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Sediment profiles of less commonly determined elements measured by Laser Ablation ICP-MS

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ABSTRACT

Anthropogenic influences on trace element profiles in dated sediments from estuaries have been often documented, with the vast majority of studies focusing on a short list of high-abundance trace elements. Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) provides a new approach that minimizes sample preparation and contamination while yielding data on a much larger list of elements simultaneously. We present concentrations and enrichment factor profiles for 22 elements at a locality that is 50 km southeast of Baltimore, the principal industrial city on Chesapeake Bay. Samples representing deposition over almost the entire 20th century were obtained from two archived cores collected 20 years apart. The following elements exhibit profiles consistent with a strong anthropogenic influence, i.e. enrichment after 1920 followed by decline after ca.1980, possibly reflecting increased regulatory efforts: Mn, Co, Cu, Zn, Ag, Cd, In, Sn, Sb, Te, Tl, Pb and Bi. As expected, the redox-sensitive elements: Mo, Re and U have similar profiles to one another. Previously, the potentially hazardous elements, Ag, In, Sb, Te, Tl and Bi, have been measured only rarely in estuarine sediments and never in Chesapeake Bay. Our discovery that their profiles track those of well-known pollutants underscores a need to investigate their sources, transport and biogeochemical behavior. Several rarely determined trace elements, Ga, Ge and Nb, exhibit trendless profiles, as do the major elements, Ti and Fe.

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1. Introduction

The goal of this investigation is to harness the analytical power of Laser Ablation ICP-MS to explore the behavior of a large suite of trace elements in Chesapeake Bay sediment cores. The cores cover the 20th century and can provide useful historic information about anthropogenic effects and redox conditions in the Bay.

Chesapeake Bay is the largest estuary in the United States and one of the largest in the world. It was the first estuary in the United States to be occupied permanently by Europeans. Chesapeake Bay has been adversely affected by over-fishing and pollution from a variety of sources such as manufacturing plants, agricultural runoff and atmospheric deposition of contaminants from sources such as inland coal-fired power-plants. The extensive efforts to restore the Bay such as the “Save the Bay” initiative have had limited success.

Numerous other authors have explored concentrations of trace elements in Chesapeake Bay. Those concerned with pollution and remediation have focused on a rather narrow list of elements: e.g. Cr, Ni, Cu, Zn, As, Cd, Hg and Pb, (Helz et al., 1975; Helz, 1976; Sinex and Helz, 1981, 1982; Riedel et al., 1997, 1999; Riedel

and Sanders, 1998; Beyer et al., 1998; Lawson and Mason, 2001; Lawson et al., 2001; Zheng et al., 2003; Mason et al., 2004). Those concerned with redox conditions (Miller, 1992; Colodner et al., 1993; Shaw et al., 1994; Adelson, 1997; Adelson et al., 2001) have focused on Mo, Re and U.

The power of LA-ICP-MS affords an opportunity to greatly expand these lists of trace elements. In LA-ICP-MS, a laser beam is focused onto a sample and material is removed through a series of photochemical, photothermal and physiochemical processes, which results in the formation of a nanosecond plasma jet above the sample followed by condensation of submicron-sized particles and transport of these particles to the plasma torch of the mass spectrometer. These particles are introduced into the torch where they are disassociated into atoms and turned into ions, which are then introduced into the orifice of the mass spectrometer; there positive ions are separated from electrons and then mass-separated and counted.

From its inception, LA-ICP-MS has been used to characterize geological materials such as rocks, minerals and mineral inclusions (Gray, 1985; Darke et al., 1989; Balaram et al., 1990), soils and sediments (Crain et al., 1992; Durrant and Ward, 1993; Baker et al., 1999; Lee et al., 2003; Rauch et al., 2006) and ice cores (Reinhardt et al., 2001, 2003). LA-ICP-MS has been used to determine mercury in sediments from Minamata Bay, Japan, with a precision of about

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5% (Tao et al., 2002). Lake sediment cores have been analyzed using the spatial resolution capabilities of LA-ICP-MS (Rauch et al., 2006). In that work, two core sections were analyzed to produce concentration profiles for Al, Si, Fe, S, As, Cu and Zn at a resolution of 0.25 mm. Such detailed resolution was possible because the layering of the accumulated sediments was preserved by freeze-coring.

