Sustainable Oil and Grease Removal from Synthetic Stormwater Runoff Using Bench-Scale Bioretention Studies

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ABSTRACT: One of the principal components of the contaminant load in urban stormwater runoff is oil and grease (O&G) pollution, resulting from vehicle emissions. A mulch layer was used as a contaminant trap to remove O&G (dissolved and particulate-associated naphthalene, dissolved toluene, and dissolved motor oil hydrocarbons) from a synthetic runoff during a bench-scale infiltration study. Approximately 80 to 95% removal of all contaminants from synthetic runoff was found via sorption and filtration. Subsequently, approximately 90% of the sorbed naphthalene, toluene, oil, and particulate-associated naphthalene was biodegraded within approximately 3, 4, 8, and 2 days after the event, respectively, based on decreases in contaminant concentrations coupled with increases of microbial populations. These results indicate the effectiveness and sustainability of placing a thin layer of mulch on the surface of a bioretention facility for reducing O&G pollution from urban stormwater runoff. *Water Environ. Res.,* **78,** 141 (2006).

KEYWORDS: urban stormwater runoff, oil and grease, hydrocarbons, bioretention, mulch, sorption, filtration, biodegradation.

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Introduction

Urban stormwater runoff deleteriously affects the quality of receiving water bodies by carrying a significant load of various pollutants, which have accumulated on urban surfaces (Line et al., 1996; Sansalone and Buchberger, 1995; Vogt, 1995; Wu et al., 1998). Oil and grease (O&G) pollution is one of the critical components of the contaminant load in urban stormwater runoff. In fact, available data indicate that urban stormwater runoff has been responsible for a considerable portion of the anthropogenic input of O&G to the environment, representing a major contributor of petroleum hydrocarbons to the oceans (Stenstrom et al., 1984). The hydrocarbons from urban runoff may later be found in aquatic sediments (e.g., Wakeham, 1977) and open water, and ultimately may accumulate in the tissues of aquatic life, resulting in a variety of negative environmental effects (e.g., DiSalvo et al., 1976).

Of the various sources of hydrocarbons to urban stormwater runoff, one of the major contributors is O&G emissions from vehicles, mostly from crankcase oils (MacKenzie and Hunter, 1979; Stenstrom et al., 1984; Wakeham, 1977). Residual petroleum products are deposited on impervious surfaces in urbanized areas, especially in areas with extensive automotive uses, such as roadways, parking areas, and commercial properties. Indeed, the amount of petroleum-derived hydrocarbons discharged with runoff has been found to be in proportion to the surrounding urbanization and technological development (Department of Environmental Resources, 1993; Stenstrom et al., 1984). Therefore, proper management of O&G discharges from impervious automotive-intensive "hotspots" is a critical issue that has significant potential for reducing the total amount of O&G discharged in urban stormwater runoff.

Presently, a number of infiltration-based technologies are being promoted to reduce stormwater runoff volume and to improve runoff quality. Bioretention is one of these stormwater best management practices (BMPs). Bioretention systems—plant- and soil-based runoff treatment and infiltration facilities for use in developed areas—are designed for water filtration and evapotranspiration, and pollutant removal by soil filtering, sorption, and other mechanisms. Studies using pilot- and full-scale bioretention facilities have demonstrated good-to-excellent removal of contaminants, including heavy metals, phosphorous, total Kjeldahl nitrogen, and ammonia (Davis et al., 2001 and 2003). However, there has been no work to date evaluating the removal of O&G in bioretention systems.

Typically, bioretention systems are installed with a surface-mulch layer, which protects the soil layer below by preventing erosion and drying of soil, and, furthermore, assists in the removal of some constituents, such as metals (Davis et al., 2001). This mulch layer can be further exploited as a medium for hydrocarbon trapping because mulch has a high content of lignin, which has a strong affinity for nonionic organic compounds (Garbarini and Lion, 1986). Therefore, in this research, a thin surface-mulch layer was evaluated as an O&G removal medium, with the hypothesis that bioretention systems in automotive-intensive "hotspots" can be engineered to capture and remove O&G from runoff to prevent O&G discharges to receiving waters.

A two-step O&G treatment process was envisioned and investigated. First, the mulch layer was evaluated for its capacity to capture O&G from infiltrating runoff via sorption and filtration. Filtration is important because a high percentage (approximately 74 to 90%) of the hydrocarbons in urban stormwater runoff is often associated with particulates (Eganhouse and Kaplan, 1981; Hoffman et al., 1984; MacKenzie and Hunter, 1979; Wakeham, 1977). The second step examined the subsequent destruction of the trapped O&G through microbial mineralization in a sustainable ecological process. Thus, the goal was to take advantage of a "depot effect" by providing a coarse, high-organic-carbon mulch layer capable of filtering out particulate-associated hydrocarbon contaminants and storing by sorption dissolved hydrocarbon contaminants, both of which are later made available for biodegradation by desorption. Importantly, the mulch layer must support a significant population of hydrocarbon-degrading microbes and allow sufficient contact time between these microorganisms and the hydrocarbons, without reducing the hydrocarbon bioavailability.

Table 1—Synthetic stormwater runoff characteristics (Davis et al., 2001).

Component	Source	Supplier	Value
pH	Hydrochloric acid (HCl)/ sodium hydroxide (NaOH)	Fisher Scientific (Fair Lawn, New Jersey)	7.0
Nutrients			
NO_3^-	Sodium nitrate ($NaNO_3$)	Fisher Scientific (99.9%)	2 mg/L as N
Organic N	Glycine	Fisher Scientific	4 mg/L as N
Phosphorus	Sodium phosphate dibasic (Na_2HPO_4)	J. T. Baker (100%) (Phillipsburg, New Jersey)	0.6 mg/L as P
Dissolved solids	$CaCl_2$	Fisher Scientific (100.4%)	120 mg/L
Petroleum contaminants*			
Naphthalene	—	Acros Organics (99%) (Geel, Belgium)	Approx. 1.6 mg/L
Toluene	—	Acros Organics (Reagent ACS)	Approx. 2.7 mg/L
Motor oil	—	Shell (SAE Grade 10W-40) (Houston, Texas)	Approx. 30.8 mg/L

* Each experiment used one of the three sources of petroleum contaminants listed.

The specific objectives of this study were to (1) evaluate the capacity of a mulch layer to capture dissolved and particulate-associated O&G contaminants via physical and chemical mechanisms during a simulated storm event; and (2) evaluate the rate and extent of O&G biodegradation that occurs between events in the mulch layer. A mass-balance approach was used to evaluate the fate of three different hydrocarbon contaminants during the storm events and to quantify the amount of contaminant biodegraded after the events.

Materials and Methods

Synthetic Runoff and Model Contaminants. In each experiment, synthetic runoff was used to provide controlled input conditions. The synthetic runoff was made using dechlorinated tap water with the supplemental chemical components listed in Table 1. The concentrations used followed the recipe of Davis et al. (2001), which was based on previously reported stormwater characteristics (Department of Environmental Resources, 1993); however, unlike Davis et al. (2001), none of the heavy metals typically found in urban stormwater runoff were included because the focus of this work was on O&G contaminants. Nonetheless, inferences regarding the influence of trace metals on microbial activity can be made based on the inhibited studies performed with mercury (Hg), as discussed further below. The model hydrocarbons selected included naphthalene and toluene because of their toxicity and common presence in stormwater runoff (Delzer et al., 1996; Hoffman et al., 1984; Stenstrom et al., 1984) and a commercial automobile motor oil.

Runoff solutions for dissolved contaminant experiments were made by direct addition of the selected contaminants. For the oil experiments, an oil layer was placed on the surface of synthetic runoff, and the water was gently stirred without breaking the oil layer to allow the oil to dissolve. For particulate-associated experiments, Berryland Oe soil (organic carbon content, 34.1%; and texture, organic) (Levin, 1994) was added to a naphthalene-water solution (approximately 25 mg/L), and the suspension was stirred for approximately 3 days to allow sufficient sorption. Soil particles with sorbed naphthalene were removed from the suspension by centrifugation, then added to synthetic runoff, resulting in total influent naphthalene concentrations of 1.5 to 1.6 mg/L and total suspended solid (TSS) concentrations of 270 to 340 mg/L. Because this resuspension of naphthalene-sorbed soil in ''clean'' synthetic runoff was likely to result in desorption of some naphthalene, both total and dissolved naphthalene concentrations in the influent and effluent were measured to determine the amount of particulate-associated naphthalene. For preliminary experiments with suspended solids only, Othello Ap silt loam (Yoo and James, 2002) was used. Both soils were obtained from Bruce R. James of the Department of Natural Resource Sciences and Landscape Architecture, University of Maryland (College Park), and sieved to 4 mm before storage.

