper limit dictated by particle density and electrolyte viscosity, the lower limit by environmental conditions). Applicable apeture sizes are: 20, 100, 140, and 200 µm. Apeture sizes larger than 200 µm or smaller than 20 µm require special procedures not covered in this method. Each apeture allows the measurement of particles in the nominal diameter range of 2 to 60% of the apeture diameter.

Matrix

The sample matrix is urban stormwater.

Expected Accuracy and Precision

Accuracy: ± 0.5%
Precision: < 1.0% RSD

Terminology

A general knowledge of fundamental statistical terminology is sufficient

Summary of Method

This method determines number and size of particles suspended in a conductive liquid by monitoring the electrical current between two electrodes immersed in the conductive liquid on either side of a small apeture, through which a suspension of the particles is forced to flow. As each particle passes through the apeture, it changes the impedance between the electrodes and produces an electrical pulse of short duration having a magnitude essentially proportional to the particle volume. The series of pulses is electronically scaled, counted, and accumulated in a number of size related channels which, when their contents are displayed on an integral visual display, produces a size distribution curve. <u>Only those individuals who have reviewed instrument documentation and have passed a laboratory practicum administered by Dr. Parmer on this instrument are authorized to utilize this method</u>.

Significance and Use

This method is intended to characterize particles and agglomerated state particles in urban stormwater. Since a large fraction of toxic compounds and constituents of interest in surface water are commonly found adsorbed to the surface of particles, it is important and significant to have a characterization method that provides data on volume and diameter of particles that are not spherical. Many particle sizing methods are based on the assumption that counted particles are spherical (most diffraction or forward scattering techniques). When these methods encounter non-spherical particles, a bias is introduced[1]. This technique uses the Electrical Sensing Zone Method which has been utilized and verified for many decades in the medical and health services industries,

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[1] ASTM Annual Book of Standards V 14.02, 1993,

particularly in characterizing particles in parenteral fluids and cell counting and distribution. The British Standards Institution has also published British Standard 3406:Part 5:1983; "Determination of Particle Size Distribution: Recommendations for Electrical Sensing Zone Method (the Coulter Principle)". Copies can be obtained from Sales Office, British Standards Institution, Linford Wood, Milton Keynes, MK14 6LE, telephone:(0908) 221166.

Interferences

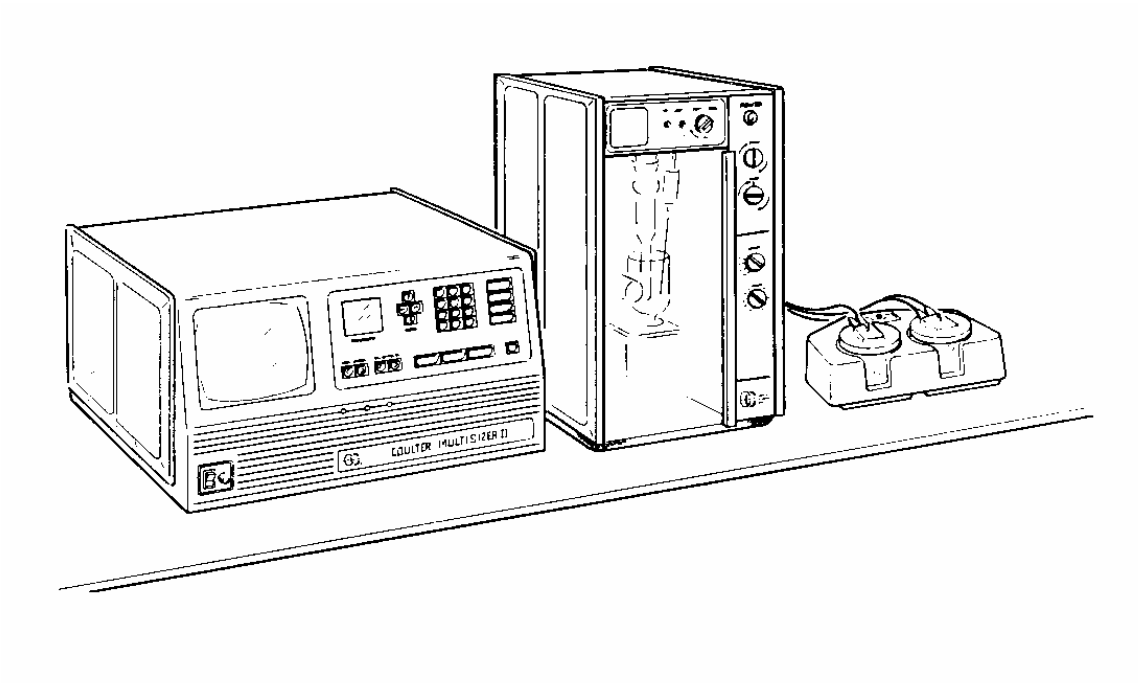
Particles in the diluent inside the aperture tube do not normally generate pulses in the analyzer, since the flow is in one direction only. However, large dense particles may settle at the bottom of the aperture tube. The jet effect of the aperture flow can stir up these settled particles so that some pass through the sensing zone on the inner side of the aperture and cause interference. This effect can be detected by making a blank count, on clean electrolyte, after each hour of use. Periodic flushing with the auxiliary stopcock will eliminate the problem. Inner particle buildup may be indicated by an excessive variation in repeat counts. In extreme cases, remove and clean the aperture tube.

Aperture blockage results in lower than expected counts, no count, or constant sounding of the threshold alarm. If aperture blockage is suspected, inspect the aperture image on the aperture viewing screen. Apertures can be cleaned by back-flushing, brushing, burning, or other methods. Refer to the Coulter Counter Analyzer Reference Manual.

When more than one particle passes through the aperture at the same time, it is called coincidence. Coincidence is detected by the Multisizer II by the unique properties of coincident signals and reports the level of coincidence as a measurement is being made. Coincidence levels of 5-10% are normal. The Multisizer II reports coincidence level, raw count and coincidence corrected count as part of the size distribution report. If coincidence levels are too high, the sample must be diluted. If there is no coincidence, then the sample is not concentrated enough and a larger aliquot of sample must be diluted.

Apparatus

The Multisizer II comprises a sampling stand, with its associated Vacuum Control Unit and the main electronics unit, which has a provision for connecting an optional X/Y plotter, Data Terminal and Video Printer, allowing hard copy to be made of any display and associated data. Any data terminal capable of receiving RS-232 signals will allow for ASCII text and numerical data to be transferred from the Multisizer to the data terminal. This method utilizes Accucomp® software from Coulter Electronics, Inc. to capture data from the Multisizer II and to prepare, print, and store reports and data analysis. An IBM compatible data terminal running Windows® is required for this software.



Coulter Multisizer II with Sample Stand and Vacuum Unit

Other apparatus required include:

Orifice tubes in 20 to 200.µm apertures.

Beakers ranging in size from 10 mL to 2 L are convenient, but only a 100 mL beaker is required in addition to the sample stand beaker.

1, 2, and 5 mL pipettes are required, or some device capable of delivering these volumes with high precision and accuracy.

Standard sieves are convenient, but not necessary unless interferences from large, dense particles are anticipated.

Reagents and Materials

Coulter ISOTON® II solution (Available from Curtin Matheson Scientific) or a filtered isotonic sodium chloride solution.

A range of polystyrene-divinylbenzene Latex® reference particles are available from Coulter. Table 1 indicates suitable calibration particles for particular orifice tubes.

Standard Orifice Tube Data

Aperture Nominal Diameter (µm)	Nominal Particle Size Range (µm)	Suitable Calibration Particles (µm)
20	0.5-12.0	2.0-3.0
30	0.6-18.0	3.0-6.0
50	1.0-30.0	3.0-10
70	1.4-42.0	5.0-15
100	2.0-60.0	10-20
140	2.8-84.0	15-40
200	4.0-120.0	20-40

Hazards and Precautions

Electrical

The instrument must be sited on a firm dry work bench, connected to 120 VAC power, and must be grounded correctly.

Main voltages and d.c. voltages exceeding 50 V are used internally. The instrument must be removed from mains before removing any cover. Refer all servicing to trained personnel.

Mechanical

Take care when handling glassware; it is fragile and if broken could cause injury.

Chemical

Mercury is used in an internal manometer to accurately regulate sample flow through the apeture. Mercury is poisonous in liquid or vapor form, as are its compounds. It is extremely mobile. Contact with human skin must be avoided. Remove spilt mercury with a proprietary mercury absorbent, contained in the spill kit. Contact Dr. Parmer in the event of any mercury spill.

Before mixing electrolyte solutions consider any possible risk.

Fire

If the instrument starts to smoke or smell, indicating a fault causing overheating, immediately switch the instrument off and disconnect from main power supply and contact Dr. Parmer.

Environment

The laboratory should be smoke free and have minimum dust.

The instrument should be operated within ambient temperature range 10 to 32°C.

Protect the electrolyte solution from airborne dust. ISOTON II diluent supplied by Coulter Electronics, Inc. (through Curtin Matheson Scientific) is essentially particle-free; other electrolyte solutions must be filtered before use to exclude particles greater than 0.5% of diameter of the aperture being used.

Sampling, Sample Preparation

A representative sample of the solution to be characterized should be obtained and placed in a polyethylene or glass container and stored at 4°C until measurement.

1, 2, or 5 mL aliquots of the sample are diluted to 100 mL with ISOTON® II solution prior to analysis.

It is important to consider that the Coulter Counter® instrument will give a size analysis of the particulate material presented to the orifice. If the material is presented as an agglomeration or flocculated form, then an untrue size analysis will result for individual particles. (In some instances however, it is important to count the particles in an agglomerated state and dispersion to the ultimate particle size is then undesirable.)

Preparation of Apparatus

Warm up time

For optimum accuracy, it is recommended that a period of 10 minutes is allowed between switching on the Multisizer II and making first measurements.

Preparation

It is advised that several preliminary measurements are performed on the Multisizer II with a sample representative of the system to be studied. For most accurate work, sample concentration should be below that at which significant coincidence occurs, preferably at approximately the 5% coincidence level. To prepare the Multisizer II for an analysis, the following procedures must be carried out.

(1) select a suitable orifice tube so that most of the particles lie within its measurement range.

(2) choose an appropriate electrolyte solution. Establish that its “background count” is acceptably low

Background and Maximum Cumulative Counts for Multisizer II Orifice Tubes

Nominal Aperture Diameter	Nominal Particle Diameter Range	Cumulative Background Count Larger than 2% of Aperture Diameter	Counts per second for 5% Aperture Coincidence	Max. Cumulative Count for 5% Aperture Coincidence
20	0.5-12.0	800 @ 0.5 µm per 0.05 mL	7800	250,000 per 0.05 mL
30	0.6-18.0	500 @ 0.6 µm per 0.05 mL	4500	68,000 per 0.05 mL
50	1.0-30.0	250 @ 1.0 µm per 0.05 mL	3100	17,000 per 0.05 mL
70	1.4-42.0	1200 @1.4 µm per 0.5 mL	2120	58,300 per 0.5 mL
100	2.0-60.0	400 @ 2.0 µm per 0.5 mL	1600	20,000 per 0.5 mL
140	2.8-84.0	600 @ 2.8 µm per 2.0 mL	1175	7,285 per 0.5 mL
200	4.0-120.0	200 @ 4.0 µm per 2.0 mL	800	10,000 per 2.0 mL

Set Up Procedure - Automatic Mode

(1) Set the power switches of the Multisizer II and associated Sampling Stand to on, then switch on any required accessories. The "Multisizer II Setup" menu is displayed.

(2) Enter the date, using the numeric keypad.

(3) Using the MENU cursor keys, step down the menu and enter the information as follows:

Orifice size, diameter/length Enter via the key pad, the diameter of the orifice tube fitted to the sampling stand. The corresponding apeture length and calibration constant "**Kd**" applicable to the orifice tube is stored in memory.

(4) Press "**CAL**" key: The stored value of **Kd**, applicable to the tube size entered, is then displayed.

(5) Press "**SET UP**" key, and repeat as necessary, to check that all entries and selections on "Analysis Setup -1" and "Analysis Setup - 2" pages are as required. For detailed information on each of these entries please refer to the Operator's Manual.

(6) Press "**SET UP**"key to display "Multisizer II SET UP" menu, return setting for "**SET UP**" to "**AUTOMATIC**"

(7) Fill the Sample Stand beaker with enough blank electrolyte (ISOTON®II) to cover apeture and Pt electrode.

(8) Ensure that the **RESET/COUNT** switch on the Sampling Stand is set to **RESET**.

(9) Press **FULL** key on Multisizer II. The status message "**Current and Gain Auto-Set in Progress**" is displayed at the bottom of the screen when this selection is made. The message remains whilst the current and gain settings are recalculated.

Calibration and Standardization

Calibration is required only when a new tube is purchased, or an electrolyte other than ISOTON II is used. The only calibration constant is **Kd**, which is stored permanently in memory. In normal operation calibration is not required. If a new tube is purchased or a different electrolyte is used, then significant method development must be accomplished and this method is not appropriate. All instrument parameters for this method are stored in the Multisizer II and should not be altered without consultation with Drs. Parmer or Pitt.