In this work we describe a LA-ICP-MS method for the analyses of Chesapeake Bay sediments.

2. Experimental section

2.1. Samples and sampling sites

Three standard reference materials (SRM) were employed in this work. NIST 610 consists of 61 certified trace elements in a plug of polished glass and is widely used during analysis of geological materials. Details about this SRM can be obtained from the NIST website (Reed, 1992). SCo-1 is a Cody Shale powder from Natrona County, Wyoming and MAG-1 is a marine mud powder from the Wilkinson Basin of the Gulf of Maine (Schultz et al., 1976). Both of these materials were prepared by the US Geological Survey in a similar fashion which involved mechanical crushing until 80% of the material could pass through a 200-mesh screen (Flanagan, 1967). The reference values used for all three SRMs were obtained from the online database GeoReM (Jochum et al., 2005; Jochum, 2008; Jochum and Willbold, 2006). NIST610 and SCo-1 were used solely to evaluate accuracy and precision while MAG-1 was used to calculate final concentrations as described below (Dolor, 2009).

All Chesapeake materials studied were archived samples. Sample localities are depicted in Fig. 1. Core 55 (38°48.5'N; 76°23.5'W), is a gravity core collected in July 1979 by the Maryland Geological Survey in a water depth of 25 m (Helz et al., 1985a, 1985b; Adelson, 1997; Adelson et al., 2001). A mass accumulation rate of $0.41 \text{ g cm}^{-2} \text{ y}^{-1}$ was determined by Helz et al. (1985b) using excess ^{210}Pb and $^{239,240}\text{Pu}$ (after excluding a homogeneous layer deposited during Hurricane Agnes). An X-ray radiograph of the core as well as mathematical modeling of the ^{210}Pb and $^{239,240}\text{Pu}$ profiles (Officer et al., 1984) reveals no evidence of turbation. The sediment consists predominantly (>70%) of clay-sized particles (<4 μm) with the rest being silt-sized material (<63 μm).

Core RD (38°53.2'N; 76°23.5'W), is a piston core collected in November 1998 by the US Geological Survey. It was collected in a water depth of 26.5 m and was located 9.2 km north of core 55. Both core sites lie in the Bay's deep central trough which contains fine-grained mud. Owing to seasonal anoxia in this trough, the sediments are minimally disturbed by burrowing organisms. Based on excess ^{210}Pb , as confirmed by ^{137}Cs , ^{14}C , total Pb and ragweed pollen, the mass accumulation rate in core RD declines from $1.21 \text{ g cm}^{-2} \text{ y}^{-1}$ in the top 75 cm to $0.78 \text{ g cm}^{-2} \text{ y}^{-1}$ at the deepest level for which we have analyses (Zimmerman and Canuel, 2002).

In order to evaluate external influences on compositions of sediments at these sites, a number of samples from sites around the Bay were also analyzed. Three samples (Susq 8–10 cm, 28–30 cm and 44–46 cm with ^{210}Pb ages of 1977, 1972 and 1968.5, respectively) from a core in the Conowingo reservoir (39°57.0'N; 76°23'W) in the Susquehanna River were analyzed to characterize material entering the Bay from the watershed (Cantillo, 1982; Helz et al., 1985a).

Baltimore Harbor samples (B'more Harbor H, M and N; Sinex and Helz, 1982) were collected May/June 1981. Baltimore harbor has been intensely contaminated by industrial activities, and these cores in particular contain extremely high Cr and Zn concentrations.

Sediments obtained with a clamshell sampler on a traverse from shallow to deep water near cores 55 and RD (Water depths 3.4 m, 6.7 m and 26.2 m) were analyzed to see if there is an effect

of water-depth on sediment composition. These samples were collected on June 2, 1977 (Sinex, 1981; Sinex and Helz, 1981; Helz et al., 1985a).