Bench-Scale Bioretention Reactor. Stormwater runoff simulation experiments were performed using a bench-scale reactor (modified from the reactor of Mueller et al., 1991) that was constructed from a porcelain Büchner funnel (253-mm i.d., 110-mm bowl depth), and lined with stainless-steel woven wire cloth (Figure 1). A 3-cm thick layer of leaf compost mulch (approximately 550 g dry) was placed on the cloth. The leaf mulch (organic matter, 29.8%; pH, 7.1; and cation exchange capacity, 34.36 meq/100g [analyzed by the University of Maryland Soil Laboratory]), which had been composted and stored for approximately 0.5 to 1 year, was obtained from the Department of Public Works, College Park, Maryland. No microorganisms were supplemented to the mulch. To permit a contaminant-mass-balance analysis, the reactor was sealed with a Teflon lid that held inlet ports for air (1 port) and runoff (4 ports) and an outlet port for exiting air. Air was passed through the reactor headspace at 100 mL/min to maintain conditions similar to the field application where the surface of mulch would be in contact with fresh air. In addition, the flow of air through the reactor headspace facilitated quantification of the volatilized contaminants as part of the mass-balance analysis. Any volatilized hydrocarbons were captured by an activated carbon trap, with 3 g (8 g for toluene experiments) of granular activated carbon placed in the air-exit line.

To confirm the contribution of biodegradation to the observed contaminant removals, inhibited-control experiments were performed for comparison to biotic experiments. Mulch for the inhibited-control experiments was directly amended with mercuric chloride ($HgCl_2$) at a rate of 1.84 mmol/kg and also soaked in a 1000 mg/L $HgCl_2$ solution for 48 hours (Fletcher and Kaufman, 1980). To create comparable mulch conditions, mulch for biotic runs was soaked in 1000 mg/L calcium chloride ($CaCl_2$) solution for 48 hours. Mercuric chloride was also introduced to the synthetic runoff for the inhibited-control experiments at a level of 400 mg/L as $HgCl_2$ (Mihelcic and Luthy, 1988). In the toluene experiments, an additional inhibited-control experiment with autoclaved mulch (for 1 hour at 121°C on three consecutive days) was performed in an effort to demonstrate better microbial inhibition.

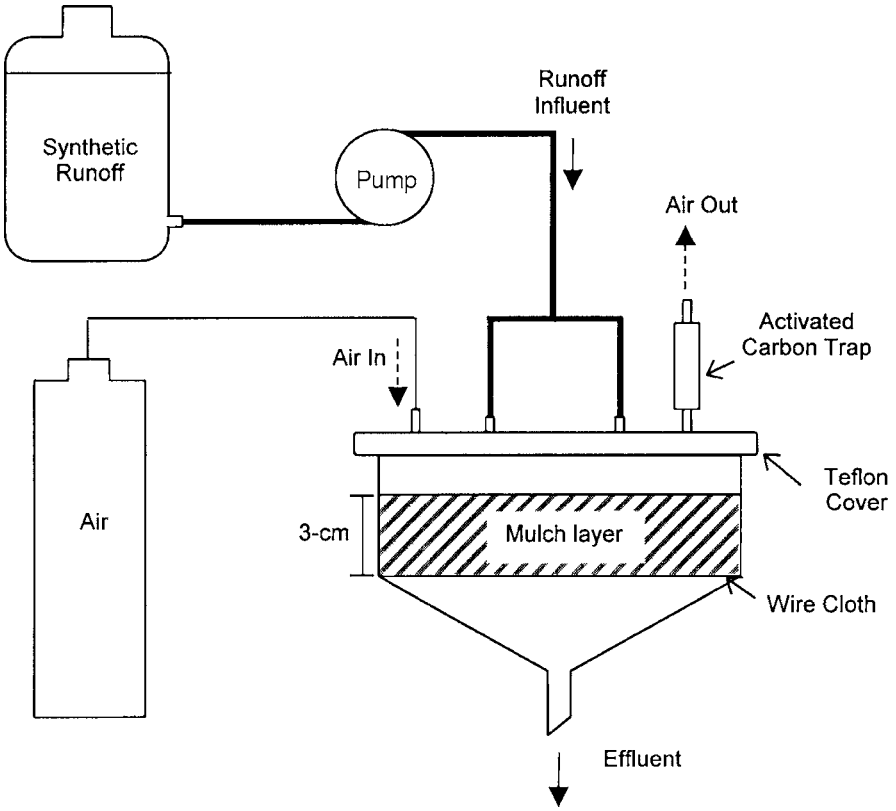

Figure 1—Schematic illustration of the mulch-based bioretention reactor (not to scale).

Stormwater-Runoff-Simulation Experiments. A mass-balance approach, which incorporated monitoring of the contaminant concentrations to the aqueous, gaseous, and solid phases, was used to quantify the contaminant fate. All experiments had two investigational phases: Phase 1, which simulated a runoff event, followed by Phase 2, simulating the time between storm events. During Phase 1, the runoff was applied to the mulch surface at 4 cm/h over 6 hours. This flowrate was based on a 1.5-cm total rainfall event over a 6-h duration, assuming a bioretention cell sized at 5% of the drainage area and a runoff coefficient of 0.8 (Davis et al., 2001). The influent and effluent from the reactor were sampled and monitored for the respective hydrocarbon concentrations. These data were used to calculate the removal efficiency from simulated runoff and, thus, the fraction of the contamination captured in the mulch. Subsequently, the reactor was sealed except for the air flow and stored at room temperature (average = 22 to 23°C, except for the particulate-associated naphthalene experiments [average = 26°C]). During Phase 2, mulch samples were taken twice per day for biotic runs and every day for inhibited-control runs to monitor the contaminant concentration (approximately 5 g wet mulch), microbial population counts (approximately 10 g wet mulch), and moisture content (APHA et al., 1995). At the end of Phases 1 and 2, the activated-carbon trap was analyzed to quantify any contaminant mass loss via volatilization. Because of the higher volatility of toluene, however, the activated carbon was analyzed daily during those Phase 2 experiments.

Typically, samples were taken and analyzed in duplicate. Thus, the results presented in the figures represent the average values for duplicate analyses, with the standard deviations shown as error bars. The biotic experiments using dissolved naphthalene and toluene were replicated and shown to be reproducible.

Analytical Methodology. Naphthalene and toluene concentrations were measured using a Hewlett-Packard (HP) gas chromatograph (GC) model 6890 (Hewlett-Packard, Wilmington, Delaware), equipped with a flame ionization detector and HP Chemstation software (version 6.03). The GC system and operating conditions used were adapted from David et al. (1993) and are described in more detail in Seagren and Moore (2003). Aqueous samples (2 mL) taken during Phase 1 experiments were extracted with 1 mL of hexane for analyses, with acenaphthene used as an internal standard. The Phase 2 mulch samples and the activated carbon were extracted with 40 mL hexane (Hong, 2002; modified from Muller et al., 1991). In all cases, 1-μL hexane-extract samples were injected to the GC in duplicate. Calibration curves for peak area versus the concentration of compounds in hexane were produced using a least-squares linear regression for both phases of each experiment. The method detection limit was 0.1 mg/L for both hydrocarbons.

Oil concentrations in aqueous samples were determined using a solid-phase extraction method (Lau and Stenstrom, 1997). Oil concentrations in mulch and activated-carbon samples were analyzed using a method modified from other studies (Mohn and Stewart, 2000; Nocentini et al., 2000; Oh et al., 2001). The samples were first extracted with hexane, followed by GC analysis of the extract after evaporation of the hexane (Hong, 2002). The TSS concentrations were measured using Standard Method 2540D (APHA et al., 1995).

Preliminary sorption isotherm experiments showed that the extraction efficiencies of naphthalene and toluene from the mulch samples were nearly 100 and 90%, respectively, within the concentration ranges used (data not shown). Because different methods were used for the aqueous and solid samples in the oil experiments, a mass balance was not established, and, instead, the concentration was only compared between biotic and inhibited-control samples.

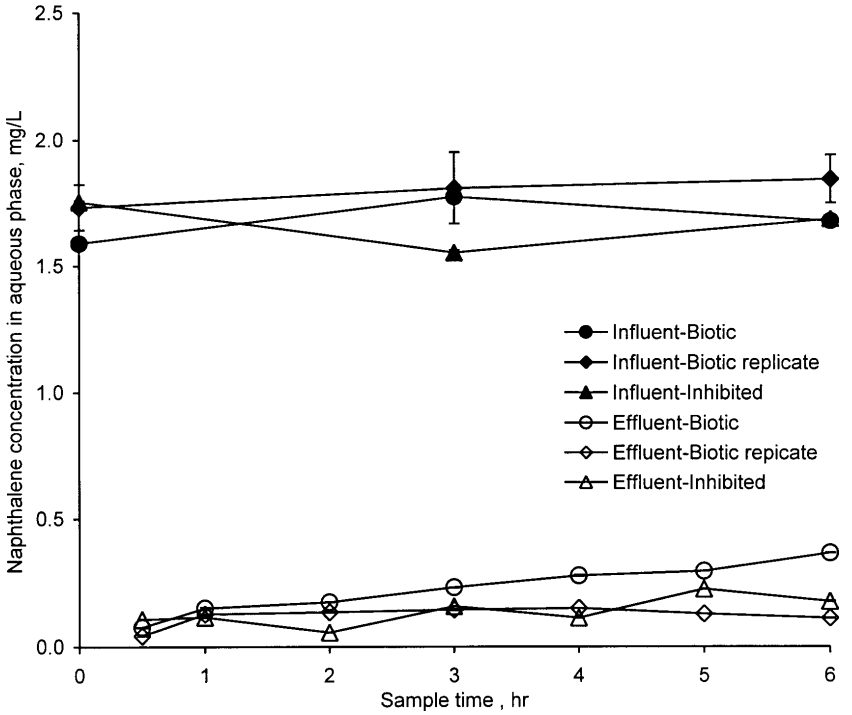

Figure 2—Influent and effluent average naphthalene concentrations in the aqueous phase during the Phase 1 simulated storm event in the biotic, biotic replicate, and inhibited-control reactors. Error bars represent ± one standard deviation.