Procedure

(1) With the required options selected on the "**Full Range**" menu and the preparation procedure completed, press "**RESET**" if any existing data is accumulated in the Full Range mode is to be deleted. Any data not deleted will be added to the results of the new measurement.

(2) Pipette 1.0 mL of sample into a 100 mL beaker and add 99.0 mL of ISOTON II.

(3) Place the sample to be analyzed on the beaker platform of the Sampling Stand. Adjust the height of the platform, as necessary, to immerse the aperture in the sample.

(4) Set "**RESET/COUNT**" on the Sampling Stand to **RESET**.

(5) Press "**START**" key on Multisizer II. The Multisizer will "beep" when measurement is completed and display the distribution of particle sizes on the Multisizer II screen.

(6) Insure that the Accucomp for Windows software is running on the PC connected to the Multisizer II.

(7) Input file name and sample descriptors of interest on the acquire menu of the Accucomp software and press the acquire file button on the screen, the Accucomp software will then wait for a file to be sent from the Multisizer II.

(8) Press "**PRINT**" button on Multisizer II. The file will be transferred to the PC and the PC will print out a hard copy of the report for the sample. A copy of the file is also stored on the PC's hard drive.

Demonstration of Statistical Control

Since the calibration of these tubes does not change significantly with time, the only technique to assure statistically sound measurements is the absence of raggedness in consecutive channels. A smooth distribution is obtained with approximately 100,000 counts in 64 channels and 700,000 in 128-256 channels occur. This method utilizes a 30 second counting period. Previous experience with urban runoff samples has indicated that when 1 mL is diluted to 100 mL, sufficient counts are obtained to insure a smooth distribution. If a distribution exhibits raggedness (usually for the largest particle sizes in the sample), generally there are not enough counts per channel to insure smoothness. In this case additional sample is required and a 2 or 5 mL aliquot may be used instead of a 1 mL aliquot.

Calculations

All calculations are performed by Accucomp software available from Coulter Electronics, Ltd. For specific details of calculation please refer to the Accucomp software manual[2].

A listing of all pertinent instrument parameters is printed with each report as well as:

A graph of the volume per mL vs. particle diameter (cumulative and individual channel count)

A graph of the surface area per mL vs particle diameter (cumulative and channel count)

Number statistics, including mean, median, mean/median ratio, mode, specific surface area, 95% confidence limits, standard deviation, variance, coefficient of variation, skewness, and kurtosis

Volume statistics, including mean, median, mean/median ratio, mode, specific surface area, 95% confidence limits, standard deviation, variance, coefficient of variation, skewness, and kurtosis

Surface area statistics including mean, median, mean/median ratio, mode, specific surface area, 95% confidence limits, standard deviation, variance, coefficient of variation, skewness, and kurtosis

Particle diameters are listed as differential number %, differential volume %, differential volume per mL, differential number per mL, and differential surface area per mL. A typical report is 3 pages of 8.5 x 11 inch paper per sample.

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[2] Coulter Multisizer AccuComp Color Software Reference Manual, Part # 4235890 (January 1989), Coulter Electronics, Inc.

The data is also stored on magnetic media for archive and re-evaluation as needed.

Assignment of Uncertainty

The major causes of error in this method are due to a low particle count, high coincidence, or occlusion of the orifice.

Low particle counts are easily remedied by increasing sample concentration.

High coincidence is remedied by decreasing sample concentration.

Occlusion of the orifice is easily detected by inspection of the aperture screen.

References

ASTM Annual Book of Standards V 14.02, Calibration of Particle Size Measuring Devices, 1993

Coulter Multisizer AccuComp Color Software Reference Manual, Part # 4235890 (January 1989), Coulter Electronics, Inc.

Coulter Multisizer II Operator's Manual

Coulter Multisizer II Fine Particle Applications Notes

Coulter Multisizer II Reference Manual

British Standard 3406:Part 5:1983; "Determination of Particle Size Distribution: Recommendations for Electrical Sensing Zone Method (the Coulter Principle)".

Attachment 6

COLOR

EPA Method 110.3 (Spectrophotometric)

Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. It must be used for industrial wastes that cannot be determined by the Platinum Cobalt method.

Summary ofMethod

2.1 Color characteristics are measured at pH 7.6 and at the original pH by obtaining the visible absorption spectrum of the sample on a spectrophotometer. The percent transmission at certain selected wavelengths is used to calculate the results.

2.2 The results are expressed in terms of dominant wavelength, hue, luminance, and purity.

Interferences

3.1 Since very slight amounts of turbidity interfere with the determination, samples must be filtered before analysis.

Sample Handling and Preservation

4.1 Since biological activity may change the color characteristics of a sample, the determination should be made as soon as possible. Refrigeration at 4°C is recommended.

Reference

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 17th Edition, p. 66, Method 204B (1975).

Attachment 7

CONDUCTANCE

EPA Method 120.1 (Specific Conductance, μmhos/cm at 25°C)

Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition).

Summary of Method

2.1 The specific conductance of a sample is measured by use of a self- contained conductivity meter, Wheatstone bridge -type, or equivalent.

2.2 Samples are preferable analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C.

Comments

3.1 Instrument must be standardized with KCl solution before daily use.

3.2 Conductivity cell must be kept clean.

3.3 Field measurements with comparable instruments are reliable.

3.4 Temperature variations and corrections represent the largest source of potential error.

Sample Handling and Preservation

4.1 Analyses can be performed either in the field or laboratory.

4.2 If analysis is not completed within 24 hours of sample collection, sample should be filtered through a 0.45-micron filter and stored at 4°C. Filter and apparatus must be washed with high quality distilled water and pre-rinsed with sample before use.

Apparatus

5.1 Conductivity bridge, range 1 to 1000 μmho per centimeter.

5.2 Conductivity cell, cell constant 1.0, or micro dipping type cell with 1.0 constant.

5.3 YSI#3403 or equivalent.

5.4 Thermometer

Reagents

6. 1 Standard potassium chloride solutions, 0.01 M: Dissolve 0.7406 gm of pre-dried (2 hour at 105°C) KCl in distilled water and dilute to 1 liter at 25°C.

Cell Calibration

7.1 The analyst should use the standard potassium chloride solution (6.1) and the table below to check the accuracy of the cell constant and conductivity bridge.

Conductivity 0.01 M KCl

°C	Micromhos/cm
21	1305
22	1332
23	1359
24	1386
25	1413
26	1441
27	1468
28	1496

Procedure

8.1 Follow the direction of the manufacturer for the operation of the instrument.

8.2 Allow samples to come to room temperature (23 to27°C), if possible.

8.3 Determine the temperature of samples within 0.5°C. If the temperature of the samples is not 25°C, make temperature correction in accordance with the instruction in Section 9 to convert reading to 25°.

Calculation

9.1 These temperature corrections are based on the standard KCl solution.

9.1.1 If the temperature of the sample is below 25°C, add 2% of the reading per degree.

9.1.2 If the temperature is above 25°C, subtract 2% of the reading per degree.

9.2 Report results as Specific Conductance, µmhos/cm at 25°.

Precision and Accuracy

10.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results:

Increment as Specific Conductance	Precision as Standard Deviation	Accuracy as	
		Bias, %	Bias, µmhos/cm
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2 In a single laboratory (EMSL) using surface water samples with an average conductivity of 536 µmhos/cm at 25°C, the standard deviation was ±6.

Bibliography

1. The procedure to be used for this determination is found in:

Annual Book of ASTM Standards Part 31, "Water," Standard D1125 -64, p. 120 (1976).

2.Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 71, Method 205 (1975).

3. Instruction Manual for YSI Model 31 Conductivity Bridge.

4. Peden, M.E., and Skowron. "Ionic Stability of Precipitation Samples," Atmospheric Environment, Vol. 12, p. 2343 -2344, 1978.

Attachment 8

HARDNESS, Total (mg/l as $CaCO_3$)

EPA Method 130.2 (Titrimetric, EDTA)

Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25 mg $CaCO_3$.

1.3 Automated titration may be used.

Summary of Method

2.1 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction is detected by means of Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are squestered.

Sample Handling and Preservation

3.1 Cool to 4°C, HNO_3 to pH <2.

Comments

4.1 Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide.

4.1.1 Routine addition of sodium cyanide solution (Caution: deadly poison) to prevent potential metallic interference is recommended.

Apparatus

5.1 Standard laboratory titrimetric equipment.

Reagents

6.1 Buffer solution

6.1.1 If magnesium EDTA is available: Dissolve; 16.9 g NH,Cl in 143 ml conc. NH_40H in a 250 m1 volumetric, add 1.25 g of magnesium salt of EDTA and dilute to the mark with distilled water. Then go to 6. 1 .3.

6.1.2 If magnesium EDTA is unavailable: Dissolve 1.119 g disodium EDTA (analytical reagent grade) and 780 mg $MgSO_4$ $7H_2O$ (or 644 mg $MgCl_26H_2O$) in 50 ml distilled water. Add this solution to a 250 ml volumetric flask containing 16.9 g NH_4Cl and 143 ml conc. NH_4OH with mixing and dilute to the mark with distilled water.

6.1.3 Store in a tightly stoppered plastic bottle; stable for approximately one month. Dispense with bulb operated pipette. Discard when 1 or 2 m1 added to sample fails to produce a pH of 10.0 ± 0.1 at endpoint of titration.

6.1.4 Commercially available "odorless buffers" which are more stable, may be used.

6.2 Inhibitors: For most waters inhibitors are not necessary. If interfering ions are present use one of the following:

6.2.1 Inhibitor I: NaCN powder. (Caution: extremely poisonous). Flush solutions or sample containing this down drain using large quantities of water. Make sure no acids are present which might liberate HCN gas.

6.2.2 Inhibitor II: Dissolve 5.0 g Na_2S_9 H_2O or 3.7 g Na_2S $5H_2O$ in 100 ml distilled water. Exclude air with tightly fitted rubber stopper. This gives sulfide precipitates which may obscure the end point if large quantities of heavy metals are present. Deteriorates rapidly through air oxidation.

6.2.3 Inhibitor III: Dissolve 4.5 g hydroxylamine hydrochloride in 100 ml of 95% ethanol or isopropanol.

6.3 Indicator: Use a commercially available indicator such as Calmagite indicator (Mallinckrodt) or one of the formulations described below (6. 3. 1 A. 3. 3)

6.3. 1 Mix 0.5 g Eriochrome Black T with 4.5 g hydroxylamine hydrochloride. Dissolve in 100 m1 of 95% ethanol or isopropanol.

6.3.2 Dissolve 0.5 to 1.0 g Eriochrome Black T in an appropriate solvent such as triethanolamine or 2-methoxyethanol. Stable approximately one week.

6.3.3 Mix together 0.5 g Eriochrome Black T and 100 g NaC1.

6.4 Standard EDTA titrant, 0.02N: Place 3.723 g analytical reagent grade disodium ethylenediamine tetraacetate dihydrate, Na2H2C10H1208N_2 $2H_20$ in a 1 liter volumetric flask and dilute to the mark with distilled water. Check with standard calcium solution (6.4.1) by titration (6.4.5). Store in polyethylene. Check periodically because of gradual deterioration.

6.4.1 Standard calcium solution 0.02 N: Place 1.000 g anhydrous calcium carbonate (primary standard low in metals) in a 500 ml flask. Add, a little at a time, 1 + 1 HCL (6.4.2) until all of the $CaCO_3$ has dissolved. Add 200 ml distilled water. Boil for a few minutes to expel CO_2. Cool. Add a few drops of methyl red indicator (6.4.3) and adjust to intermediate orange color by adding 3N NH_40H (6.4.4) or 1 + 1 HCl (6.4.2) as required. Quantitatively transfer to a 1 liter volumetric flask and dilute to mark with distilled water.

6.4.2 Hydrochloric acid solution, 1 + 1.

6.4.3 Methyl red indicator: Dissolve 0.10 g methyl red in distilled water in a 100 ml volumetric flask and dilute to the mark.

6.4.4 Ammonium hydroxide solution, 3 N: Dilute 210 ml of conc. NH_4OH to 1 liter with distilled water.

6.4.5 Standardization titration procedure: Place 10.0 ml standard calcium solution (6.4.1) in vessel containing about 50 ml distilled water. Add 1 ml buffer solution (6. 1). Add 1-2 drops indicator (6.3) or small scoop of dry indicator (6.3.3). Titrate slowly with continuous stirring until the last reddish tinge disappears; adding last few drops at 3 -5 second intervals. At end point the color is blue. Total titration duration should be 5 minutes from the time of buffer addition.

N of EDTA= 0.2/ml of EDTA

6.5 Ammonium Hydroxide, lN: Dilute 70 ml of conc. NH_4OH to 1 liter with distilled water.

Procedure

7.1 Pretreatment

7.1.1 For drinking waters, surface waters, saline waters, and dilution thereof, no pretreatment steps are necessary. Proceed to 7.2.

7.1.2 For most wastewaters, and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual. Following this digestion, proceed to 7.2.

7.1.2 Titration of sample- normal to high hardness:

7.2.1 Sample should require' <15 ml EDTA titrant (6.4) and titration should be completed within 5 minutes of buffer addition.

7.2.2 Place 25.0 m1 sample in titration vessels, neutralize with 1 N ammonium hydroxide (6. 5) and dilute to about 50 m1.