Core PC-6 (38°32.66'N; 76°23.14'W) was collected about 30 km south of core 55 in 20 m water depth (Helz et al., 2000; Adelson et al., 2001). These samples were from horizons deposited before the 18th century (as determined from pollen evidence). They were analyzed to obtain further information on the background levels of the elements of interest before eutrophication and industrial pollution.

A Miocene shore deposit was also analyzed (Fairhaven unit of the Calvert Formation). One of the major sources of sediment to northern Chesapeake Bay is erosion of unconsolidated sediments of the Atlantic Coastal Plain (Biggs, 1970; Schubel, 1968) This sample is rich in redox-sensitive elements, probably due to a period of high productivity along the Atlantic Coast approximately 15 million years ago (Ferri, 1977; Helz et al., 2000).

All samples except those from core RD were dried (110 °C) and then crushed with a mullite mortar and pestle to eliminate clumps formed during drying. Subsequently, samples were stored in glass bottles at room temperature. Core RD samples were stored frozen until needed and then dried, crushed and packaged in polyethylene bags.

2.2. Procedures

Most previous authors have incorporated binding agents into powdered samples prior to pressing them into pellets for Laser Ablation (Crain et al., 1992; Denoyer, 1992; Williams and Jarvis, 1993; Morrison et al., 1995; Lee et al., 2003; Rauch et al., 2006). Binding agents can create high blanks. Additionally, using a binding agent dilutes the sample (Denoyer, 1992; Rauch et al., 2006). In this work we avoided binding agents and their associated analytical issues, relying on the ~3% organic matter inherent in our samples to provide sufficient binding during pelletization. Other authors have done this and reported precise and accurate results (Durrant and Ward, 1993; Tao et al., 2002).

To make 9 mm circular pellets, approximately 50 mg of a sample was inserted into a die (316 stainless steel) that is commonly used to make KBr pellets for infrared spectroscopy. The die was placed into a workbench clamp and tightened with a wrench. This formed pellets robust enough to remain whole during ablation. Between samples the die was cleaned with deionized water followed by acetone to accelerate drying.

The LA-ICP-MS instrument included a New Wave Nd-YAG (Neodymium doped: Yttrium aluminum garnet; Nd:Y₃Al₅O₁₂) laser and a Thermo ELEMENT2 double focusing magnetic sector field ICP-MS (Brenan et al., 2005). An ultraviolet laser was used since it produced less elemental fractionation than infrared lasers (Cromwell and Arrowsmith, 1995). The output of the Nd:YAG laser (1064 nm) was frequency quintupled (to 213 nm) using non-linear crystals. Typical laser settings are outlined in Table 1.

The ablation cell of the laser system was flushed with helium, which has been found to enhance sensitivity compared to argon (Eggins et al., 1998; Gunther and Heinrich, 1999; Bleiner and Gunther, 2001; Brenan et al., 2005). Laser power output was evaluated daily during tuning and was not changed throughout the course of the day. This value was usually 45% (equivalent to ~2 J cm⁻²). Tuning to optimize instrument output was performed by monitoring ^{43}Ca , ^{238}U , ^{232}Th and $^{232}\text{Th}^{16}\text{O}$ while ablating NIST 610. Desired values were $\text{Ca} \geq 50,000$ counts per second (cps), $\text{U} \geq 150,000$ cps, and $\text{ThO/Th} \leq 0.03$. Table 1 also summarizes typical instrument parameters.