The heterotrophic plate count (HPC) method (APHA et al., 1995) with R2A agar was used to estimate the total heterotrophic microbial population in the mulch. Naphthalene- and toluene-degrader plate counts (NDPC and TDPC, respectively) were performed using mineral medium (Seagren et aZzure and computer program of Haines et al. (1996).

Results and Discussion

General Observations. Several general observations were common to all the experiments that warrant discussion. First, simulated-runoff-effluent flow was observed within a few minutes after starting the experiments, and the effluent flowrates were constant and identical to the influent flowrate throughout Phase 1. These observations indicate that the permeability of the mulch layer was sufficient to keep the retention time of influent solutions very short. Second, in all cases, the color of the effluent was initially brown, with a high solids content based on visual observations, although the initial concentrations of contaminants in effluent were always low (discussed below); however, as time elapsed, the color faded, and the solids content decreased sufficiently that the solution visibly became almost clear with a yellowish color. Third, moisture contents of the mulch ranged from approximately 40 to 70% by mass during the Phase 2 studies, which is much higher than the 2 to 5% that has been shown to significantly affect the rate of hydrocarbon biodegradation in soil (Davis and Madsen, 1996), suggesting that the moisture level did not limit the rate of biodegradation.

Dissolved Naphthalene Experiments. Experiments performed with an influent concentration of approximately 1.6 mg/L dissolved naphthalene (approximately 3.2 mg/h surface loading) demonstrated approximately 90% removal from the aqueous phase via sorption to the mulch layer during Phase 1 (Figure 2). Both the biotic and inhibited-control experiments demonstrated similar removal efficiencies in Phase 1, suggesting that the inhibition treatment did not significantly affect the sorptive capacity of the mulch. In both cases, however, although the sorbed naphthalene loading was less than the naphthalene sorption capacity (based on isotherm studies [Hong, 2002]), a small portion of the naphthalene introduced (less than 10%) remained in the effluent, likely because of mass-transfer limitations.

Naphthalene mass in each material phase was calculated to perform the mass-balance analysis. The mass of naphthalene in the influent and effluent aqueous phases, M_{aq} (mg), was calculated as follows:

$$M_{aq} = \sum [C_{aq} \times Q \times \Delta t] \quad (1)$$

Where

C_{aq} = naphthalene concentration (mg/L),
Q = runoff flowrate (L/h), and
Δt = time increment (h).

In addition, the measured naphthalene concentrations in the mulch (C_m) and activated carbon (C_v-representing volatilized hydrocarbon) (mg/dry g) were used to calculate the total naphthalene mass in the reactor, M_m, and trap, M_v (mg), respectively, as follows:

$$M_m = C_m m_m \quad (2a)$$
$$M_v = C_v m_v \quad (2b)$$

Where

m_m = dry mass of mulch (dry g), and
m_v = dry mass of activated carbon (dry g).

Table 2—Mass-balance of contaminants at the end of the simulated storm event (Phase 1).

	Naphthalene (mg)			Toluene (mg)				Particulate-associated naphthalene (mg)	
Sample	Biotic	Biotic (replicate)	Control ($HgCl_2$)	Biotic	Biotic (replicate)	Control ($HgCl_2$)	Control (autoclaved)	Biotic	Control ($HgCl_2$)
Influent mass[a]	20.6 ± 0.1	21.4 ± 0.05	20.4 ± 0.1	31.3 ± 0.3	34.2 ± 0.6	30.8 ± 0.1	33.7 ± 0.5	19.6 ± 0.05	17.9 ± 0.03
Effluent mass[a]									
Aqueous	2.7 ± 0.007[b]	1.5 ± 0.004	1.7 ± 0.004	4.3 ± 0.03	6.9 ± 0.07	3.8 ± 0.04	14.6 ± 0.1	0.6 ± 0.005	0.1 ± 0.003
Mulch	18.0 ± 2.5[c]	19.4 ± 0.6	23.0 ± 0.5	18.5 ± 0.9	18.6 ± 0.6	14.6 ± 0.7	14.8 ± 0.2	18.6 ± 3.4	17.5 ± 0.1
Volatilized	0.0037 ± 3.3×10^{-5}[d]	0.001 ± 4.3×10^{-5}	0.0036 ± 6.9×10^{-6}	4.3 ± 1.8	5.0 ± 0.4	2.7 ± 0.02	2.7 ± 0.4	—	—
Total	20.7	20.9	24.7	27.1	30.5	21.1	32.1	19.2	17.6
Recovery (%)	100	97.7	121	86.6	89.2	68.5	95.3	98.0	98.3

[a] Average ± standard deviation.
[b] Standard deviation calculated from standard deviation of duplicate GC injections of hexane extracts of single aqueous samples, and propagation of error in eq 1.
[c] Standard deviation calculated from standard deviation of duplicate GC injections of hexane extracts of duplicate mulch samples.
[d] Standard deviation calculated from standard deviation of duplicate GC injections of hexane extracts of single-activated carbon samples.

Therefore, for the Phase 1 runoff application, the hydrocarbon mass balance is given as follows:

$$M_{aq\text{-}in} = M_{aq\text{-}out} + M_m + M_v \quad (3)$$

The naphthalene mass-balance results are presented in Table 2. These data demonstrate that most of the naphthalene from the aqueous influent was sorbed to the mulch layer (>87%) and confirm that volatilization of naphthalene during Phase 1 was negligible (less than 0.02% of the total mass). In the two biotic studies, the recovered naphthalene equaled greater than 97% of the input. In the inhibited-control experiment, however, the recovered mass was 21% higher than the input mass, possibly because of some heterogeneity in the distribution of the naphthalene, which may have resulted in the mulch phase samples, in this case, having material that was predominantly taken from higher concentration regions in the mulch layer (e.g., the mulch surface).

Although the results were similar between the biotic and inhibited-control experiments during Phase 1, they differed during the post-storm event period (Phase 2), as expected. In the two biotic experiments, greater than 92% naphthalene removal occurred in the mulch layer within 62 hours following the end of Phase 1, which was approximately twice as fast as in the inhibited-control [Figure 3(a)]. In particular, removal of naphthalene in the biotic run proceeded rapidly during the first 48 hours, comparable to other published data for soil systems (Guerin and Boyd, 1997; Wang and Vipulanandan, 2001; Zhang and Bouwer, 1997). Loss of naphthalene also occurred in the inhibited-control, but at a slower rate, suggesting that biodegradation was not completely eliminated in spite of the $HgCl_2$ loadings. Losses resulting from volatilization were negligible during Phase 2 (0.012 to 0.013 mg), supporting the assumption that the fast degradation of naphthalene in the biotic reactor occurred because of microbial activity.

Additional evidence supporting the occurrence of biodegradation is provided by the gradual increase in the populations of total heterotrophic bacteria and naphthalene-degrading bacteria in the mulch with time, in all cases [Figure 3(b)]. No initial lag time was observed for the NDPC in the biotic reactor, although there was a lag phase for the HPC. Importantly, the changes in microbial numbers correlated to the loss of naphthalene [Figure 3(a)]. In particular, the increase of the NDPC data correlates well with the decrease of naphthalene. Similar results were observed in the replicated biotic run (data not shown) (Hong, 2002). Furthermore, comparison of the microbial counts indicates that the addition of $HgCl_2$ did inhibit the microbial growth in the control reactor, consistent with the reduced rate and extent of naphthalene removal. Nonetheless, naphthalene-degrading bacteria were still present in the control and did increase with time, explaining the slow disappearance of naphthalene. The observations of microbial growth in the reactors after introducing the naphthalene, and reduced growth and naphthalene removal in the control, support the hypothesis that the rapid degradation of naphthalene is primarily a result of the microbial activities in the mulch.