7.2.3 Add 1 to 2 ml buffer solution (6.1).

7.2.4 If end point is not sharp (as determined by practice run) add inhibitor at this point (see 7.4).

7.2.5 Add 1 to 2 drops indicator solution (6.3. 1 or 6.3.2) or small scoop of dried powder indicator formulation (6.3.3).

7.2.6 Titrate slowly with continuous stirring with standard EDTA titrant (6.4) until last reddish tint disappears. Solution is normally blue at end point.

7.3 Titration of sample-low hardness (less than 5 mg/1)

7.3.1 Use a larger sample (100 ml)

7.3.2 Use proportionately larger amounts of buffer, inhibitor and indicator.

7.3.3 Use a micro-burette and run a blank using re-distilled, distilled or de-ionized water.

7.4 To correct for interferences:

7.4.1 Some metal ions interfere by causing fading or indistinct end points. Inhibitors reduce this in accord with the scheme below for 25.0 ml samples diluted to 50 ml.

Maximum Concentrations of Interferences Permissible with Various Inhibitors[a]

Interfering Substance	Maximum Interference Concentration mg/L		
	Inhibitor I	Inhibitor II	Inhibitor III
Aluminum	20	20	20
Barium	b	b	b
Cadmium	b	20	b
Cobalt	over 20	0.3	0[c]
Iron	over 30	5	20
Lead	b	20	b
Manganese	b	1	1
Nickel	over 20	0.3	0[c]
Strontium	b	b	b
Zinc	b	200	b
Polyphosphate		10	

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[a] based on 25-ml sample diluted to 50 ml.

[b] titrates as hardness.

[i]nhibitor fails if substance is present.

7.4.2 Inhibitor I: At step 1.2.4 add 250 mg NaCN. Add sufficient buffer to achieve pH 10.0 ± 0.1 to offset alkalinity resulting from hydrolysis of sodium cyanide.

7.4.3 Inhibitor II: At step 7.2.4 add 1 ml of inhibitor II (6.2.2)

7.4.4 Inhibitor III: At step 1.2.4 add 1 m 1 of inhibitor III (6.2.3).

Calculations

Hardness (EDTA) as mg $CaCO_3$/L = A x N x 50,000/ml sample

where:

A = ml EDTA titrant (6.4)

N = normality of EDTA titrant.

Precision and Accuracy

9.1 Forty-three analysts in nineteen laboratories analyzed six synthetic water samples containing exact increments of calcium and magnesium salts, with the following results:

Increment as Total Hardness mg/L, $CaCO_3$	Precision as Standard Deviation mg/L, $CaCO_3$	Accuracy as	
		Bias, %	Bias, mg/L, $CaCO_3$
31	2.87	-0.87	-0.003
33	2.52	-0.73	-0.24
182	4.87	-0.19	-0.4
194	2.98	-1.04	-2.0
417	9.65	-3.35	-13.0
444	9.73	-3.23	-14.3

(FWPCA Method Study 1, Mineral and Physical Analyses)

9.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 194 mg $CaCO_3$/L, the standard deviation was ± 3.

9.3 A synthetic unknown sample containing 610 mg/L total hardness as $CaCO_3$ contributed by 108 mg/L Ca and 82 mg/L Mg, and the following supplementary substances: 3.1 mg/L K, 19.9 mg/L Na, 241 mg/L chloride, 0.25 mg/L nitrite N, 1.1 mg/L nitrate N, 259 mg/L sulfate, and 42.5 mg/L total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 56 laboratories by the EDTA titrimetric method with a relative standard deviation of 2.9% and a relative error of 0.8%.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 202, Method 309B (1975).

2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1126-67, p 161, Method B (1976).

Attachment 9

pH

EPA Method 150.1 (Electrometric)

Scope and Application

1. 1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition).

Summary of Method

2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.

Sample Handling and Preservation

3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.

3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.

Interferences

4.1 The glass electrode, in general, is not subject to solution interference from color, turbidity, colloidal matter, oxidants, reductants or high salinity.

4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.

4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (l + 9) may be necessary to remove any remaining film.

4.4 Temperature effects on the electrometric measurement of pH arise from two sources.

The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled it should therefore be noted by reporting both the pH and temperature at the time of analysis.

Apparatus

5.1 pH Meter -laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

5.2 Glass electrode.

5.3 Reference electrode-a calomel, silver-silver chloride or other reference electrode of constant potential may be used.

NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel type filling materials that require minimal maintenance.

5.4 Magnetic stirrer and Teflon-coated stirring bar.

5.5 Thermometer or temperature sensor for automatic compensation.

Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[3] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

Calibration

7.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.

7.2.1 Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.

Procedure

8. 1 Standardize the meter and electrode system as outlined in Section 1.

8.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.

8.2.1 If field measurements are being made the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element as indicated by drift free (< 0.1 pH) readings.

8.3 If the sample temperature differs by more than 2°C from the buffer solution the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer’s instructions.

8.4 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and

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[3] National Bureau of Standards Special Publication 260.

temperature. Repeat measurement on successive volumes of sample until values differ by less than 0. 1 pH units. Two or three volume changes are usually sufficient.

8.5 For acid rain samples it is most important that the magnetic stirrer is not used. Instead, swirl the sample gently for a few seconds after the introduction of the electrode(s). Allow the electrode(s) to equilibrate. The air-water interface should not be disturbed while measurement is being made. If the sample is not in equilibrium with the atmosphere, pH values will change as the dissolved gases are either absorbed or desorbed. Record sample pH and temperature.

Calculation

9.1 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest °C.

Precision and Accuracy

10.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as	
		Bias, %	Bias, pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2 In a single laboratory (EMSL), using surface water samples at an average pH of 1.1, the standard deviation was ±0.1.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).

2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293-65, p 178 (1976).

3. Peden, M. E. and Skowron, L. M., Ionic Stability of Precipitation Samples, Atmospheric Environment, Vol. 12, pp. 2343-2349, 1978.

Attachment 10

RESIDUE, FILTERABLE

EPA Method 160.1 (Gravimetric, Dried at 180°C)

Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The practical range of the determination is 10 mg/L to 20,000 mg/L.

Summary of Method

2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.

2.2 If Residue, Non- Filterable is being determined, the filtrate from that method may be used for Residue, Filterable.

Definitions

3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.

Sample Handling and Preservation

4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.

Interferences

5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.

5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.

5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

Apparatus

6.1 Glass fiber filter discs, 4.7 cm or 2.1 cm, without organic binder, Reeve Angel type 934-AH, Gelman type A/E, or quivalent.

6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.

6.3 Suction flask, 500m1.

6.4 Goochcrucibles, 25ml (if 2.1 cm filter is used).

6.5 Evaporating dishes, porcelain, 100 ml volume. (Vycor or platinum dishes may be substituted).

6.6 Steam bath.

6.7 Drying oven, 180°C ±2°C.

6.8 Desiccator.

6.9 Analytical balance, capable of weighing to 0.1 mg.

Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.

7.2 Preparation of evaporating dishes: If Volatile Residue is also to be measured heat the clean dish to 550 ±50°C for one hour in a muffle furnace. If only Filterable Residue is to be measured heat the clean dish to 180 ± 2°C for one hour. Cool in desicator and store until needed. Weigh immediately before use.

7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 mL to the funnel by means of a 100 mL graduated cylinder. If total filterable residue is low, a larger volume may be filtered.

7.4 Filter the sample through the glass fiber filter, rinse with three 10 mL portions of distilled water and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

7.5 Transfer 100 mL (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

7.6 Dry the evaporated sample for at least one hour at 180 ±2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

Calculation

8. 1 Calculate fllterable residue as follows:

Filterable residue, mg/L = (A - B)x1,000/C

where:

A = weight of dried residue + dish in mg

B = weight of dish in mg

C = volume of sample used in mL

Precision and Accuracy

9. 1 Precision and accuracy are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 92, Method 208B, (1975).

RESIDUE, NON- FILTERABLE

EPA Method 160.2 (Gravimetric, Dried at 103-105°C)

Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The practical range of the determination is 4 mg/L to 20,000 mg/L.

Summary of Method

2. 1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103-105°C.

2.2 The filtrate from this method may be used for Residue; Filterable.

Definitions

3.1 Residue, non -filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103-105°C.

Sample Handling and Preservation

4.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.

4.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.

Interferences

5.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.

5.2 Samples high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter (7.5) minimizes this potential interference.

Apparatus

6.1 Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.

NOTE: Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size", collection efficiencies and effective retention are used to define this property in glass fiber fllters. Values for these parameters vary for the filters listed above.

6.2 Filter support: filtering apparatus with reservoir and a coarse (40-60 microns) fritted disc as a filter support.

NOTE: Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Buchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse frilled disc.

6.3 Suction flask.

6.4 Drying oven, 103-105°C.

6.5 Desiccator.

6.6 Analytical balance, capable of weighing to 0.1 mg.

Procedure

7.1 Preparation of glass fiber filter disc: Place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103-105°C for one hour. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0. 5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only.

7.2 Selection of Sample Volume

For a 4.7 cm diameter filter, filter 100 mL of sample. If weight of captured residue is less than 1.0 mg, the sample volume must be increased to provide at least 1.0 mg of residue. If other filter diameters are used, start with a sample volume equal to 7 ml/cm^2 of filter area and collect at least a weight of residue proportional to the 1.0 mg stated above.

NOTE: If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 minutes, the following scheme is recommended: Use an unweighed glass fiber filter of choice affixed in the filter assembly. Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. Twenty-five mL increments for timing are suggested. Continue to record the time and volume increments until titration rate drops rapidly. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate. Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.

7.3 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the frilled support.

7.4 Shake the sample vigorously and quantitatively transfer the predetermined sample volume selected in 7.2 to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.

7.5 With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

NOTE: Total volume of wash water used should equal approximately 2 ml per cm^2. For a 4.1 cm filter the total volume is 30 mL

7.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103-105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

Calculations

8.1 Calculate non-filterable residue as follows:

Non- filterable residue, mg/L = (A-B)xl000/C

where:

A = weight of filter (or filter and crucible) + residue in mg

B = weight of filter (or filter and crucible) in mg

C = mL of sample filtered

Precision and Accuracy

9. 1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

Bibliography

1. NCASI Technical Bulletin No. 291, March 1977. National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Ave., NY.

RESIDUE, TOTAL

EPA Method 160.3 (Gravimetric, Dried at 103-105°C)

Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The practical range of the determination is from 10mg/L to 20,000 mg/L.

Summary of Method

2.1 A well mixed aliquot of the sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105°C.

Definitions

3.1 Total Residue is defined as the sum of the homogenous suspended and dissolved materials in a sample.

Sample Handling and Preservation

4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.

Interferences

5.1 Non-representative particulate such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.

5.2 Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.

Apparatus

6.1 Evaporating dishes, porcelain, 90mm, l00 mL capacity. (Vycor or platinum dishes may be substituted and smaller size dishes may be used if required .)

Procedure

7.1 Heat the clean evaporating dish to 103-105°C for one hour, if Volatile Residue is to be measured, heat at 550 ± 50°C for one hour in a muffle furnace. Cool, desiccate, weigh and store in desiccator until ready for use.

7.2 Transfer a measured aliquot of sample to the pre-weighed dish and evaporate to dryness on a steam bath or in a drying oven.

7.2.1 Choose an aliquot of sample sufficient to contain a residue of at least 25 mg. To obtain a weighable residue, successive aliquots of sample may be added to the same dish.

7.2.2 If evaporation is performed in a drying oven, the temperature should be lowered to approximately 98°C to prevent boiling and splattering of the sample.

7.3 Dry the evaporated sample for at least 1 hour at 103-105°C. Cool in a desiccator and weigh. Repeat the cycle of drying at 103-105°C, cooling, desiccating and weighing until a constant weight is obtained or until loss of weight is less than 4% of the previous weight, or 0.5 mg, whichever is less.

Calculation

8.1 Calculate total residue as follows:

Total residue, mg/L = $(A - B) \times 1{,}000/C$

where:

A = weight of sample + dish in mg

B = weight of dish in mg

C = volume of sample in mL

Precision and Accuracy

9. 1 Precision and accuracy data are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 91, Method 208A, (1975).

RESIDUE, VOLATILE

EPA Method 160.4 (Gravimetric, Ignition at 550°C)

Scope and Application

1.1 This method determines the weight of solid material combustible at 550°C.

1.2 The test is useful in obtaining a rough approximation of the amount oforganic matter present in the solid fraction of sewage, activated sludge, industrial wastes, or bottom sediments.

Summary of Method

2.1 The residue obtained from the determination of total, filterable or non-filterable residue is ignited at 550°C in a muffle furnace. The loss of weight on ignition is reported as mg/ L volatile residue.

Comments

3.1 The test is subject to many errors due to loss of water of crystal1ization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

3.2 The results should not be considered an accurate measure of organic carbon in the sample, but may be useful for other purposes.

3.3 The principal source of error in the determination is failure to obtain a representative sample.

Sample Handling and Preservation

4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decompostion of solids is recommended.

Precision and Accuracy

5.1 A collaborative study involving three laboratories examining four samples by means of ten replicates showed a standard deviation of ±11 mg/L at 170 mg/L volatile residue concentration.

Reference

6. 1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 95, Method 208E, (1975).