Spot size, ablation frequency and power output of the laser system was adjusted to ensure that the power density remained at optimal values of between 1.5 and 2.5 J cm⁻². This photon fluence

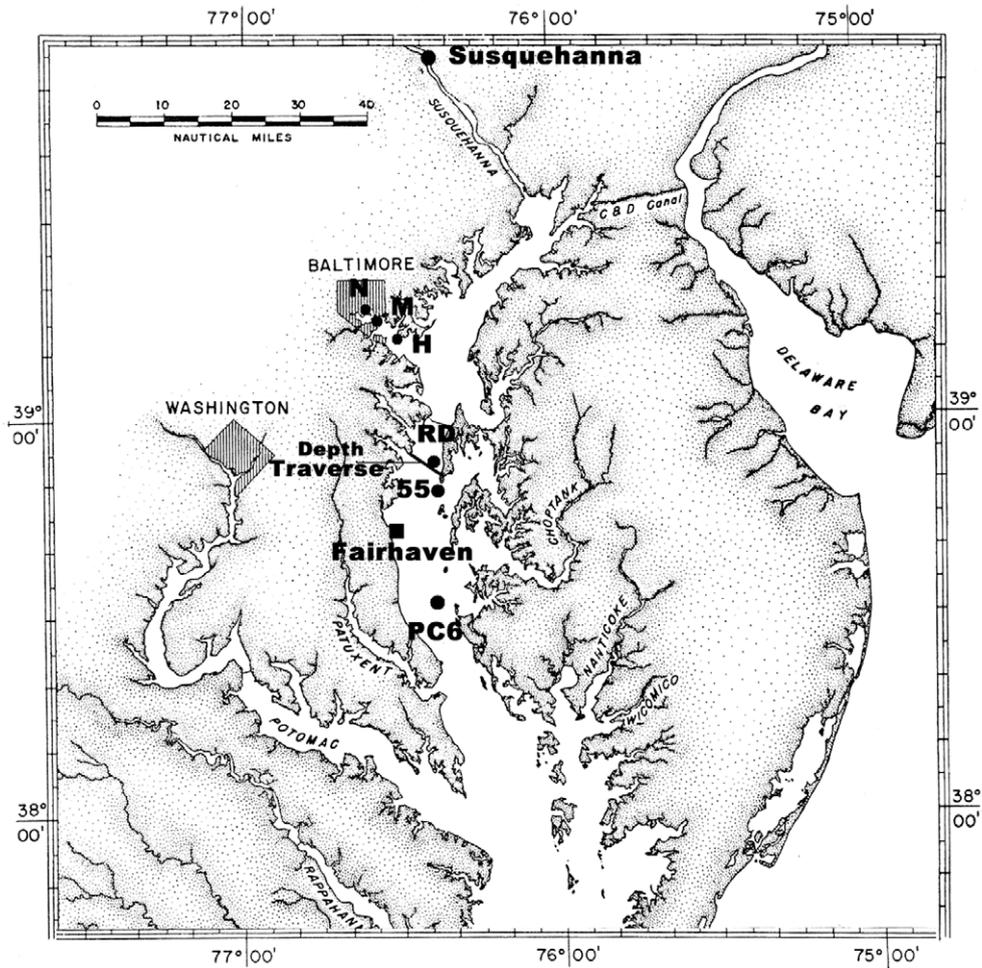


Fig. 1. Map showing location of samples.

produces sufficient energy to ensure effective photon-material coupling during ablation. Laser line widths of 100 μm were used for MAG-1, SCo-1 and samples, while widths of 15 μm were used for NIST 610. In the first two cases, larger line widths were used because of weak signals from low concentrations of Re, Te, and Ag. In preliminary experiments an ablation frequency of 8 Hz was used, but this required 40 μm line widths for NIST 610 in order to obtain

sufficient signal for all elements, and we expected to need at least 250 μm spot sizes for MAG-1, SCo-1 and sediment samples. Increasing the ablation frequency from 8 to 20 Hz produced satisfactory results, and further experiments with different line widths and frequencies were not undertaken.

The particular isotopes analyzed (Table 2) were chosen on the basis of prior knowledge of isobaric interferences, as well as a

Table 1
LA-ICP-MS operating conditions.