The rapid biodegradation of sorbed naphthalene observed in this study in the mulch after the simulated storm event is consistent with the findings of other studies (e.g., Guerin and Boyd, 1997; Park et al., 2001 and 2002) and indicates that the sorbed naphthalene was available to the microorganisms. Only the biodegradation of freshly sorbed naphthalene was considered here, but that is representative of the manner in which the mulch layer will work in a functional bioretention system.

Dissolved Toluene Experiments. The influent aqueous phase concentration of approximately 2.7 mg/L dissolved toluene (approximately 5.4 mg/h surface loading) was reduced by greater than approximately 80% during Phase 1, in both the biotic reactors and the control run amended with $HgCl_2$ (Figure 4). However, a lower removal efficiency (approximately 56%) was observed in the autoclaved control experiment. Other researchers have similarly observed that autoclaving soils may change the characteristics of soils, causing lower sorption capacity (e.g., Wolf et al., 1989).

The Phase 1 toluene mass balance demonstrates that a large fraction (approximately 50 to 60%) of the influent toluene was sorbed to the mulch layer (Table 2). In all four experiments, a greater portion of the influent toluene (approximately 8 to 15%) was volatilized than

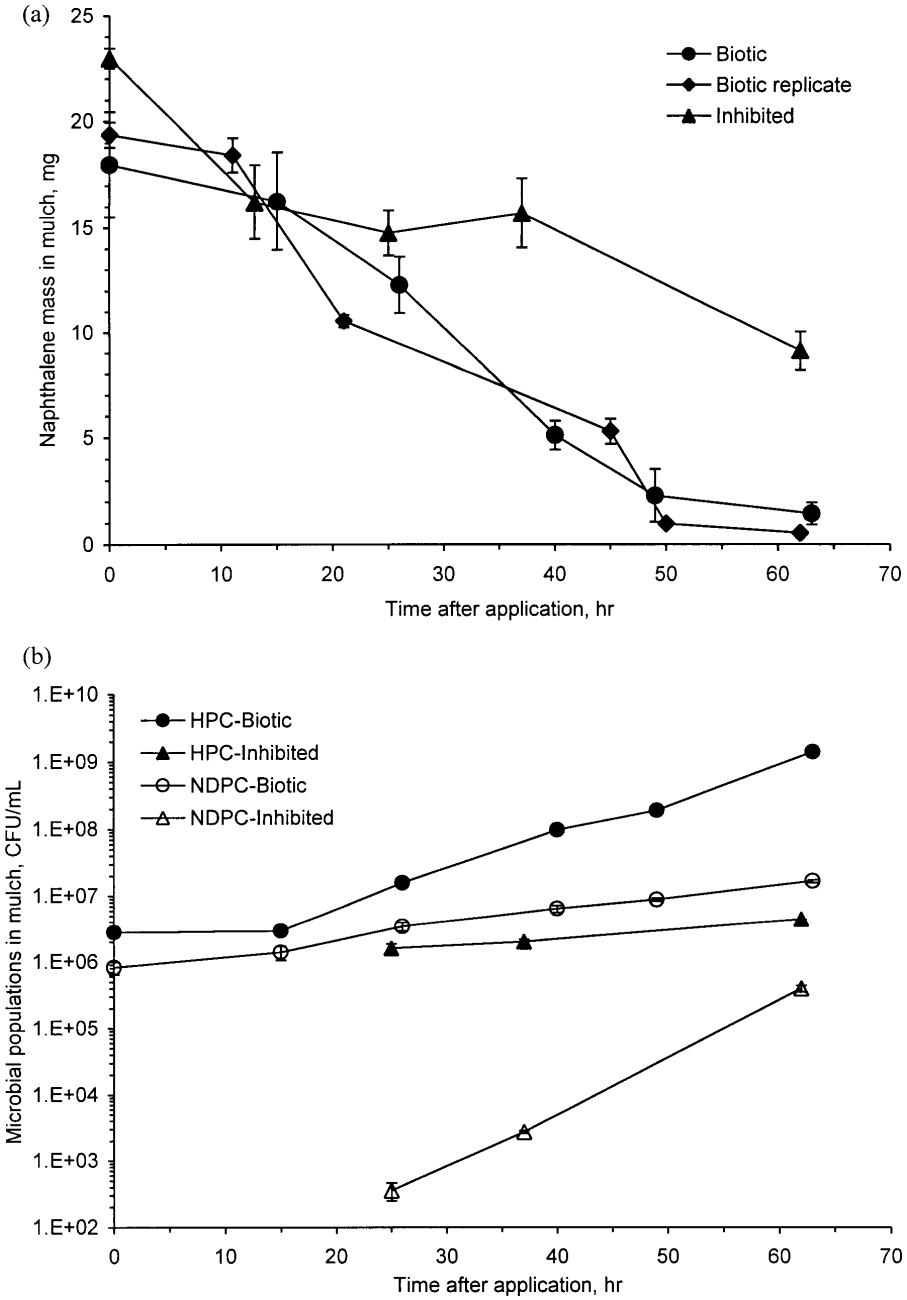

Figure 3—Phase 2 results for the dissolved naphthalene experiments: (a) Average mass of naphthalene in the mulch of the biotic, biotic replicate, and inhibited-control reactors; and (b) average total heterotrophic plate counts (HPC) and naphthalene-degrader plate counts (NDPC) in the mulch of the biotic and inhibited-control reactors (biotic replicate data not shown for clarity). Error bars represent ± one standard deviation.

in the naphthalene experiments, and, accordingly, a less accurate mass balance was established with toluene.

Because of the volatilization losses, the Phase 2 data for toluene are presented in Figure 5(a) as the sum of the toluene mass found on the mulch and activated carbon versus time. Thus, the lost mass is considered to have been biodegraded. In the biotic reactors, toluene removal via biodegradation occurred most rapidly during the first 2 to 3 days, with a total of approximately 79 to 62% of the initial toluene lost because of biodegradation. In comparison, greater amounts of the toluene were left after three days in the control experiments, and the total decreases in toluene due to biodegradation were obviously less, particularly in the autoclaved control experiment.

Corresponding trends between the toluene mass data and the microbial-plate-count data (Figure 5) provide strong evidence for the importance of biodegradation. The microbial populations in the biotic reactor increased with time, based on both the HPC and the TDPC [Figure 5(b)]. In the replicate experiment, the population of toluene degraders (data not shown) increased approximately one order of magnitude during Phase 2, as observed in the original biotic experiment (Hong, 2002). No lag time was observed for the

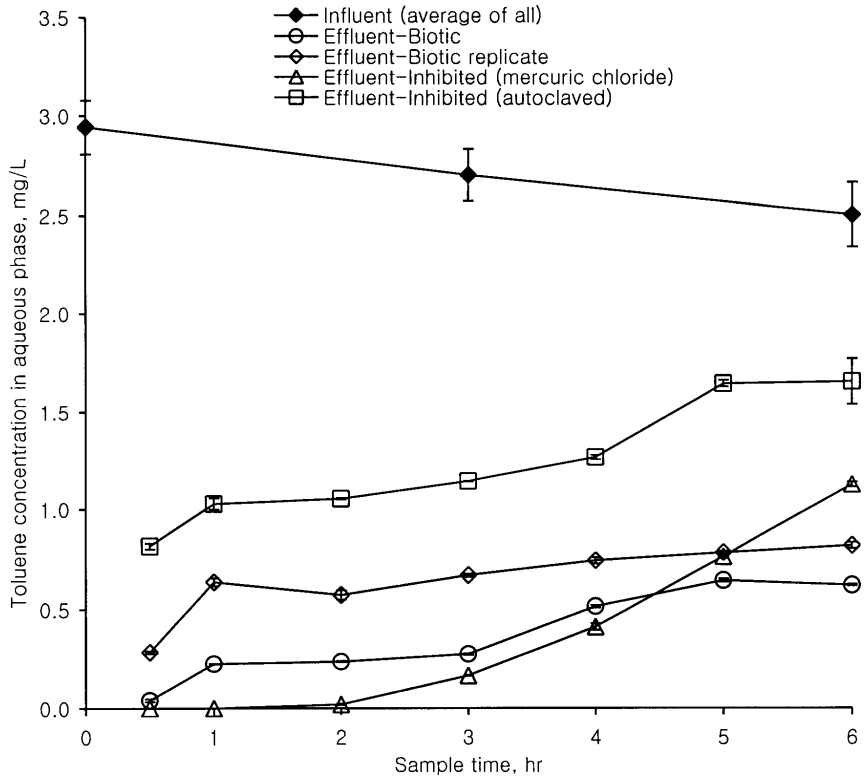

Figure 4—Influent and effluent average toluene concentrations in the aqueous phase during the Phase 1 simulated storm event in the biotic, biotic replicate, and inhibited-control reactors. Error bars represent ± one standard deviation.

microorganisms to degrade the toluene, as in the naphthalene experiments, being consistent with the findings of Zhang and Bouwer (1997). In addition, the changes in microbial numbers, particularly the toluene degraders, correspond well to the loss of toluene.