Attachment 11

TURBIDITY

EPA Method 180.1 (Nephelometic)

Scope and Application

1.1 Thismethod is applicable to drinking, surface, and saline waters in the range of turbidity from 0 to 40 nephelometric turbidity units (NTU). Higher values may be obtained with dilution of the sample.

NOTE 1: NTU's are considered comparable to the previously reported Formazin Turbidity Units (FTU) and Jackson Turbidity Units (JTU).

Summary of Method

2.1 The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings, in NTU's, are made in a nephelometer designed according to specifications outlined in Apparatus. A standard suspension of Formazin, prepared under closely defmed conditions, is used to calibrate the instrument.

2.1.1 Formazin polymer is used as the turbidity reference suspension for water because it is more reproducible than other types of standards previously used for turbidity standards.

2.1.2 A commercially available polymer standard is also approved for use for the National Interim Primary Drinking Water Regulations. This standard is identified as AMCO-AEPA-l available from Amco Standard International, Inc.

Sample Handling and Preservation

3.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.

Interferences

4.1 The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles will affect the results in a positive manner.

4.2 The presence of true color, that is the color of water which is due to dissolved substances which absorb light, will cause turbidities to be low, although this effect is generally not significant with finished waters.

Apparatus

5.1 The turbidimeter shall consist ofa nephelometer with light source for illuminating the sample and one or more photoelectric detectors with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. The turbidimeter should be so designed that little stray light reaches the detector in the absence of turbidity and should be free from significant drift after a short warm-up period.

5.2 The sensitivity of the instrument should permit detection of a turbidity difference of 0.02 unit or less in waters having turbidities less than 1 unit. The instrument should measure from 0 to 40 units turbidity. Several ranges will be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities.

5.3 The sample tubes to be used with the available instrument must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched. They must not be handled at all where the light strikes them, but should be provided with sufficient extra length, or with a protective case, so that they may be handled.

5.4 Differences in physical design of turbidimeters will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, the following design criteria should be observed:

5.4.1 Light source: Tungsten lamp operated at a color temperature between 2200-3000°K.

5.4.2 Distance traversed by incident light and scattered light within the sample tube: Total not to exceed 10 cm.

5.4.3 Detector: Centered at 90° to the incident light path and not to exceed ±30° from 90°. The detector, and filter system if used, shall have a spectral peak response between 400 and 600 nm.

5.5 The Hach Turbidimeter, Model 2100 and 2100 A, is in wide use and has been found to be reliable; however, other instruments meeting the above design criteria are acceptable.

Reagents

6.1 Turbidity-free water: Pass distilled water through a 0.45µ pore size membrane filter if such filtered water shows a lower turbidity than the distilled water.

6.2 Stock formazin turbidity suspension:

Solution 1: Dissolve 1.00 g hydrazine sulfate, $(NH_2)_2 \bullet H_2SO_4$, in distilled water and dilute to 100 mL in a volumetric flask.

Solution 2: Dissolve 10.00 g hexamethylenetetramine in distilled water and dilute to 100 mL in a volumetric flask.

In a 100 mL volumetric flask, mix 5.0 ml Solution 1 with 5.0 ml Solution 2. Allow to stand 24 hours at 25 ±3°C, then dilute to the mark and mix.

6.3 Standard formazin turbidity suspension: Dilute 10.00 ml stock turbidity suspension to 100 mL with turbidity-free water. The turbidity of this suspension is defined as 40 units. Dilute portions of the standard turbidity suspension with turbidity -free water as required.

6.3.1 A new stock turbidity suspension should be prepared each month. The standard turbidity suspension and dilute turbidity standards should be prepared weekly by dilution of the stock turbidity suspension.

6.4 The AMCO-AEPA-l standard as supplied requires no preparation or dilution prior to use.

Procedure

7.1 Turbidimeter calibration: The manufacturer's operating instructions should be followed. Measure standards on the turbidimeter covering the range of interest. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration scales. At least one standard should be run in each instrument range to be used. Some instruments permit adjustments of sensitivity so that scale values will correspond to turbidities. Reliance on a manufacturer's solid scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges. If a pre-calibrated scale is not supplied, then calibration curves should be prepared for each range of the instrument.

7.2 Turbidities less than 40 units: Shake the sample to thoroughly disperse the solids. Wait until air bubbles disappear then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

7.3 Turbidities exceeding 40 units: Dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor. For example, if 5 volumes of turbidity-free water were added to 1 volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample was 180 units.

7.3.1 The Hach Turbidimeters, Models 2100 and 2100A, are equipped with 5 separate scales:0-0.2, 0-1.0, 0-100, and 0-1000 NTU. The upper scales are to be used only as indicators of required dilution volumes to reduce readings to less than 40 NTU.

NOTE 2: Comparative work performed in the MDQAR Laboratory indicates a progressive error on sample turbidities in excess of 40 units.

Calculation

8.1 Multiply sample readings by appropriate dilution to obtain final reading.

8.2 Report results as follows:

NTU	Record to Nearest:
0.0- 1.0	0.05
1-10	0.1
10-40	1
40-100	5
100- 400	10
400-1000	50
> 1000	100

Precision and Accuracy

9.1 In a single laboratory (EMSL), using surface water samples at levels of 26, 41, 75 and 180 NTU, the standard deviations were ±0.60, ±0.94, ±1.2 and ±4.7 units, respectively.

9.2 Accuracy data are not available at this time.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D1889 -71, p 223 (.1976).

2. Standard Methods for the Examination of Water and Wastewater, 14th Fdition, p 132, Method 214A, (1975).

Attachment 12

DETERMINATION OF TRACE ELEMENTS BY STABILIZED TEMPERATURE GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

UAB METHOD 200.9

SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of dissolved and total recoverable elements in ground water, surface water, drinking water and wastewater. This method is also applicable to total recoverable elements in sediment, sludge, biological tissues, and solid waste samples.

1.2 Dissolved elements are determined after suitable filtration and acid preservation. Acid digestion procedures are required prior to the determination of total recoverable elements. Appropriate digestion procedures for biological tissues should be utilized prior to sample analysis.

1.3 This method is applicable to the determination of the following elements by stabilized temperature graphite furnace atomic absorption spectrometry (STGFAA).

Metals determined by STGFAA

Element	Chemical Abstract Services Registry Numbers (CASRN)
Cadmium (Cd}	7440-43-9
Chromium (Cr)	7440-47-3
Copper (Cu)	7440-50-8
Lead (Pb)	7439-92-1
Nickel (Ni)	7440-02-0
Zinc (Zn)	7440-66-6

NOTE: Method detection limit and instrumental operating conditions for the applicable elements are listed in Table 2. These are intended as a guide to instrumental detection limits typical of a system optimized for the element employing commercial instrumentation. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

1.4 The sensitivity and limited linear dynamic range (LDR) of GFAA often implies the need to dilute a sample prior to the analysis. The actual magnitude of the dilution as well as the cleanliness of the labware used to perform the dilution can dramatically influence the quality of the analytical results. Therefore, samples types requiring large dilution should be analyzed by an alternative analytical method which has a larger LDR or which is inherently less sensitive than GFAA.

1.5 This method should be used by analysts experienced in the use of GFAA.

SUMMARY OF METHOD

2.1 This method describes the determination of applicable elements by stabilized temperature platform graphite furnace atomic absorption (STPGFAA). In STPGFAA the sample (and the matrix modifier, if required) is first pipetted onto the platform or a device which provides delayed atomization. The sample is then dried at a relatively low temperature (≈120°C) to avoid spattering. Once dried, the sample is normally pretreated in a char or ashing step which is designed to minimize the interference effects caused by the concomitant sample matrix. After the char step the furnace is allowed to cool prior to atomization. The atomization cycle is characterized by rapid heating of the furnace to a temperature where the metal (analyte) is atomized from the pyrolytic graphite surface. The resulting atomic cloud absorbs the element specific atomic emission produced by a hollow cathode lamp (HCL) or a electrodeless discharge lamp (EDL). Because the resulting absorbance usually has a nonspecific component associated with the actual analyte absorbance, an instrumental background correction device is necessary to subtract from the total signal the component which is nonspecific to the analyte. In the absence of interferences, the background corrected absorbance is directly related to the concentration of the analyte. Interferences relating to STPGFAA (Sect. 4) must be recognized and corrected. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the method of standard addition (Sect. 11.5).

DEFINITIONS

3.1 DISSOLVED - Material that will pass through a 0.45-μm membrane filter assembly, prior to sample acidification.

3.2 TOTAL RECOVERABLE - The concentration of analyte determined on an unfiltered sample following treatment with hot dilute mineral acid.

3.3 INSTRUMENT DETECTION LIMIT (IDL) - The concentration equivalent of an analyte signal equal to three times the standard deviation of the calibration blank signal at the selected absorbance line.

3.4 METHOD DETECTION LIMIT (MDL) - The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.5 LINEAR DYNAMIC RANGE (LDR) - The concentration range over which the analytical working curve remains linear.

3.6 LABORATORY REAGENT BLANK (LRB) - An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, and reagents that are used with samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.

3.7 CALIBRATION BLANK - A volume of ASTM type I water acidified such that the acid(s) concentration is identical to the acid(s) concentration associated with the calibration standards.

3.8 STOCK STANDARD SOLUTION - A concentrated solution containing one analyte prepared in the laboratory using an assayed reference compound or purchased from a reputable commercial source.

3.9 CALIBRATION STANDARD (CAL) - A solution prepared from the stock standard solution which is used to calibrate the instrument response with respect to analyte concentration.

3.10 LABORATORY FORTIFIED BLANK (LFB) - An aliquot of reagent water to which a known quantity of each method analyte is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the method is within accepted control limits.

3.11 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) - An aliquot of an environmental sample to which a known quantity of each method analyte is added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.12 QUALITY CONTROL SAMPLE (QCS) - A solution containing a known concentration of each method analyte derived from externally prepared test materials. The QCS is obtained from a source external to the laboratory and is used to check laboratory performance.

3.13 MATRIX MODIFIER - A substance added to the graphite furnace along with the sample in order to minimize the interference effects by selective volatilization of either analyte or matrix components.

INTERFERENCES

4.1 Several interference sources may cause inaccuracies in the determination of trace elements by GFAA. These interferences can be classified into three major subdivisions, namely spectral, nonspectral and memory.

4.1.1 Spectral Interferences resulting from the absorbance of light by a molecule and/or an atom which is not the analyte of interest. Spectral interferences caused by an element only occur if there is a spectral overlap between the wavelength of the interfering element and the analyte of interest. Fortunately, this type of interference is relatively uncommon in STPGFAA because of the narrow atomic line widths associated with STPGFAA. In addition, the use of appropriate furnace temperature programs and high spectral purity lamps as light sources can minimize the possibility of this type of interference. However, molecular absorbances can span over several hundred nanometers producing broadband spectral interferences. This type of interference is far more common in STPGFAA. The use of matrix modifiers, selective volatilization and background correctors are all attempts to eliminate unwanted non- specific absorbance. The non-specific component of the total absorbance can vary considerably from sample type to sample type. Therefore, the effectiveness of a particular background correction device may vary depending on the actual analyte wavelength used as well as the nature and magnitude of the interference.

Spectral interferences are also caused by the emission from black body radiation produced during the atomization furnace cycle. This black body emission reaches the photomultiplier tube producing erroneous results. The magnitude of this interference can be minimized by proper furnace tube alignment and monochromator design. In addition, atomization temperatures which adequately volatilize the analyte of interest without producing unnecessary black body radiation can help reduce unwanted background emission produced during atomization.

Note: A spectral interference may be manifested by extremely high backgrounds (1.0 abs[*]) which may exceed the capability of the background corrector and/or it may be manifested as a non-

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[*] This background level is given as a guide and is not intended to serve as an absolute value which may be applied in all situations

analyte element which may cause a direct spectral overlap with the analyte of interest. If a spectral interference is suspected, the analyst is advised to:

1. Dilute the sample if the analyte absorbance is large enough to sacrifice some of the sensitivity. This dilution may dramatically reduce a molecular background or reduce it to the point where the background correction device is capable of adequately removing the remaining nonspecific component. If the non-specific component is produced by a spectral overlap with an interfering element, the change in absorbance caused by dilution of the sample should decrease in a linear fashion, provided the undiluted and diluted sample are both within the linear range of the interfering element.

2. If dilution is not acceptable because of the relatively low analyte absorbance readings or the dilution produces a linear decrease in the nonspecific absorbance, the analyst is advised to investigate another analyte wavelength which may eliminate the suspected spectral interference(s).

3. If dilution and alternative spectral lines are not acceptable, the analyst is advised to attempt to selectively volatilize the analyte or the nonspecific component thereby eliminating the unwanted interference(s) by atomizing the analyte in an interference-free environment.

4. If none of the above advice is applicable and the spectral interference persists, an alternative analytical method which is not based on the same type of physical / chemical principle may be necessary to evaluate the actual analyte concentration.