ELEMENT2 ICP-MS	
Rf power	1200 W
Cooling gas (Ar) flow rate	16 L/min
Auxiliary gas (Ar) flow rate	0.8–1.2 L/min
Sample gas (Ar) flow rate	0.6–1.0 L/min
Additional 1 (He) flow rate	1.06–1.10 L/min
Monitoring ions	Refer to Table 2
Acquisition type	Peak hopping
Samples per peak	1
Sample time for most elements*	10 ms
Sample time for Re and Te	40 ms
Laser Ablation	
LA system	New wave Nd-YAG
Wavelength	213 nm
Scan method	Translational line
Ablation frequency	20 Hz
Power density	1.5–2.5 J cm ⁻²
Measurement delay	25 s
Spot size	15 and 100 μm
Stage translation speed	10 μm/s

Table 2
Isotopes analyzed via LA-ICP-MS.

Isotope	Isotopic mass	Isotopic abundance	Isotope	Isotopic mass	Isotopic abundance
S	33	0.75	Mo	95	15.90
CaO	43	0.14	Mo	97	9.60
Ti	49	5.50	Ag	107	51.80
V	51	100.00	Cd	111	12.80
Mn	55	100.00	In	115	95.70
Fe	57	2.14	Sn	118	24.10
Co	59	100.00	Sb	121	57.21
Ni	60	26.10	Sb	123	42.79
Cu	63	69.20	Te	125	7.00
Zn	66	27.90	W	184	30.70
Ga	69	60.10	Re	185	37.40
Ge	72	27.40	Re	187	62.60
As	75	100.00	Tl	205	70.50
Se	77	7.60	Pb	208	52.40
Nb	93	100.00	Bi	209	100.00
			U	238	99.30

desire to reduce differences in signal size between major and minor elements of interest. For major components (Ti and Fe) one of the less abundant isotopes was selected. For elements where more than one isotope was analyzed (Mo, Sb and Re), the abundance corrected concentrations were averaged. This was possible because there was good agreement between the abundance corrected concentrations for these elements.

Each analysis consisted of 20–40 s with the laser on with the shutter closed to obtain a background signal, followed by 70–90 s with the shutter open to collect the ablation signal (Fig. 2). Horizontal translation of the sample stage (at a rate of $10 \mu\text{m s}^{-1}$) during sampling resulted in a track that was approximately 1.5 mm long. A 50–70 s steady plateau of counts was extracted from the ablation signal to determine element concentrations (Lundstrom et al., 2006).

The method of data analysis used in this work requires prior knowledge of the concentration of one element in both the samples and the calibration materials (SRM's). This internal standard is used to correct for variations in ablation efficiency. A common practice has been to create an internal standard by adding a swamping concentration of one element to each sample. We wished to avoid such sample amendments and therefore, used natural Mn concentrations, which were measured in the fine-grained sediments and SRMs via ICP-MS analyses as described in Section 2.3. Manganese occurs in sediments largely as Mn-oxyhydroxide grain coatings and thus tends to be evenly dispersed in sediments. Fig. 2 demonstrates that the Mn signal, although subject to fluctuations, displays no irregularities suggestive of spatial heterogeneities that are large at the scale of a $100 \mu\text{m}$ laser beam.

For solution analyses a Finnigan Element 2 ICP-MS instrument, interfaced with a cyclonic spray chamber was used to determine the internal standard, Mn, in bulk sediment samples. Approximately 0.2 g of each sediment sample was digested via the open-vessel digestion method (Langmyhr, 1967; Van-Loon, 1985) using Trace Metal Grade or better purity acids. A seven-point external calibration curve was used and both samples and standards were spiked with a 3 ppb yttrium internal standard to monitor analytical-drift (Dolor, 2005).