Similar to the naphthalene experiments, microbial counts indicate that the inhibition techniques were moderately effective. In particular, the slower decrease of toluene with time, coupled with a lower initial microbial population and less microbial growth (with the exception of the HPC data) indicate that autoclaving of the mulch better inhibited the native microorganisms than the $HgCl_2$ amendment.

Based on these results, the freshly sorbed toluene appears to be readily bioavailable in the mulch layer, similar to the findings of the naphthalene experiments. This observation is consistent with the findings of other studies, which have demonstrated that sorption of toluene to humic acid, especially humin in soil, involves non-covalent interactions and is reversible and diffusion controlled (Chang et al., 1997; Shih and Wu, 2002).

Dissolved-Motor-Oil Experiments. Experiments performed with an influent concentration of approximately 27 mg/L dissolved-motor-oil hydrocarbons (55 mg/h surface loading) demonstrated approximately 80% removal from the aqueous phase via sorption to the mulch during the Phase 1 in the biotic run. In comparison, the removal was 90% from 34 mg/L dissolved hydrocarbons in the $HgCl_2$-control run. Again, the addition of $HgCl_2$ did not appear to significantly affect the sorptive capability of the mulch. After the completion of Phase 1, oil affiliated with the surface of the mulch layer could be visually observed.

An oil-mass balance during Phase 1 could not be established because extractions of mulch samples always overestimated the oil mass, apparently because of extraction of natural oil and grease or organic matter in the mulch. This only occurred when oil was added to the mulch, not when the native mulch was analyzed. Volatilization of oil measured via the carbon trap was found to be negligible during both Phase 1 and Phase 2, as expected.

Gas chromatograms of the hexane extracts from the mulch samples were used to compare the change in the oil content with time during Phase 2 (Figure 6). The cone-like rise and fall of the detector response represents various compounds with similar molecular masses that were not resolved into individual peaks (Nakles et al., 1996). These chromatograms differed only in concentration (height), while the distribution of the components in the mixture and the chromatographic profile remained the same (e.g., Nocentini et al., 2000). Moreover, no peaks were observed to increase with time, indicating that no measurable accumulation of detectable biodegradation byproducts occurred (Eiermann and Bolliger, 1995). The peak heights clearly decreased with time in the biotic chromatograms [Figures 6(a-d)], especially during the first 2 to 3 days. Similar observations were made by Nocentini et al. (2000), who documented a decrease in the hydrocarbon concentration with no shift of the peaks in the chromatogram over time resulting from the biodegradation of motor oil sorbed on soils. In the inhibited-control experiment, however, there was no significant change in the chromatograms throughout Phase 2 [Figures 6(e-g)].

Using a more quantitative approach, the oil mass in the mulch was monitored by calculating the total chromatogram area, excluding the hexane solvent, to observe the total mass decrease

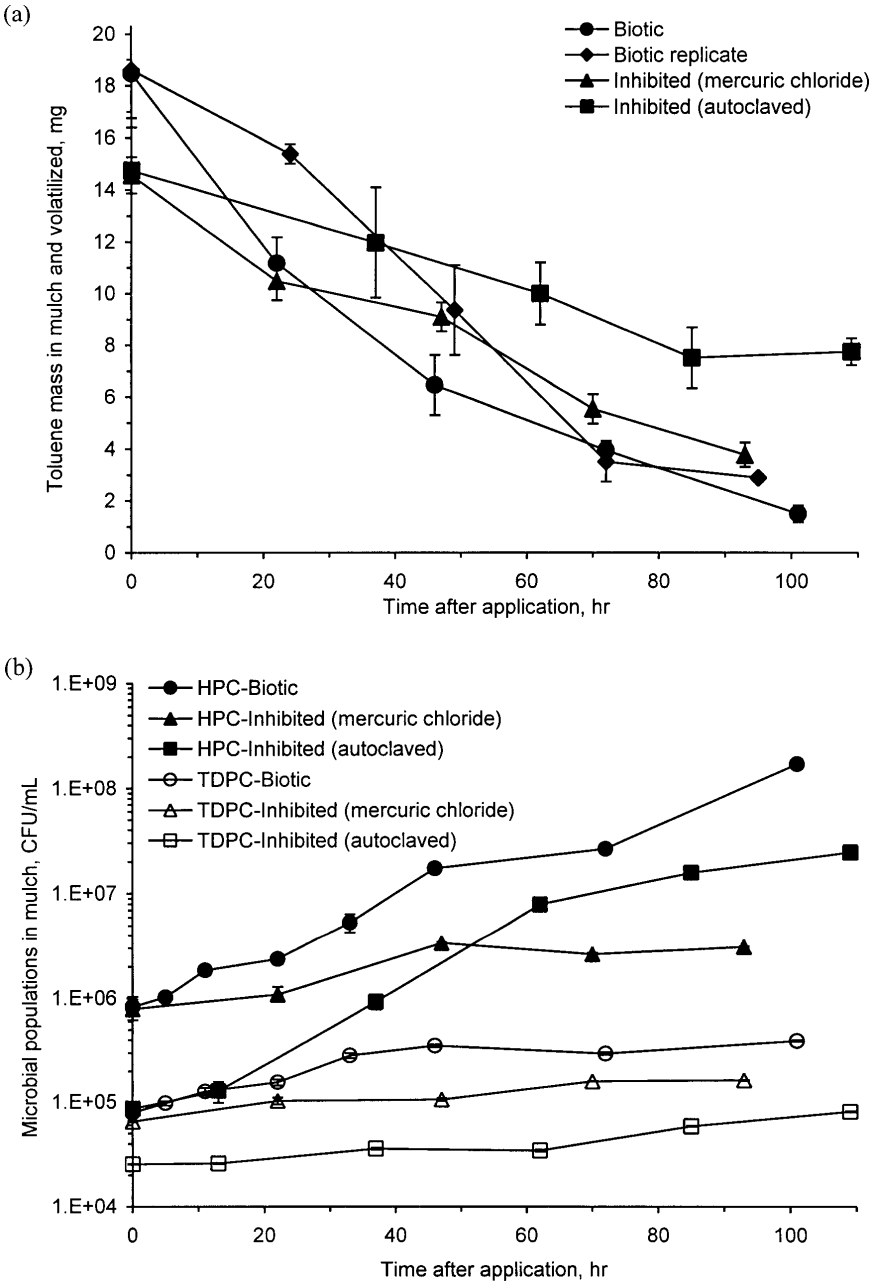

Figure 5—Phase 2 results for the dissolved toluene experiments: (a) Average mass of toluene in the mulch and activated carbon of the biotic, biotic replicate, and inhibited-control reactors, and (b) average total heterotrophic plate counts (HPC) and toluene-degrader plate counts (TDPC) in the mulch of the biotic and inhibited-control reactors (biotic replicate data not shown for clarity). Error bars represent ± one standard deviation.

of oil during Phase 2. The results of this analysis show a significant amount of experimental variability [Figure 7(a)], possibly because of the mulch not being mixed sufficiently to provide a homogeneous oil distribution for the sampling after Phase 1 (although this did not cause any noticeable problems in the other experiments). Based on these data, approximately 92% removal of oil from the mulch occurred in the biotic reactor 10 days after the end of Phase 1. Removal of most oil in the biotic reactor was found to occur during the first few days, with more than half of the oil degraded within 3 days. Based on the relatively short retention times observed for naphthalene and toluene (6.1 and 2.1 minutes, respectively), most of the peaks appearing in the oil chromatograms (Figure 6) between 10 and 50 minutes may be because of large aliphatic hydrocarbons (Koma et al., 2001), which are considered to be easily biodegradable under aerobic conditions (Eweis et al., 1998). On the other hand, only approximately 20% removal of oil was observed in the control reactor within 9 days. In fact, although the analytical deviations are large in some samples, no obvious decrease in oil mass in the inhibited-control experiment was noted in Phase 2 through day 9. Overall, these results indicate that the sorbed oil was bioavailable and that no significant biodegradation of oil occurred during the inhibited-control experiment.