4.1.2 Non-spectral -Interferences caused by sample components which inhibit the formation of free atomic analyte atoms during the atomization cycle. The use of a delayed atomization device which provides stabilized temperatures is required, because these devices provide an environment which is more conducive to the formation of free analyte atoms and thereby minimize this type of interference. This type of interference can be detected by analyzing a sample plus a laboratory fortified sample matrix early within any analysis set. From this data, immediately calculate the percent recovery (Sect. 1 0. 4. 2). If the percent recovery is out side the laboratory determined control limits (Sect. 10.3.3) a potential problem should be suspected. If the result indicates a potential matrix effect, the analyst is advised to:

1. Perform the method of standard additions (see Sect. 11.5); if the "percent recovery" from the method of standard addition is drastically different from the percent recovery from LFM, then lab contamination or another lab related problem should be suspected and corrected.

NOTE: If contamination is suspected, analyze the LFB and calculate a percent recovery.

2. If the two recoveries are approximately equal and the response from the standard addition is dramatically different than that which would be calculated from the calibration curve, the sample should be suspected of a matrix induced interference and analyzed by the method of standard addition (Sect. 11.5).

The limitations listed in Sect. 11.5 must be met in order to apply these recommendations.

4.1.3 Memory interferences resulting from analyzing a sample containing a high concentration of an element (typically a high atomization temperature element) which cannot be removed quantitatively in one complete set of furnace steps. The analyte which remains in the furnace can produce false positive signals on subsequent sample(s). Therefore, the analyst should establish the analyte concentration which can be injected into the furnace and adequately removed in one complete set of furnace cycles. This concentration represents the maximum concentration of analyte within a sample which will not cause a memory interference on the subsequent sample(s). If this concentration is exceeded, the sample should be diluted and a blank should be analyzed (to assure the memory affect has been eliminated) before reanalyzing the diluted sample.

Note: Multiple clean out furnace cycles may be necessary in order to fully utilize the LDR for certain elements.

4.1.4 Specific Element Interferences

Cadmium: The HCl present from the digestion procedure can influence the sensitivity for Cd. A 1% HCl solution with Pd used as a modifier results in a 70% loss in sensitivity relative to the analyte in a 1% HNO_3 solution. The use of Pd/Mg/H as a modifier reduces this suppression to less than 10%.

Copper: Pd lines at 324.27 nm and 325.16 nm may produce an interference on the Cu line at 324.8 nm[5].

Lead: The HCl present from the digestion procedure can influence the sensitivity for Pb. A 1% HCl solution with Pd used as a modifier results in a 70% loss in sensitivity relative to the analyte response in a 1% HNO_3 solution. The use of Pd/MS/H2 as a modifier reduces this suppression to less than 10%.

SAFETY

5.1 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as 1ow as reasonably achievable. Each 1aboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method[1,2]. A reference fi1e of material data handling sheets is available to all personnel involved in the chemical analysis.

5.2 The graphite tube during atomization emits intense UV radiation. Suitable precautions should be taken to protect personnel from this hazard.

5.3 The use of argon/hydrogen gas mixture during the dry and char steps may evolve a considerable amount of HCl gas. Therefore, adequate ventilation is required.

APPARATUS AND EQUIPMENT

6.1 GRAPHITE FURNACE ATOMIC ABSORBANCE SPECTROPHOTOMETER

6.1.1 The GFAA spectrometer must be capable of programmed heating of the graphite tube and the associated delayed atomization device. The instrument should be equipped with an adequate background correction device capable of removing undesirable non-specific absorbance over the spectral region of interest. The capability to record relatively fast (< 1 see) transient signals and evaluate data on a peak area basis is preferred. In addition, a recirculating refrigeration bath is recommended for improved reproducibility of furnace temperatures. The data shown in the tables were obtained using the stabilized temperature platform and Zeeman background correction. This method utilizes Smith-Heiftje background correction.

6.1.2 Single element hollow cathode lamps or single element electrodeless discharge lamps along with the associated power supplies.

6.1.3 Argon gas supply (high-purity grade, 99.99%).

6.1.4 A 5% hydrogen in argon gas mix and the necessary hardware to use this gas mixture during specific furnace cycles.

6.1.5 Autosampler - Although not specifically required, the use of an autosampler is highly recommended.

6.1.6 Microwave digestion apparatus.

6.1.7 Microwave vessels.

6.2 GRAPHITE FURNACE OPERATING CONDITIONS-- A guide to experimental conditions for the applicable elements are shown in Table 2

6.3 SAMPLE PROCESSING EQUIPMENT

6. 3. 1 Balance - Analytical, capable of accurately weighing to 0.1 mg.

6.3.2 Hot Plate - Corning PClOO or equivalent.

6.3.3 Centrifuge - Steel cabinet with guard bowl, electric timer and brake.

6.3.4 Drying Oven capable of ±3°C temperature control.

6.4 LABWARE - The determination of trace level elements requires a consideration of potential sources of contamination and analyte losses. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. **A clean laboratory work area designated for trace element sample handling must be used**. Sample containers can introduce positive and negative errors in the determination of trace elements by contributing contaminants through surface desorption or leaching and/or depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, Teflon, etc. .), including the sample container, should be cleaned prior to use. Labware should be soaked overnight and thoroughly washed with laboratory -grade detergent and water, rinsed with water, and soaked for four hours in a mixture of dilute nitric and hydrochloric acid (1+2+9), followed by rinsing with ASTM type I water and oven drying.

NOTE: Chromic acid must not be used for cleaning glassware.

6.4.1 Glassware - Volumetric flasks and graduated cylinders.

6.4.2 Assorted calibrated pipettes.

6.4.3 Conical Phillips beakers, 250-mL with 50-mm watch glasses. Griffin beakers, 250-mL with 15-mm watch glasses.

6.4.4 Storage bottles - Narrow mouth bottles, Teflon FEP (fluorinated ethylene propylene) with Tefzel ETFE (ethylene tetrafluorethylene) screw closure, 125-mL and 250-mL capacities.

6.4.5 Wash bottle - One piece stem, Teflon FEP bottle with Tefzel ETFE screw closure, 125-mL capacity.

REAGENTS AND CONSUMABLE MATERIALS

7.1 REAGENTS - Reagents may contain elemental impurities which might affect analytical data. Because of the high sensitivity of GFAA, high- purity reagents should be used whenever possible. All acids used for this method must be ultra high- purity grade. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation.

7.1.1 Nitric acid, concentrated (sp. gr. 1.41) (CASRN 169l-37-2).

7.1.2 Nitric acid (1+1) - Add 500 mL conc. nitric acid to 400 mL of ASTM type I water and dilute to 1 L.

7.1.3 Nitric acid (1+9) - Add 100 mL conc. to 400 mL of ASTM type I water and dilute to 1 L.

7.1.4 Hydrochloric acid, concentrated (sp.gr. 1.19) (CASRN 1641-01-0).

7.1.5 Hydrochloric acid (1+4) - Add 200 mL conc. hydrochloric acid to 400 mL ASTM type I water and dilute to 1000 mL.

7.1.6 Tartaric acid. ACS reagent grade (CASRN 87-69-4).

7.1.7 Matrix Modifier, dissolve 300 mg Palladium (Pd) powder in concentrated HNO_3 (l mL of HNO adding 10 mL of concentrated HCl if necessary). Dissolve 200 mg of $Mg(N0_3)_2$ in ASTM type 1 water. Pour the two solutions together and dilute to 100 mL with ASTM type 1 water.

Note: It is recommended that the matrix modifier be analyzed separately in order to assess the contribution of the modifier to the overall laboratory blank.

7.1.8 Ammonium hydroxide, concentrated (sp.gr. 0.902) (CASRN 1336-21-6).

7.2 WATER - For all sample preparation and dilutions, ASTM type I water (ASTM D1193) is required. Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.

7.3 STANDARD STOCK SOLUTION - May be purchased from a reputable commercial source or prepared from ultra high- purity grade chemicals or metal (99.99- 99.999% pure). All salts should be dried for 1 h at 105°C, unless otherwise specified. (CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling). The stock solution should be stored in Teflon bottles. The following procedures may be used for preparing standard stock solutions:

NOTE: Some metals, particularly those which form surface oxides, require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled repeatedly, rinsed with water, dried and weighed until the desired weight is achieved.

7.3.1 Cadmium solution, stock, 1 mL = 1000 µg Cd: Pickle Cd metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.2 Chromium solution, stock, 1 mL = 1000 µg Cr : Dissolve 0.1923g CrO_3 in a solution mixture of 10 mL ASTM type I water and 1 mL conc. nitric acid. Dilute to 100 mL with ASTM type I water.

7.3.3 Copper solution, stock, 1 mL = 1000 µg Cu: Pickle Cu metal in (1+9) nitric acid to an exact weight of 0.100g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.4 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 0.1599g $PbNO_3$ in 5 mL (1+1) nitric acid. Dilute to 100 mL with ASTM type I water.

7.3.5 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 0.100g nickel powder in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7. 3.6 Zinc solution, stock, 1 mL = 1000 µg Zn : Pickle zinc metal in (1+9) nitric acid to an exact weight of 0.100g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.4 PREPARATION OF CALIBRATION STANDARDS - Fresh calibration standards (CAL Solution) should be prepared every two weeks or as needed. Dilute each of the stock standard solutions to levels appropriate to the operating range of the instrument using the appropriate acid diluent (see note). The element concentrations in each CAL solution should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. The instrument calibration should be initially verified using a quality control sample (Sect. 7.6).

NOTE: The appropriate acid diluent for dissolved elements in water samples is 1% HNO_3. For total recoverable elements in waters the appropriate acid diluent is 2% HNO_3 and 1% HCl. Finally, the appropriate acid diluent for total recoverable elements in solid samples is 2% HNO_3 and 2% HCl. The reason for these different diluents is to match the types of acids and the acid concentrations of the samples with the acid present in the standards and blanks.

7.5 BLANKS - Two types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve and the laboratory reagent blank (LRB) is used to assess possible contamination from the sample preparation procedure and to assess spectral background. All diluent acids should be made from concentrated acids (Sects. 7.1.1, 7.1.4) and ASTM type I water.

7.5.1 Calibration blank - Consists of the appropriate acid diluent (Sect. 7.4 note) (HCl/HNO_3) in ASTM type I water.

7.5.2 Laboratory reagent blank (preparation blank) must contain all the reagents in the same volumes as used in processing the samples. The preparation blank must be carried through the entire sample digestion and preparation scheme.

7.6 QUALITY CONTROL SAMPLE - Quality control samples are available from various sources. Dilute (with the appropriate acid (HCl/HNO_3) blank solution) an appropriate aliquot of analyte such that the resulting solution will result in an absorbance of approximately 0.1.

7.7 LABORATORY FORTIFIED BLANK - To an aliquot of laboratory reagent blank, add an aliquot of the stock standard to provide a final concentration which will produce an absorbance of approximately 0.1 for the analyte. The fortified blank must be carried through the entire sample digestion and preparation scheme.

SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1 Prior to sample collection, consideration should be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration, acid preservation etc. should be performed at the time of sample collection or as soon thereafter as practically possible.

8.2 For the determination of dissolved elements, the sample should be filtered through a 0.45-µm membrane filter. Use a portion of the sample to rinse the filter assembly, discard and then collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to a pH of less than two.

8.3 For the determination of total recoverable elements in aqueous samples, acidify wi th (1+1) nitric acid at the time of col1ection to a pH of less than two. The sample should not be filtered prior to analysis.

NOTE: Samples that cannot be acid preserved at the time of collection because of sampling limitations or transport restrictions, should be acidified with nitric acid to pH <2 upon receipt in the laboratory (normally, 3 mL of (1+1) nitric acid per liter of sample is sufficient for most ambient and drinking water samples). Following acidification, the sample should be held for a minimum of 16 h before withdrawing an aliquot for sample processing.

8.4 Solid samples usually require no preservation prior to analysis other than storage at 4°C.

CALIBRATIONAND STANDARDIZATION

9.1 CALIBRATION - Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required periodically throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a calibration check is required at the beginning of each period during which analyses are performed.

9.1.1 Initiate proper operating configuration of instrument and data system. Allow a period of not less than 30 min for the instrument to warm up if an EDL is to be used.

9.1.2 Instrument stability must be demonstrated by analyzing a standard solution of a concentration 20 times the IDL a minimum of five times with the resulting relative standard deviation of absorbance signals less than 5%.

9.1.3 Initial calibration. The instrument must be calibrated for the analyte to be determined using the calibration blank (Sect. 7.5.1) and calibration standards prepared at three or more concentration levels within the linear dynamic range of the analyte.

9.2 INSTRUMENT PERFORMANCE - Check the performance of the instrument and verify the calibration using data gathered from analyses of calibration blanks, calibration standards and the quality control sample.

9.2.1 After the calibration has been established, it must be initially verified for the analyte by analyzing the QCS (Sect. 7.6). If measurements exceed ±10% of the established QCS value, the analysis should be terminated, the source of the problem identified and corrected, the instrument recalibrated, and the new calibration must be verified before continuing analyses.

9.2.2 To verify that the instrument is properly calibrated on a continuing basis, analyze the calibration blank and an intermediate concentration calibration standard as surrogate samples after every ten analyses. The results of the analyses of the standard will indicate whether the calibration remains valid. If the indicated concentration of any analyte deviates from the true concentration by more than 10%, the instrument must be recalibrated and the response of the QCS checked as in Sect. 9.2.1. After the QCS sample has met specifications, the previous ten samples must be reanalyzed in groups of five with an intermediate concentration calibration standard analyzed after every fifth sample. If the intermediate concentration calibration standard is found to deviate by more than 10%, the analyst is instructed to identify the source of instrumental drift.