2.3. Data analysis

Raw counts per second data from the LA-ICP-MS instrument were imported into the LAMTRACE program (Brenan et al., 2003; Coedo et al., 2004; Wheeler et al., 2006). This program calculates the concentration of element, X, in the sample ($C_{X,SAM}$) relative to the literature value of the concentration of X in the standard refer-

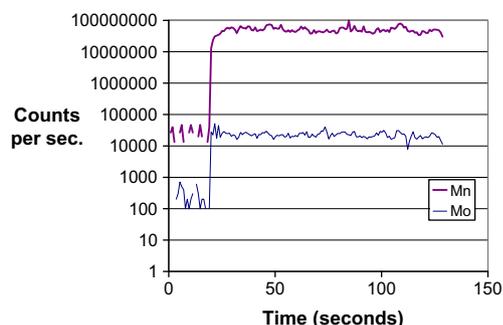


Fig. 2. Time-resolved LA-ICP-MS spectra illustrating background vs. signal levels and uniformity of counts in a Chesapeake Bay sample. Each analysis consisted of 20–40 s with the laser on and the shutter closed to obtain a background signal, followed by 70–90 s with the shutter open to collect the ablation signal. While the shutter was opened, the laser traversed $1.0 \text{ mm} \times 0.1 \text{ mm} = 0.1 \text{ mm}^2$ of area on the sample surface.

ence material ($C_{X,SRM(LIT)}$) (Longerich et al., 1996). In our work, MAG-1 was the SRM. The internal standard, Mn, is employed to correct for ablation efficiency differences between the sample and standard.

Eqs. (1)–(3) outline the calculations performed by LAMTRACE. The background corrected signal from element X in the sample ($I_{X,SAM}$) was calculated by subtracting the mean signal obtained before the laser impinged on the sample from the mean signal obtained while the sample was being ablated (see Fig. 2). The background corrected signal of Mn in the sample ($I_{Mn,SAM}$) was calculated in the same manner. Because the concentration of Mn in the sample ($C_{Mn,SAM}$) is known, a provisional value for the concentration of X in the sample ($C_{X,SAM}^*$) can be obtained:

$$C_{X,SAM}^*/C_{Mn,SAM} = I_{X,SAM}/I_{Mn,SAM} \quad (1)$$

$C_{X,SAM}^*$ would be a correct determination of the concentration of X in the sample only if the instrumental efficiency for both X and Mn were identical, which need not be true.

An instrumental efficiency correction is applied by making use of an SRM. First, a provisional value of the concentration of X in the SRM is determined just as the equivalent quantity was determined in the sample:

$$C_{X,SRM}^*/C_{Mn,SRM} = I_{X,SRM}/I_{Mn,SRM} \quad (2)$$

Then the true concentration of X in the sample ($C_{X,SAM}$) is calculated by assuming that the ratio of true to provisional concentrations is the same in the sample and the SRM. The true concentration of X in the SRM is taken to be the certified or recommended value obtained from the literature:

$$C_{X,SAM}/C_{X,SAM}^* = C_{X,SRM(LIT)}/C_{X,SRM}^* \quad (3)$$

Inherent in this approach is an assumption that relative instrumental efficiency for X and Mn in the sample and the SRM are the same. Therefore, the sample and SRM should have similar physical and chemical properties. This requirement dictated the choice of MAG-1, a fine-grained marine sediment, as the SRM.

3. Results and discussion

We present the concentrations of the elements in Table 3. The uncertainties shown are standard deviations of four replicate analyses obtained from different laser tracks over the same sample pellet.

In Fig. 3 we present some method comparisons based on previously published independent analyses of the same samples analyzed in this work. The vertical axis indicates results obtained by different operators at different times using several single-element methods; the horizontal axis indicates our results obtained simultaneously by Laser Ablation. The alternate methods were: Mn and Zn, Direct-Current Plasma Emission Spectroscopy (Cantillo, 1982, 1984); Pb, Atomic Absorption Spectroscopy (Zimmerman, 2000; Marcantonio et al., 2002); Cu, Flame Atomic Absorption Spectroscopy; and Mo, Isotope Dilution ICP-MS (Adelson, 1997; Adelson et al., 2001). Fig. 3 illustrates the impressive dynamic range of LA-ICP-MS. Concentrations spanning three orders of magnitude were determined simultaneously and agreed reasonably with results from diverse single-element methods. Except for Mo, deviations of points from the 1:1 line appear to be non-systematic, suggesting that they arise simply from random error in one or both methods being compared. The Mo points appear to lie along a line with a slope of 1.12, implying that the isotope dilution method is determining on average 12% more Mo than our LA-ICP-MS method. This kind of deviation could be caused by a systematic error in determining the Mo concentration by one of these methods.