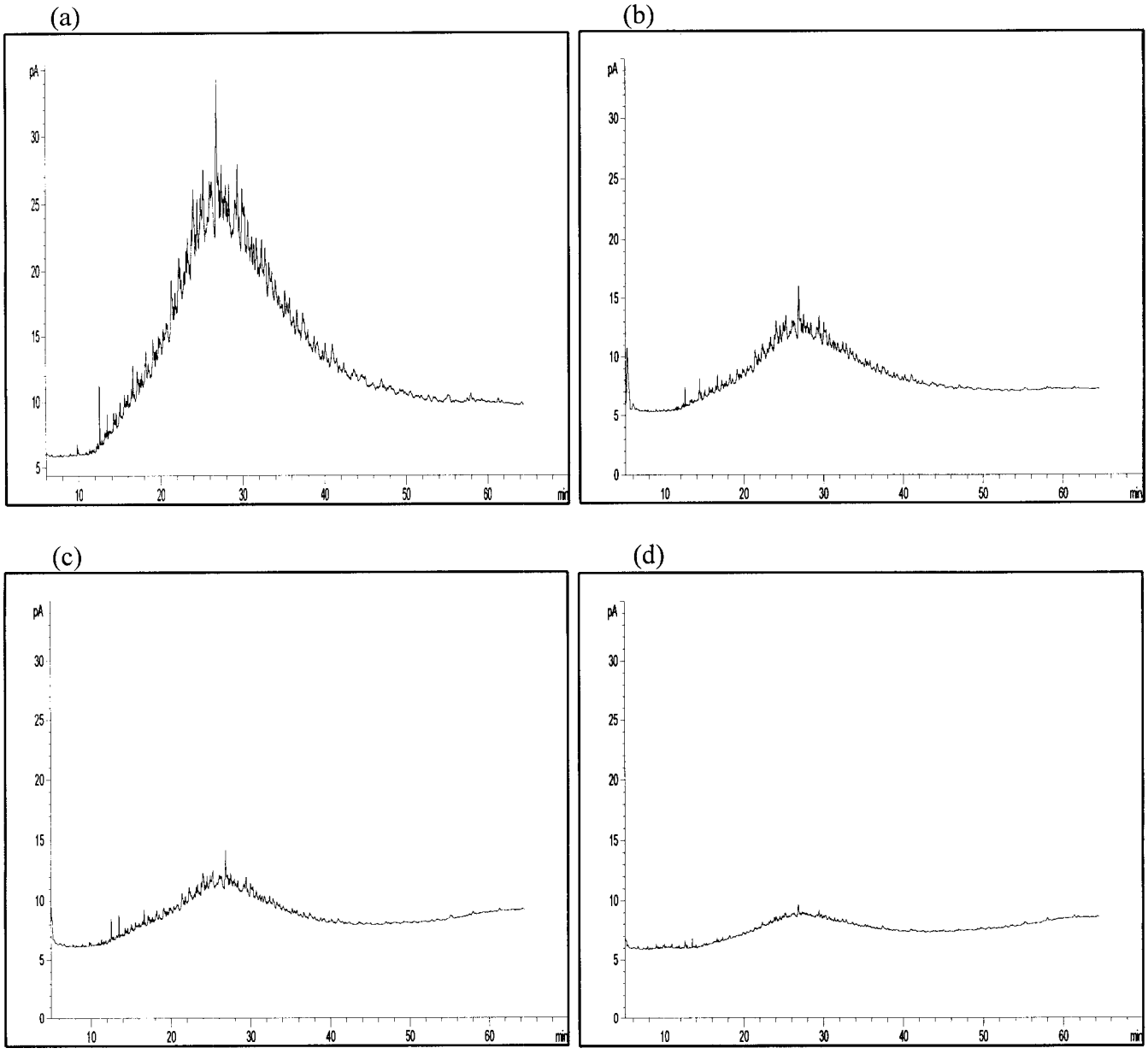

Figure 6—Representative gas chromatograms of oil extracted from the mulch during Phase 2 in the biotic experiment at times (a) 0, (b) 2, (c) 3, and (d) 10 days, and in the inhibited-control experiment at times (e) 0, (f) 5, and (g) 11 days.

Interestingly, the oil-degrader MPN count and HPC data showed an initial increase followed by decreasing trends after a few days in the biotic reactor [Figure 7(b)]. The increases in the first 1 to 2 days correlate well with the initial loss of the majority of oil. In general, the native microorganisms seemed to tolerate and use the new carbon source quickly, with no lag time. This immediate growth of oil degraders after the introduction of oil is consistent with the findings of other investigators using soils (e.g., Delille and Delille, 2000; Margesin and Schinner, 1999). On the other hand, in the inhibited-control, a lag for oil-degrading bacterial growth appeared, and microbial activities of the oil degraders were significantly inhibited throughout Phase 2.

The time to reach approximately 90% removal of oil (approximately 8 days) in the biotic reactor was much longer than that of naphthalene (approximately 3 days) and toluene (approximately 4 days). The oil is a complex mixture of hydrocarbons, some of which require more time for biodegradation. In addition, substrate interactions between petroleum hydrocarbons may inhibit biodegradation (Yerushalmi and Guiot, 1998). However, it is also possible that the longer time needed for degradation is simply because of the higher concentration of dissolved oil hydrocarbons that was introduced in this experiment, as compared to the concentrations of the individual target compounds.

Particulate-Associated Naphthalene Experiments. Particulate-associated naphthalene experiments were performed with a total influent concentration of approximately 1.6 mg/L naphthalene (3.2 mg/h surface loading), of which 17 and 27%, respectively, was sorbed onto the soil in the influent of the biotic and inhibited-control experiments. The results of both experiments demonstrated approximately 98% removal of total and dissolved naphthalene

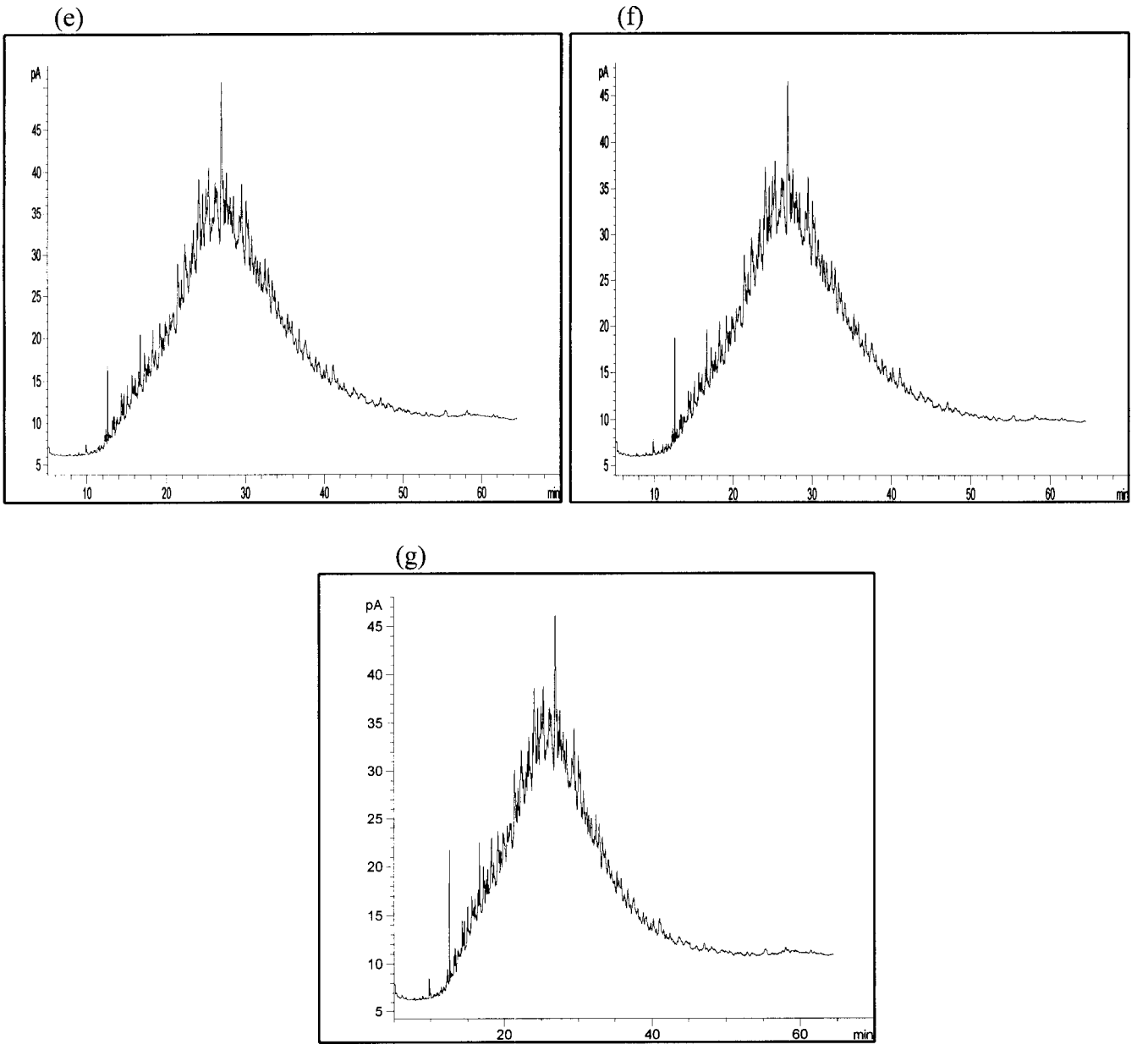

Figure 6—Continued.

during Phase 1 [Figure 8(a)]. The higher removal efficiency of total naphthalene from the influent in these experiments (approximately 98%) compared to the dissolved naphthalene experiments (approximately 90%) may be attributed to the excellent filtration of naphthalene-sorbed particulates. In both experiments, the influent TSS concentrations increased with time because not all the solids were homogeneously distributed in the influent bottle, even though mixing was provided, causing an accumulation of solids as time elapsed [Figure 8(b)]. The effluent TSS concentration data support the visual observations of filtration of solids by the mulch layer. All of the effluent TSS concentrations, including those for a preliminary experiment (influent TSS = 190 mg/L) with no hydrocarbon contaminant (data not shown) and a control without the input of particulates, demonstrated similar trends [Figure 8(b)], decreasing to very low levels (approximately 2.3 to 10.5 mg/L) at the end of the Phase 1. This suggests that the residual solids in the effluent were mainly resulting from the particles flushed from the mulch and not from the soil particles introduced. Initial effluent TSS concentrations were extremely high, exceeding 1000 mg/L in all experiments, but they dropped quickly to less than 100 mg/L within 1 hour. These results demonstrate that the particulates in the synthetic runoff, which may contain associated contaminants, will be filtered by the mulch layer in a bioretention system, with the potential for even further removal by the underlying soil layer. Even though most particulates appeared to be accumulated on the surface of the mulch, little water-head buildup was observed on the mulch. From a practical perspective, this provides a real benefit of using mulch as a top layer material on a bioretention system.