NOTE: If the sample matrix is responsible for the calibration drift and/or the sample matrix is affecting analyte response, it may be necessary to perform standard additions in order to assess an analyte concentration (Sect. 11.5).

QUALITY CONTROL (QC)

10.1 FORMAL QUALITY CONTROL - The minimum requirements of this QC program consist of an initial demonstration of laboratory capability, and the analysis of laboratory reagent blanks and fortified blanks and samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

10.2 INITIAL DEMONSTRATION OF PERFORMANCE

10.2.1 The initial demonstration of performance is used to characterize instrument performance (MDLs and linear calibration ranges) for analyses conducted by this method.

10.2.2 Method detection limits (MDL) - The method detection limit should be established for the analyte, using reagent water (blank) fortified at a concentration of two to five times the estimated detection limits. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$MDL = (t) \times (S)$

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom [$t = 3.14$ for seven replicates],

S = standard deviation of the replicate analyses.

Method detection limits should be determined every six months or whenever a significant change in background or instrument response is expected.

10.2.3 Linear calibration ranges - Linear calibration ranges are metal dependent. The upper limit of the linear calibration range should be established by determining the signal responses from a minimum of four different concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined every six months or whenever a significant change in instrument response maybe expected.

10.3 ASSESSING LABORATORY PERFORMANCE - REAGENT AND FORTIFIED BLANKS

10.3.1 Laboratory reagent blank (LRB) - The laboratory must analyze at least one LRB (Sect. 7.5.2) with each set of samples. Reagent blank data are used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing. If an analyte value in the reagent blank exceeds its determined MDL, then laboratory or reagent contamination should be suspected. Any determined source of contamination should be corrected and the samples reanalyzed.

10.3.2 Laboratory fortified blank (LFB) - The laboratory must analyze at least one LFB (Sect. 7.7) with each set of samples. Calculate accuracy as percent recovery (Sect. 10.4.2). If the recovery of any analyte falls outside the control limits (Sect. 10.3.3), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

10.3.3 Until sufficient data (usually a minimum of 20 to 30 analyses) become available, a laboratory should assess laboratory performance against recovery limits of 80- 120%. When sufficient internal performance data become available, develop control limits from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data are used to establish upper and lower control limits as follows:

UPPER CONTROL LIMIT = $x + 3S$

LOWER CONTROL LIMIT =$x - 3S$

After each 5-10 new recovery measurements, new control limits should be calculated using only the most recent 20 to 30 data points.

10.4 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

10.4.1 The laboratory must fortify a minimum of 10% of the samples or one fortified sample per set, whichever is greater. Ideally for solid samples, the concentration added should be approximately equal to 0.1 abs units after the solution has been diluted. In other words if the sample (after dilution) results in an absorbance of 0.05, ideally the laboratory fortified sample wi11 result in an absorbance of 0.150 (after dilution). Over time, samples from all routine sample sources should be fortified.

10.4.2 Calculate the percent recovery for the analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the control limits established in Sect. 10.3.3 for the analyses of LFBs. Fortified recovery calculations are not required if the fortified concentration is less than 10% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$R = [(Cs - C)/S] \times 100$

where,

R = percent recovery.

Cs = fortified sample concentration.

C = sample background concentration.

S = concentration equivalent of the fortified sample.

10.4.3 If the recovery of the analyte on the fortified sample falls outside the designated range, and the laboratory performance on the LFB for the analyte is shown to be in control (Sect. 10.3) the recovery problem encountered with the fortified sample is judged to be matrix related (Sect. 4), not system related. The data obtained for that analyte should be verified with the methods of standard additions (Sect. 11.5).

10.5 QUALITY CONTROL SAMPLES (QCS) - Each quarter, the laboratory should analyze one or more QCS (if avai1able). If criteria provided with the QCS are not met, corrective action should be taken and documented.

PROCEDURE

SAMPLE PREPARATION - DISSOLVED ELEMENTS

11.1.1 For the determination of dissolved elements in drinking water, wastewater, ground and surface waters, take a 50-mL(± l mL) aliquot of the filtered acid preserved sample, and add 1 mL of concentrated nitric acid. The sample is now ready for analysis. Allowance should be made in the calculations for the appropriate dilution factors.

NOTE: If a precipitate is formed during acidification, transport or storage, the sample aliquot must be treated using the procedure in Sect. 11.2.1 prior to analysis.

SAMPLE PREPARATION - TOTAL RECOVERABLE ELEMENTS.

11.2.1 For the determination of total recoverable elements in water or waste water, take a 50-mL (± 1 mL) aliquot from a well mixed, acid preserved sample and transfer it to a Teflon microwave digestion vessel Add 1 mL of concentrated HNO_3. Seal the vessel per the manufacturer's instructions.

NOTE: Microwave digestion requires the use of a program that has been verified for a particular sample type. Please insure that Dr. Parmer has approved any new programs. After digestion, the sample is now ready for analysis. Prior to the analysis of samples the calibration standards must be analyzed and the calibration verified using a QC sample (Sect. 9). Once the calibration has been verified, the instrument is ready for sample analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, samples should be analyzed as soon as possible after preparation.

11.2.2 For the determination of total extractable elements in solid samples (sludge, soils, and sediments), mix the sample thoroughly to achieve homogeneity and weigh accurately a 0.5±0.01g portion of the sample. Transfer to a Teflon microwave digestion vessel. Add 45 mL RO water followed by 1 mL nitric acid. Digest as with a liquid sample

NOTE: Determine the percent solids in the sample for use in calculations and for reporting data on a dry weight basis.

11.2.3 Appropriate digestion procedures for biological tissues should be utilized prior to sample analysis.

11.3 For every new or unusual matrix, it is highly recommended that an inductively coupled plasma atomic emission spectrometer be used to screen for high element concentrations. Information gained from this may be used to prevent potential damage of the instrument and better estimate which elements may require analysis by graphite furnace.

11.4 Samples having concentrations higher than the established linear dynamic range should be di1uted into range and re-analyzed. If methods of standard additions are required, follow the instructions in Sect. 11.5.

11.5 STANDARD ADDITIONS - If methods of standard addition are required, the following procedure is recommended.

11.5.1 The standard addition technique[4] involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. <u>It will not correct for additive interference which causes a baseline shift</u>. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration C_S. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_x = S_B V_S C_S / (S_A - S_B) V_x$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S. should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_x and thus C_S. is much greater than C_x to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. <u>For the results from this technique to be valid, the following limitations must be taken into consideration:</u>

1. The analytical curve must be linear.

2. The chemical form of the analyte added must respond the same as the analyte in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

CALCULATIONS

12.1 Do not report element concentrations below the determined MDL.

12.2 For aqueous samples prepared by total recoverable procedure (Sect.11.2.1), multiply solution concentrations by the appropriate dilution factor. Round the data to the tenths place and report the data in µg/L with up to three significant figures.

12.3 For solid samples prepared by total recoverable procedure (Sect.11.2.2) round the solution concentration (µg/L in the analysis solution) to the tenths place and multiply by the dilution factor. Data should be reported to a tenth mg/kg up to three significant figures taking into account the percent solids if the data are reported on a dry weight basis.

The dry weight should be determined on a separate sample aliquot if the sample is available. The dry weight can be determined by transferring a uniform 1-g aliquot to an evaporating dish and drying the sample to a constant weight at 103-105°C.

12.4 If additional dilutions were performed, the appropriate dilution factor must be applied to sample values.

12.5 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

PRECISION AND ACCURACY

13.1 Instrument operating conditions used for single laboratory testing of the method and MDLs are listed in Table 3.

13.2 Data obtained from single laboratory testing of the method are summarized in Table 2A-C for three solid samples consisting of SRM 1645 River Sediment, EPA Hazardous Soil and EPA Electroplating Sludge. Samples ware prepared using the procedure described in Sect. 11.2.2 of the EPA METHOD. For each matrix, five replicates were analyzed and an average of the replicates used for determining the sample background concentration. Two further pairs of duplicates were fortified at different concentration levels. The sample background concentration, mean spike percent recovery, the standard deviation of the average percent recovery and the relative percent difference between the duplicate fortified determinations are listed in Table 2A-C. In addition, Table 2D-F contains a si ngle 1aboratory testing of the method in aqueous media including drinking water, pond water and well water. Samples were prepared using the procedure described in Sect. 11.2.1. For each aqueous matrix, five replicates were analyzed and an average of the replicates used for determining the sample background concentration. Four samples were fortified at the levels reported in Table 2D-F. A percent relative standard deviation is reported in Table 2D-F for the fortified samples. An average percent recovery is also reported in Tables 2D-F.

Precision and recovery for NBS River Sediment 1645

Solid Sample	Certified Value	Avg. Sed Conc (mg/kg)	%RSD	Avg % Rec (20 mg/kg)^x	S (r)	RPD	Avg % Rec (100 mg/kg)^x	S (r)	RPD
Cadmium	10.2	10.8	3.7	*	-	-	110.7	0.7	1.7
Chromium	29600	32800	1.6	99.1	14.2	0	*	-	-

Copper	109	132	4.8	*	-	-	111.5	3.6	2.6

Precision and recovery for EPA Hazardous Soil 884

Solid Sample	Avg. Sed Conc (mg/kg)	%RSD	Avg % Rec (20 mg/kg)^x	S (r)	RPD	Avg % Rec (100 mg/kg)^x	S (r)	RPD
Cadmium	1.8	10.3	115.4	0.8	1.4	99.0	4.3	12.1
Chromium	84.0	4.2	95.5	33.8	17.9	120.8	6.6	8.9
Copper	127	4.3	108.0	15.2	2.6	117.7	5.4	5.7

Precision and recovery data for EPA Electroplating Sludge 286

Solid Sample	Avg. Sed Conc (mg/kg)	%RSD	Avg % Rec (20 mg/kg)^x	S (r)	RPD	Avg % Rec (100 mg/kg)^x	S (r)	RPD
Cadmium	119	1.3	81.9	7.9	3.0	112.5	3.9	4.7
Chromium	8070	4.5	*	-	-	*	-	-
Copper	887	1.6	*	-	-	99.5	21.9	6.0

%RSD	percent relative standard deviation (n=5)
S (r)	standard deviation of average percent recovery
RPD	relative percent difference between duplicate recovery determinations
*	fortified concentration < 10% of sample concentration
-	not determined
x	fortified concentration

Precision and recovery data for Pond Water

Element	Avg Conc (µg/L)	%RSD	Fortified Conc (µg/L)	%RSD @ Fortified Conc	Avg % Rec
Cd	< 0.05	*	0.5	4.5	99.1
Cr	0.75	8.7	2.5	1.8	98.5
Cu	2.98	11.2	10	2.9	101.9
Ni	2.11	6.8	20	1.6	105.6
Pb	1.24	20.5	25	1.8	101.6

Precision and recovery data for Drinking Water

Element	Avg Conc (µg/L)	%RSD	Fortified Conc (µg/L)	%RSD @ Fortified Conc	Avg % Rec
Cd	< 0.05	*	0.5	6.3	105.2
Cr	< 0.1	*	2.5	3.1	105.7
Cu	2.6	7.3	10	1.2	111.5
Ni	0.8	32.7	20	4.3	103.8
Pb	< 0.7	*	10	4.0	101.8

Precision and recovery data for Well Water

Element	Avg Conc (µg/L)	%RSD	Fortified Conc (µg/L)	%RSD @ Fortified Conc	Avg % Rec
Cd	1.8	11.9	0.5	4.6	109.3
Cr	< 0.1	*	2.5	4.0	102.6
Cu	35.9	1.2	10	0.6	90.2
Ni	11.8	3.2	20	4.0	105.7
Pb	< 0.7	*	25	0.7	102.2

<	sample concentration less than established MDL
*	not determined on sample concentration less than the MDL

Recommended operating conditions

Element	λ	Slit	Char Temp	Atom Temp	MDL (µg/L)
Cd	228.8	0.7	800	1600	0.05
Cr	357.9	0.7	1650	2600	0.1
Cu	324.8	0.7	1300	2600	0.7
Ni	232.0	0.2	1400	2500	0.6
Pb	283.3	0.7	1250	2000	0.7
Zn	213.9	0.7	700	1800	0.3

MDL determined using a 20 µL sample size and stopped flow atomization

14. REFERENCES

I. "OSHA Safety and Health Standards, General Industry," (ZSCFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January, 1976.

2. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, Federal Register, July 24, 1986.

3. Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.

4. Winefordner, J.D., "Trace Analysis: Spectroscopic Methods for Elements," Chemical Analysis, Vol. 46, pp. 41- 42.

5. Waltz, B., G. Schlemmar and J. R. Mudakavi, JAAS, 1988, 3, 695.

Attachment 13

ALKALINITY

EPA Method 310.1 (Titrimetric, pH 4.5)

Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 ml.

1.3 Automated titrimetric analysis is equivalent.

Summary of Method

2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.

Comments

3.1 The sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.

3.2 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.

3.3 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9, using the procedure in:

Annual Book of ASTM Standards, Part 31, "Water", p 115, D-1067, Method D, (1976).

3.4 Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.

Apparatus

4.1 pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH units. Standardize and calibrate according to manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25 ±2° C.