Table 3
Concentrations of elements \pm 1st standard deviation from four replicate LA-ICP-MS analyses on the same sample pellet. Mn values were determined by solution ICP-MS on a digested sub-sample of the sediment.

Depth (cm)	Year	Ti (%)	Mn ($\mu\text{g/g}$)	Fe (%)	Co ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)	Ga ($\mu\text{g/g}$)	Ge ($\mu\text{g/g}$)	Nb ($\mu\text{g/g}$)	Mo ($\mu\text{g/g}$)	Ag ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)
CORE 55													
-1	1978.6	0.43 \pm 0.08	540 \pm 40	3.8 \pm 0.6	21 \pm 4	44 \pm 9	180 \pm 40	15 \pm 3	1.9 \pm 0.6	11 \pm 3	4.3 \pm 1.4	0.37 \pm 0.05	0.68 \pm 0.22
-9	1970	0.42 \pm 0.04	720 \pm 50	3.9 \pm 0.4	20 \pm 2	47 \pm 7	220 \pm 40	15 \pm 1	1.8 \pm 0.2	11 \pm 2	2.7 \pm 0.3	0.46 \pm 0.06	1.09 \pm 0.30
-11	1967.8	0.44 \pm 0.02	940 \pm 70	4.3 \pm 0.1	26 \pm 1	48 \pm 2	240 \pm 10	17 \pm 1	2.0 \pm 0.1	13 \pm 3	2.3 \pm 0.3	0.64 \pm 0.01	0.79 \pm 0.21
-13	1965.6	0.42 \pm 0.02	820 \pm 60	4.2 \pm 0.4	25 \pm 3	49 \pm 2	240 \pm 10	14 \pm 1	1.9 \pm 0.1	11 \pm 1	4.4 \pm 0.9	0.66 \pm 0.06	1.09 \pm 0.04
-17	1964	0.47 \pm 0.06	790 \pm 60	4.8 \pm 0.1	26 \pm 1	57 \pm 2	265 \pm 10	15 \pm 1	1.9 \pm 0.1	11 \pm 2	1.5 \pm 0.1	0.72 \pm 0.06	1.02 \pm 0.22
-21	1963.1	0.43 \pm 0.02	870 \pm 60	4.7 \pm 0.2	31 \pm 2	60 \pm 3	280 \pm 10	20 \pm 1	2.2 \pm 0.1	11 \pm 1	1.7 \pm 0.2	0.85 \pm 0.09	0.91 \pm 0.05
-27	1956.8	0.43 \pm 0.01	840 \pm 60	3.9 \pm 0.2	19 \pm 1	45 \pm 2	220 \pm 10	16 \pm 1	2.0 \pm 0.3	10 \pm 1	1.8 \pm 0.1	0.38 \pm 0.01	1.74 \pm 0.16
-33	1950.8	0.47 \pm 0.05	810 \pm 60	3.8 \pm 0.2	21 \pm 1	49 \pm 4	230 \pm 10	16 \pm 1	2.0 \pm 0.1	11 \pm 1	2.1 \pm 0.6	0.48 \pm 0.09	1.41 \pm 0.26
-45	1940.1	0.41 \pm 0.01	980 \pm 70	4.1 \pm 0.2	21 \pm 1	49 \pm 1	210 \pm 10	16 \pm 1	2.0 \pm 0.1	10 \pm 1	2.4 \pm 0.1	0.16 \pm 0.02	1.10 \pm 0.12
-51	1935.1	0.45 \pm 0.02	730 \pm 50	4.2 \pm 0.2	22 \pm 1	49 \pm 1	200 \pm 10	19 \pm 1	1.9 \pm 0.1	11 \pm 1	1.4 \pm 0.2	0.17 \pm 0.01	0.75 \pm 0.06