The mass-balance analyses on naphthalene at the end of the Phase 1 are shown in Table 2. Volatilization was assumed to be negligible according to the dissolved naphthalene experiments, and these Phase 1 experiments were performed without the reactor lid

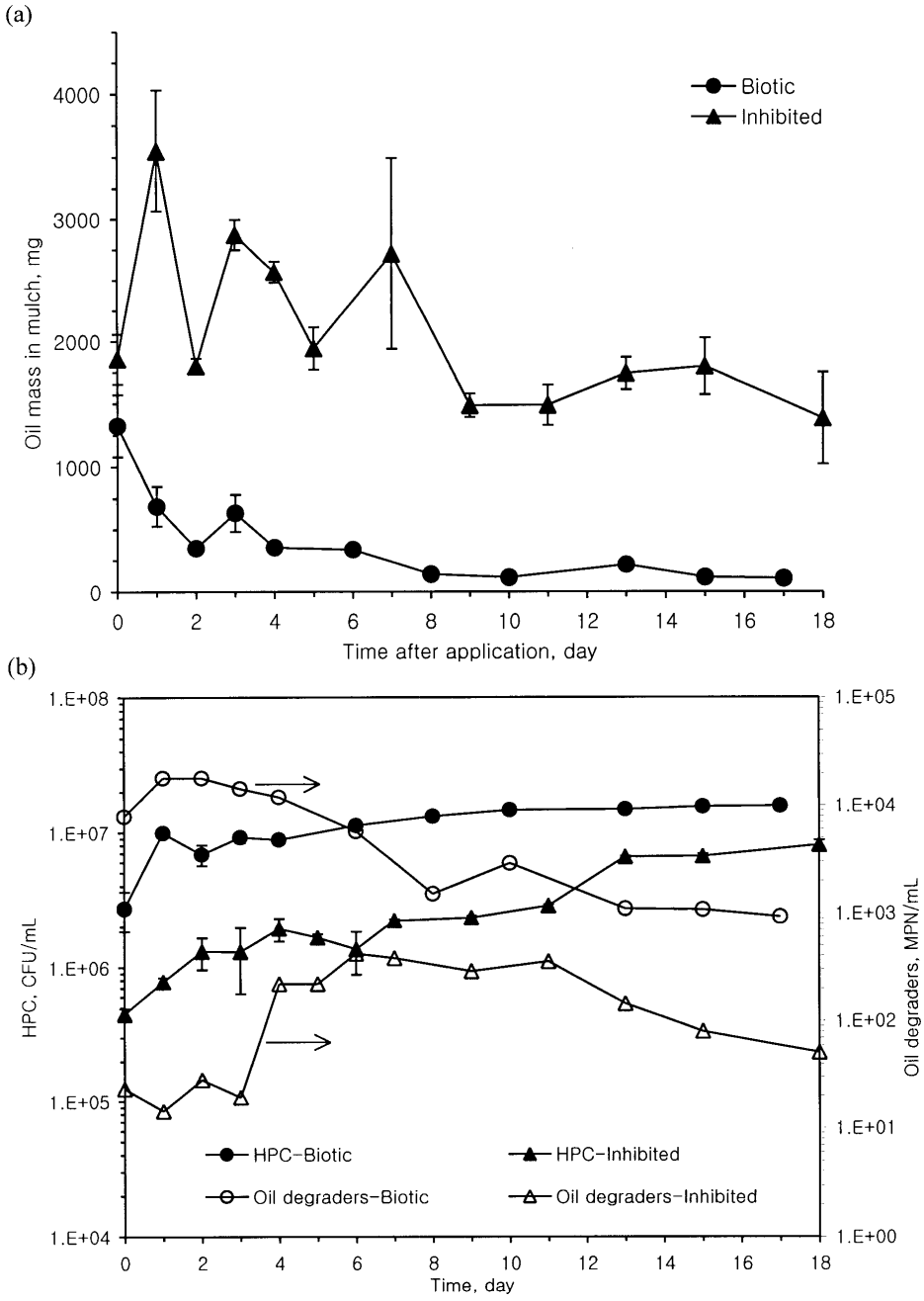

Figure 7—Phase 2 results for the motor oil experiments: (a) Average mass of oil in the mulch; and (b) average total heterotrophic plate counts (HPC) and oil-degrader counts (MPN) in the mulch. Error bars represent ± one standard deviation.

(covered with aluminum foil instead) to simplify introduction of the particulates. A higher fraction of the naphthalene remained in the mulch phase than in the dissolved naphthalene experiments because the particulate-associated naphthalene was directly filtered by the mulch layer.

The degradation patterns in the biotic and inhibited-control reactors were clearly different during Phase 2 (Figure 9), with negligible losses resulting from volatilization, in both cases. In the biotic experiment, approximately 95% naphthalene removal from the solid phase occurred via biodegradation within 3 days (62 hours), with most of the removal occurring during the first day (approximately 75%). Furthermore, the results demonstrate that biodegradation of particulate-associated naphthalene, filtered or sorbed by the mulch layer, proceeded just as did that of dissolved naphthalene trapped by sorption (compare to Figure 3). In addition, the mass of particulate-associated naphthalene input to the biotic reactor was 3.2 mg; thus, it appears that the particulate-associated naphthalene was biodegraded because the mass of naphthalene in the mulch was reduced to 0.2 mg.

Similar to the findings in the dissolved-naphthalene experiments, a gradual increase of the microbial population in the mulch was observed in the biotic reactor, without any lag time, corresponding to the loss of naphthalene. The total heterotrophic microorganisms and naphthalene degraders were inhibited by the $HgCl_2$ treatment,