4.2 Use an appropriate sized vessel to keep the air space above the solution at a minimum. Use a rubber stopper fitted with holes for the glass electrode, reference electrode (or combination electrode) and burette.

4.3 Magnetic stirrer, pipettes, flasks and other standard laboratory equipment,

4.4 Burettes, Pyrex 50, 25 and l0 ml.

Reagents

5.1 Sodium carbonate solution, approximately 0.05N: Place 2.5 ±0.2 g (to nearest mg) Na_2CO_3 (dried at 250°C for 4 hours and cooled in desiccator) into a 1 liter volumetric flask and dilute to the mark.

5.2 Standard acid (sulfuric or hydrochloric), 0.1 N: Dilute 3.0 ml cone H_2SO_4, or 8.3 ml conc HCl to 1 liter with distilled water. Standardize versus 40.0 ml of 0.05 N Na_2CO_3 solution with about 60 ml distilled water by titrating potentiometrically to pH of about 5. Lift electrode and rinse into beaker. Boil solution gently for 3-5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using:

(A x B)/(53.00 x C)

where:

A = gm Na_2CO_3 weighed into 1 liter

B = ml Na_2CO_3 solution

C = ml acid used to inflection point

5.3 Standard acid (sulfuric or hydrochloric), 0.02 N: Dilute 200.0 ml of 0.1000 N standard acid to 1 liter with distilled water. Standardize by potentiometric titration of 15.0 ml 0.05N Na_2CO_3 solution as above.

Procedure

6.1 Sample size

6.1.1 Use a sufficiently large volume of titrant (> 20 ml in a 50 ml burette) to obtain good precision while keeping volume low enough to permit sharp end point.

6.1.2 For < 1000 mg $CaCO_3$/1 use 0.02N titrant

6.1.3 For > 1000 mg $CaCO_3$/ 1 use 0.1N titrant

6.1.4 A preliminary titration is helpful.

6.2 Potentiometric titration

6.2.1 Place sample in flask by pipetting with pipette tip near bottom of flask

6.2.2 Measure pH of sample

6.2.3 Add standard acid (5.2 or 5.3), being careful to stir thoroughly but gently to allow needle to obtain equilibrium.

6.2.4 Titrate to pH 4.5. Record volume of titrant.

6.3 Potentiometric titration of low alkalinity

6.3.1 For alkalinity of < 2Q mg/l titrate 100-200 ml as above (6.2) using a 10 ml micro-burette and 0.02N acid solution (5.3).

6.3.2 Stop titration at pH in range of 4.3-4.7, record volume and exact pH. Very carefully add titrant to lower pH exactly 0.3 pH units and record volume.

Calculations

7.1 Potentiometric titration to pH 4.5

Alkalinity, mg/1 $CaCO_3$ = (A x N x 50,000)/ ml of sample

where:

A = ml standard acid

N = normality standard acid

7.2 Potentiometric titration of low alkalinity:

Total alkalinity, mg/ 1 $CaCO_3$ = (2B-C) x N x 50,000/ml of sample

where:

B = ml titrant to first recorded pH

C = total ml titrant to reach pH 0.3 units lower

N = normality of acid

Precision and Accuracy

8.1 Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

Alkalinity precision and accuracy

Increment as Alkalinity mg/L, $CaCO_3$	Precision as Standard Deviation mg/L, $CaCO_3$	Accuracy as	
		Bias, %	Bias, mg/L, $CaCO_3$
8	1.27	+10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	-8.19	-9.3
119	5.36	-7.42	-8.8

(FWPCA Method Study 1, Mineral and Physical Analyses)

8.2 In a single laboratory (EMSL) using surface water samples at an average concentration of 122 mg $CaCO_3$/1, the standard deviation was ± 3.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Fdition, p 278, Method 403, (1975).

2. Annual Book of ASTM Standards, Part31, "Water", p 113, D-1067, Method B, (1976).

Attachment 14

CHEMICAL OXYGEN DEMAND

EPA Method 410.4 (Colorimetric, Automated; Manual)

Scope and Application

1.1 This method covers the determination of COD in surface waters, domestic and industrial wastes.

1.2 The applicable range of the automated method is 3-900 mg/1 and the range of the manual method is 20 to 900 mg/L.

Summary of Method

2.1 Sample, blanks and standards in sealed tubes are heated in an oven or block digestor in the presence of dichromate at 150°C. After two hours, the tubes are removed from the oven or digestor, cooled and measured spectrophotometrically at 600 nm.

Sample Handling and Preservation

3.1 Collect the samples in glass bottles if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

3.2 Samples should be preserved with sulfuric acid to a $pH < 2$ and maintained at 4°C until analysis.

Interferences

4.1 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chlorides.

Apparatus

5.1 Drying oven or block digestor, 150°C

5.2 Coming culture tubes, 16x100 mm or 25x150 mm with Teflon lined screwcap

5.3 Spectrophotometer or Technicon AutoAnalyzer

5.4 Muffle furnace, 500°C.

Reagents

6.1 Digestion solution: Add 10.2 g $K_2Cr_20_7$, 167 ml conc. H_2SO_4 and 33.3 g $HgSO_4$ to 500 mL of distilled water, cool and dilute to 1 liter.

6.2 Catalyst solution: Add 22 g Ag_2SO_4 to a 4.09 kg bottle of conc. H_2SO_4. Stir until dissolved.

6.3 Sampler wash solution: Add 500 ml of concentrated H_2SO_4, to 500 ml of distilled water.

6.4 Stock potassium acid phthalate: Dissolve 0.850 g in 800 ml of distilled water and dilute to 1 liter. 1 mL = 1 mg COD

6.4.1 Prepare a series of standard solutions that cover the expected sample concentrations by diluting appropriate volumes of the stock standard.

Procedure

7.1 Wash all culture tubes and screw caps with 20% H_2SO_4, before their first use to prevent contamination. Trace contamination may be removed from the tubes by igniting them in a muffle oven at 500°C for 1 hour.

7.2 Automated

7.2.1 Add 2.5 mL of sample to the 16x100 mm tubes.

7.2.2 Add 1.5 ml of digestion solution (6. 1) and mix.

7.2.3 Add 3.5 ml of catalyst solution (6.2) carefully down the side of the culture tube.

7.2.4 Cap tightly and shake to mix layers.

7.2.5 Process standards and blanks exactly as the samples.

7.2.6 Place in oven or block digestor at 150°C for two hours.

7.2.7 Cool and place standards in sampler in order of decreasing concentration. Complete filling sampler tray with unknown samples.

7.2.8 Measure color intensity on AutoAnalyzer at 600 nm.

7.3 Manual

7.3.1 The following procedure may be used if a larger sample is desired or a spectrophotometer is used in place of an AutoAnalyzer.

7.3.2 Add 10 mL of sample to 25x150 mm culture tube.

7.3.3 Add 6 ml of digestion solution (6. 1) and mix.

7.3.4 Add 14 ml of catalyst solution (6.2) down the side of culture tube.

7.3.5 Cap tightly and shake to mix layers.

7.3.6 Place in oven or block digestor at 150°C for 2 hours.

7.3.7 Cool, allow any precipitate to settle and measure intensity in spectrophotometer at 600 nm. Use only optically matched culture tubes or a single cell for spectrophotometric measurement.

Calculation

8. 1 Prepare a standard curve by plotting peak height or percent transmittance against known concentrations of standards.

8.2 Compute concentration of samples by comparing sample response to standard curve.

Precision and Accuracy

9. 1 Precision and accuracy data are not available at this time.

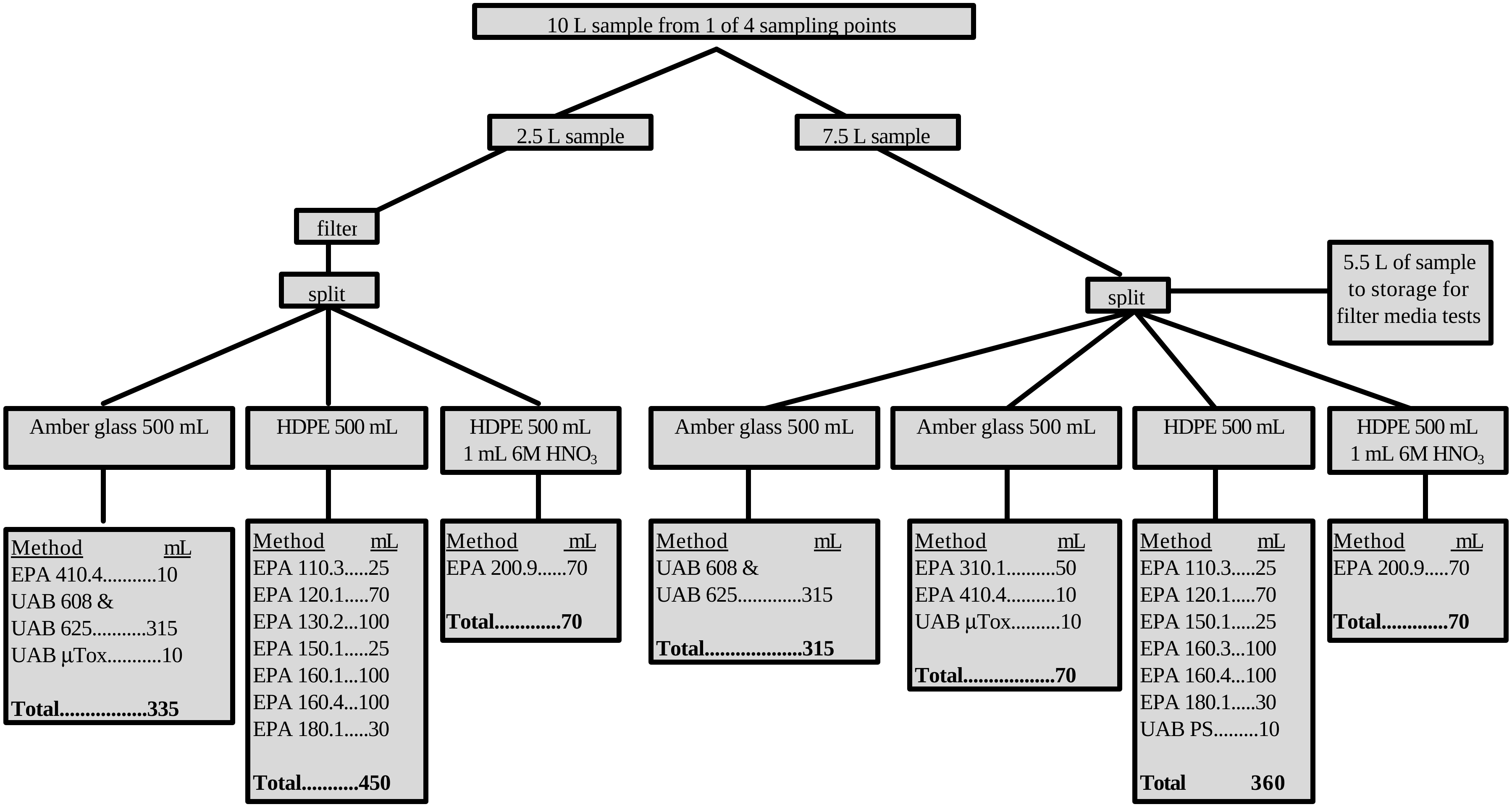
Bibliography

1. Jirka, A. M., and M. J. Garter, "Micro-Semi-Automated Analysis of Surface and Wastewaters for Chemical Oxygen Demand." Anal. Chem. 47:1397. (1975).