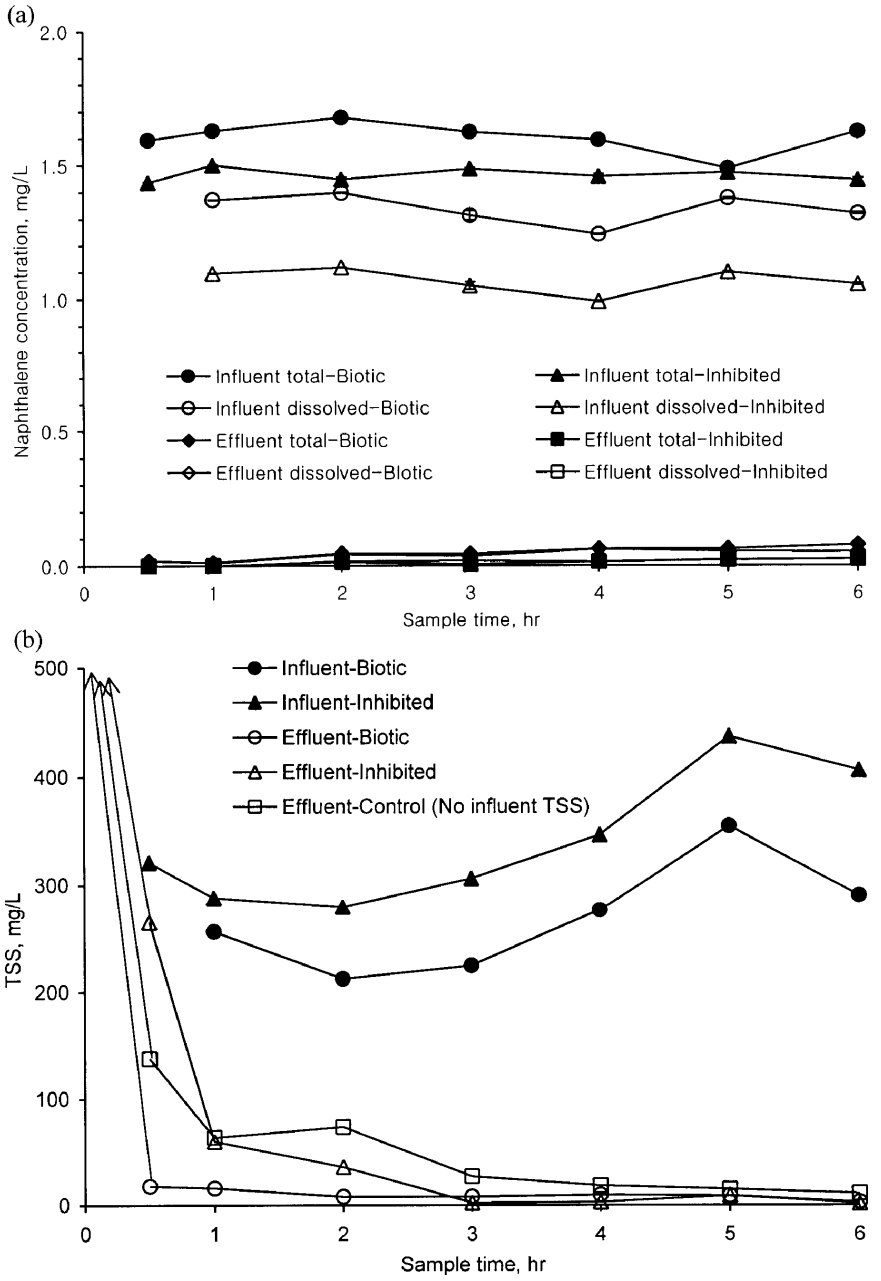

Figure 8—Naphthalene and total suspended solids (TSS) data for the aqueous phase during the Phase 1 simulated storm events in the particulate-associated naphthalene experiments: (a) Influent and effluent average total and dissolved naphthalene concentrations, and (b) influent and effluent TSS concentrations. Initial effluent TSS values (at t = 0) exceeded 1000 mg/L and are not shown. Error bars represent ± one standard deviation.

causing an approximately three and two orders of magnitude decrease in the populations, respectively, at the beginning of the Phase 2. However, the slow decrease of naphthalene with time in the control reactor mulch phase apparently occurred because of regrowth of the naphthalene degraders, despite the low initial population.

Overall, the Phase 2 results indicate that the particulate-associated naphthalene was available to the microorganisms, similar to the sorbed naphthalene on the mulch layer. However, the naphthalene was freshly sorbed to the soil particles in these simulations, whereas the compounds sorbed on the particulates under field conditions may have undergone some degree of aging, which may render them less available for desorption and biodegradation (Alexander, 1995; Steinberg et al., 1987).

Summary and Conclusions

In general, the results demonstrated that the mulch layer efficiently removed the hydrocarbon contaminants from the synthetic runoff during the simulated storm events (Phase 1) and facilitated biodegradation of these contaminants after the capture (Phase 2). This was true for all four different contaminant types and forms that were investigated: (1) dissolved naphthalene (approximately 90% removed from runoff), (2) dissolved toluene (approximately 83%),

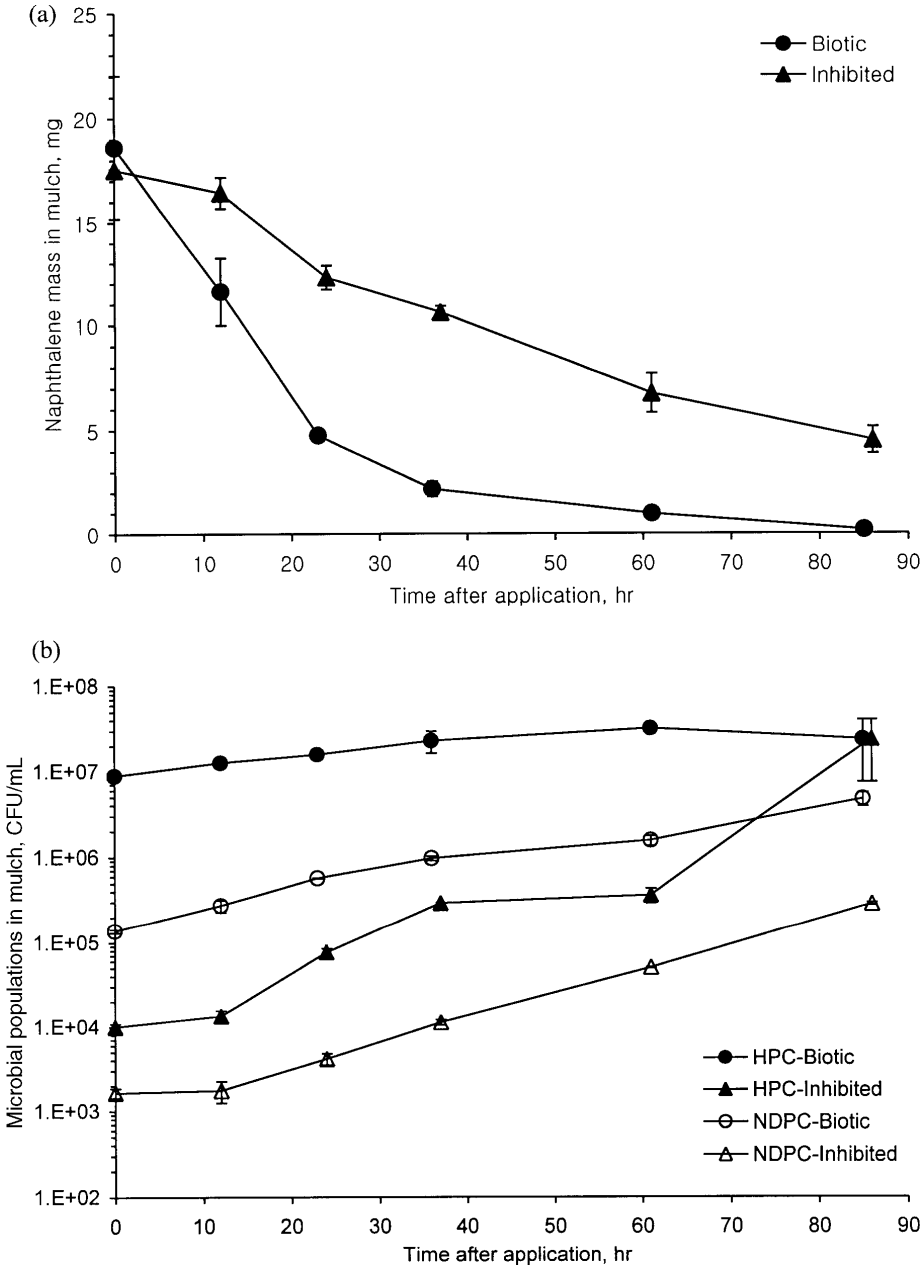

Figure 9—Phase 2 results for the particulate-associated naphthalene experiments: (a) Average mass of naphthalene in the mulch; and (b) average total heterotrophic plate counts (HPC) and naphthalene-degrader plate counts (NDPC) in the mulch. Error bars represent ± one standard deviation.

(3) dissolved motor oil (approximately 80%), and (4) particulate-associated naphthalene (approximately 97%). Biodegradation of the contaminants sorbed in the mulch layer was demonstrated by the decrease in the contaminant concentration in the mulch and the corresponding increase of the total heterotrophic microbial populations and the specific contaminant-degrader populations.

Overall, several advantages are gained by placing a thin (approximately 3 cm) surface-mulch layer on a bioretention facility (or other type of stormwater infiltration system) for O&G removal. First, it appears that high contaminant removal efficiency can be achieved by the mulch to treat both dissolved and particulate-associated hydrocarbon contaminants. Second, a relatively short time is needed (3 to 4 days with single contaminants and a maximum 10 days with the higher oil contamination) to degrade the trapped contaminants after the storm event, and no accumulation of hydrocarbons occurs, demonstrating that this is a sustainable process. Third, because the native microbial population in the mulch tested has been found to have an appropriate O&G biodegradation capacity, it is not necessary to inoculate the mulch with specific microorganisms. In addition, after exposure of the mulch to the contaminants, an increased population of contaminant-degrading microorganisms is available for biodegradation during a subsequent re-exposure. Furthermore, the moisture content of the mulch layer did not decrease drastically after the simulated storm event under an air stream, which will be beneficial for microorganisms in the mulch and in the soil below. Fourth, incomplete

inhibition of microbial populations using high levels of $HgCl_2$ suggests that the likely presence of trace levels of toxic heavy metals in stormwater runoff may not significantly decrease microbial degradation of contaminants. Fifth, the mulch layer has high permeability; therefore, it should not cause significant water-head buildup on the bioretention surface, so that the runoff can readily infiltrate to the soil layer below.

The O&G removal demonstrated in this research, coupled with the pollutant removals shown in previous studies (Davis et al., 2001 and 2003; Kim et al., 2003), suggests the great potential for water-quality improvement via conventional bioretention systems and the possibility for greater pollutant removal and sustainable operation through re-engineering.

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