Attachment 15

Sample Flowcharts

MCTT Evaluation Flow Chart



2.5 L sample, filtered and split:

Amber glass 500 mL

Method	mL
EPA 410.4	10
UAB 608 & UAB 625	315
UAB µTox	10
Total	**335**

HDPE 500 mL

Method	mL
EPA 110.3	25
EPA 120.1	70
EPA 130.2	100
EPA 150.1	25
EPA 160.1	100
EPA 160.4	100
EPA 180.1	30
Total	**450**

HDPE 500 mL 1 mL 6M HNO$_3$

Method	mL
EPA 200.9	70
Total	**70**

7.5 L sample, split:

Amber glass 500 mL

Method	mL
UAB 608 & UAB 625	315
Total	**315**

Amber glass 500 mL

Method	mL
EPA 310.1	50
EPA 410.4	10
UAB µTox	10
Total	**70**

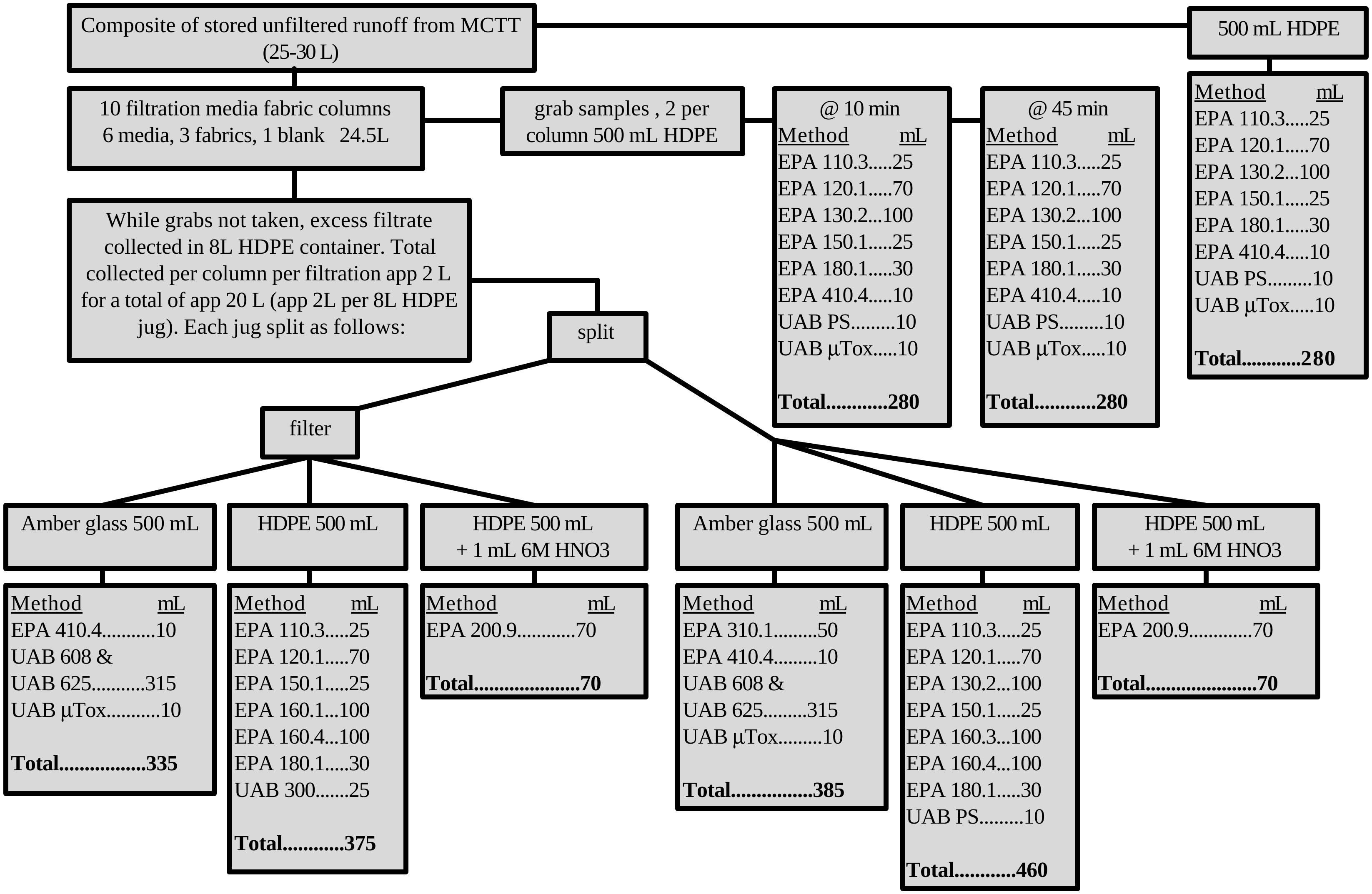
HDPE 500 mL

Method	mL
EPA 110.3	25
EPA 120.1	70
EPA 150.1	25
EPA 160.3	100
EPA 160.4	100
EPA 180.1	30
UAB PS	10
Total	**360**

HDPE 500 mL 1 mL 6M HNO$_3$

Method	mL
EPA 200.9	70
Total	**70**

Filtration Media Evaluation Flow Chart



Composite of stored unfiltered runoff from MCTT (25-30 L)

500 mL HDPE

Method	mL
EPA 110.3	25
EPA 120.1	70
EPA 130.2	100
EPA 150.1	25
EPA 180.1	30
EPA 410.4	10
UAB PS	10
UAB µTox	10
Total	**280**

10 filtration media fabric columns 6 media, 3 fabrics, 1 blank 24.5L

grab samples , 2 per column 500 mL HDPE

@ 10 min

Method	mL
EPA 110.3	25
EPA 120.1	70
EPA 130.2	100
EPA 150.1	25
EPA 180.1	30
EPA 410.4	10
UAB PS	10
UAB µTox	10
Total	**280**

@ 45 min

Method	mL
EPA 110.3	25
EPA 120.1	70
EPA 130.2	100
EPA 150.1	25
EPA 180.1	30
EPA 410.4	10
UAB PS	10
UAB µTox	10
Total	**280**

While grabs not taken, excess filtrate collected in 8L HDPE container. Total collected per column per filtration app 2 L for a total of app 20 L (app 2L per 8L HDPE jug). Each jug split as follows:

Amber glass 500 mL

Method	mL
EPA 410.4	10
UAB 608 & UAB 625	315
UAB µTox	10
Total	**335**

HDPE 500 mL

Method	mL
EPA 110.3	25
EPA 120.1	70
EPA 150.1	25
EPA 160.1	100
EPA 160.4	100
EPA 180.1	30
UAB 300	25
Total	**375**

HDPE 500 mL + 1 mL 6M HNO3

Method	mL
EPA 200.9	70
Total	**70**

Amber glass 500 mL

Method	mL
EPA 310.1	50
EPA 410.4	10
UAB 608 & UAB 625	315
UAB µTox	10
Total	**385**

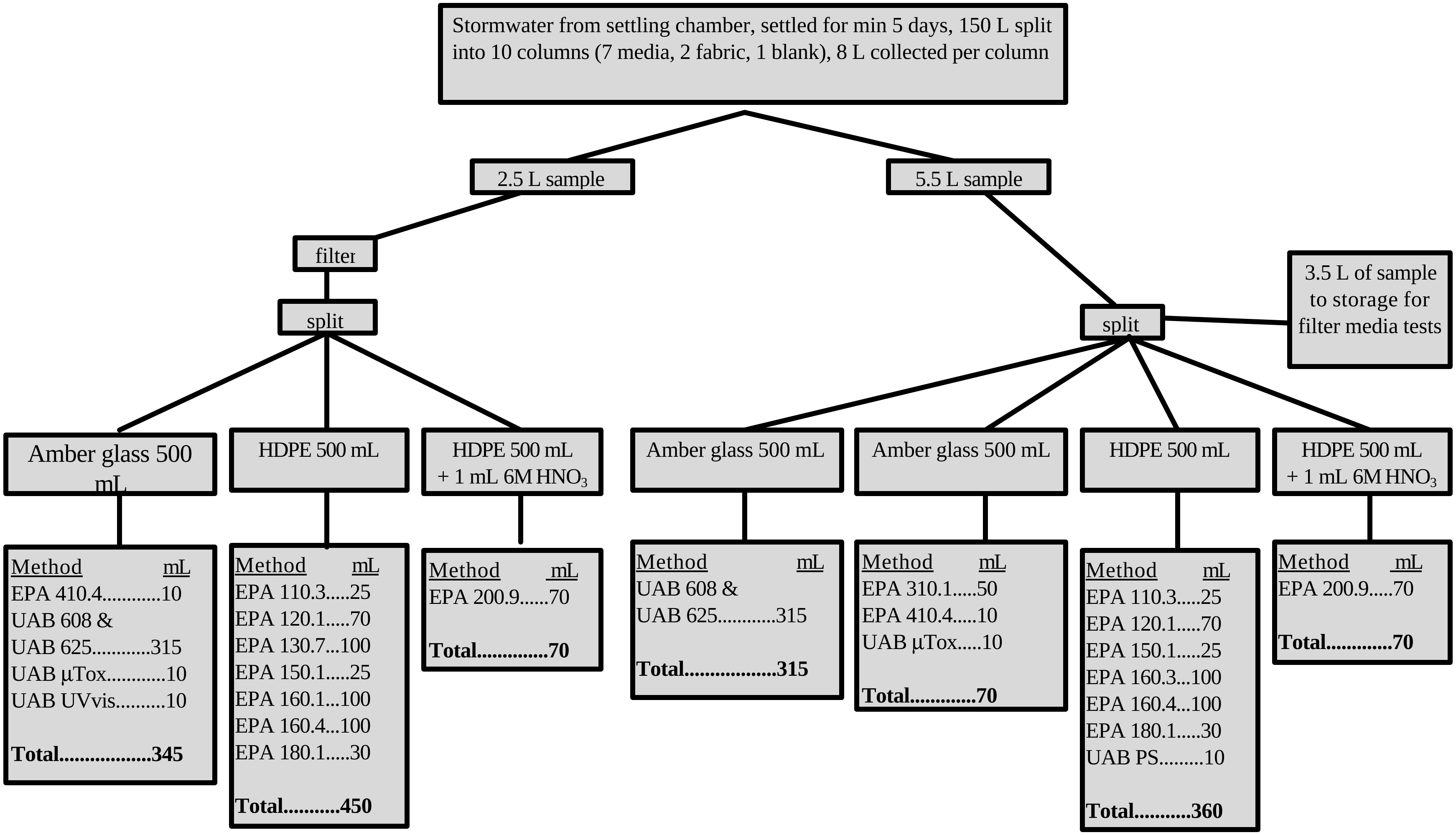
HDPE 500 mL

Method	mL
EPA 110.3	25
EPA 120.1	70
EPA 130.2	100
EPA 150.1	25
EPA 160.3	100
EPA 160.4	100
EPA 180.1	30
UAB PS	10
Total	**460**

HDPE 500 mL + 1 mL 6M HNO3

Method	mL
EPA 200.9	70
Total	**70**

On-Site Filtration Media Evaluation Flow Chart



Amber glass 500 mL (2.5 L sample, filtered):

Method	mL
EPA 410.4	10
UAB 608 & UAB 625	315
UAB µTox	10
UAB UVvis	10
Total	**345**

HDPE 500 mL (2.5 L sample, filtered):

Method	mL
EPA 110.3	25
EPA 120.1	70
EPA 130.7	100
EPA 150.1	25
EPA 160.1	100
EPA 160.4	100
EPA 180.1	30
Total	**450**

HDPE 500 mL + 1 mL 6M HNO_3 (2.5 L sample, filtered):

Method	mL
EPA 200.9	70
Total	**70**

Amber glass 500 mL (5.5 L sample):

Method	mL
UAB 608 & UAB 625	315
Total	**315**

Amber glass 500 mL (5.5 L sample):

Method	mL
EPA 310.1	50
EPA 410.4	10
UAB µTox	10
Total	**70**

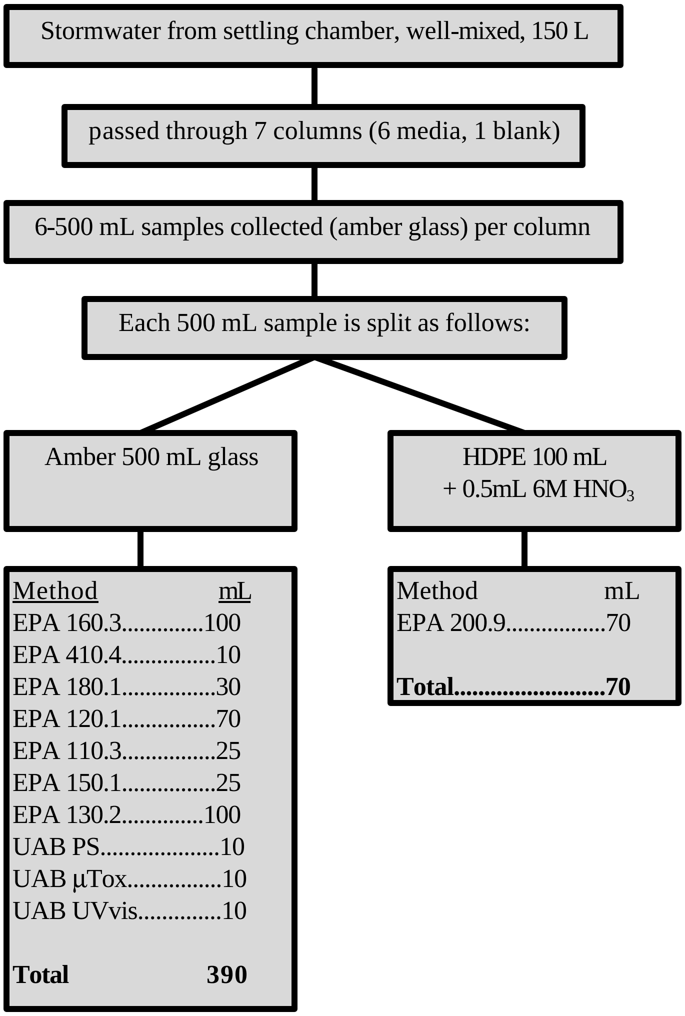
HDPE 500 mL (5.5 L sample):

Method	mL
EPA 110.3	25
EPA 120.1	70
EPA 150.1	25
EPA 160.3	100
EPA 160.4	100
EPA 180.1	30
UAB PS	10
Total	**360**

HDPE 500 mL + 1 mL 6M HNO_3 (5.5 L sample):

Method	mL
EPA 200.9	70
Total	**70**

Bench Scale Filtration Media Evaluation Flow Chart



Method	mL
EPA 160.3	100
EPA 410.4	10
EPA 180.1	30
EPA 120.1	70
EPA 110.3	25
EPA 150.1	25
EPA 130.2	100
UAB PS	10
UAB µTox	10
UAB UVvis	10
Total	**390**

Method	mL
EPA 200.9	70
Total	**70**