-55	1931.8	0.46 \pm 0.06	650 \pm 50	3.7 \pm 0.2	17 \pm 1	35 \pm 1	180 \pm 10	15 \pm 1	1.6 \pm 0.2	12 \pm 1	1.5 \pm 0.2	0.13 \pm 0.01	0.42 \pm 0.07
-59	1928.7	0.47 \pm 0.05	710 \pm 50	4.1 \pm 0.3	20 \pm 2	45 \pm 5	190 \pm 20	17 \pm 1	2.0 \pm 0.1	12 \pm 1	2.2 \pm 0.2	0.15 \pm 0.02	0.66 \pm 0.17
-69	1921	0.51 \pm 0.14	700 \pm 50	3.9 \pm 0.2	14 \pm 1	29 \pm 1	110 \pm 10	17 \pm 1	2.0 \pm 0.2	12 \pm 3	1.3 \pm 0.1	0.09 \pm 0.01	0.39 \pm 0.12
-77	1916.9	0.48 \pm 0.09	720 \pm 50	4.4 \pm 0.1	15 \pm 1	29 \pm 1	120 \pm 10	17 \pm 1	1.9 \pm 0.1	12 \pm 2	1.3 \pm 0.1	0.08 \pm 0.01	0.28 \pm 0.02
-95	1906.7	0.40 \pm 0.02	430 \pm 30	3.9 \pm 0.2	14 \pm 1	26 \pm 2	100 \pm 10	16 \pm 1	2.3 \pm 1.2	10 \pm 1	1.1 \pm 0.3	0.07 \pm 0.04	0.25 \pm 0.03
-97	1905.8	0.43 \pm 0.04	550 \pm 40	4.1 \pm 0.2	13 \pm 1	26 \pm 2	100 \pm 10	15 \pm 1	1.7 \pm 0.1	9 \pm 1	1.7 \pm 0.1	0.10 \pm 0.05	0.24 \pm 0.02
-101	1904	0.45 \pm 0.09	530 \pm 40	4.0 \pm 0.1	15 \pm 4	26 \pm 3	100 \pm 20	15 \pm 1	1.8 \pm 0.2	10 \pm 2	1.4 \pm 0.4	0.08 \pm 0.02	0.40 \pm 0.19
CORE RD													
-5	1997.8	0.40 \pm 0.05	600 \pm 40	3.6 \pm 0.2	18 \pm 1	35 \pm 2	153 \pm 6	10 \pm 1	1.7 \pm 0.1	10 \pm 1	2.3 \pm 0.4	0.22 \pm 0.04	0.59 \pm 0.18
-7	1997.3	0.39 \pm 0.04	590 \pm 40	3.7 \pm 0.2	18 \pm 1	35 \pm 1	157 \pm 6	10 \pm 1	1.8 \pm 0.1	9 \pm 1	2.2 \pm 0.4	0.24 \pm 0.03	0.64 \pm 0.05
-19	1994.6	0.44 \pm 0.05	980 \pm 70	4.2 \pm 0.3	18 \pm 1	39 \pm 2	180 \pm 8	11 \pm 1	1.8 \pm 0.1	11 \pm 3	1.9 \pm 0.1	0.32 \pm 0.10	0.63 \pm 0.16
-29	1992.3	0.51 \pm 0.16	840 \pm 60	4.8 \pm 0.6	22 \pm 1	52 \pm 5	200 \pm 20	10 \pm 1	2.1 \pm 0.2	12 \pm 2	7.0 \pm 1.9	0.33 \pm 0.08	0.79 \pm 0.20
-35	1990.9	0.42 \pm 0.05	830 \pm 60	4.0 \pm 0.3	23 \pm 1	42 \pm 2	230 \pm 10	15 \pm 1	1.7 \pm 0.1	10 \pm 1	2.4 \pm 0.3	0.51 \pm 0.11	1.31 \pm 0.48
-39	1989.8	0.46 \pm 0.14	940 \pm 70	4.1 \pm 0.3	21 \pm 2	42 \pm 3	210 \pm 10	16 \pm 2	1.9 \pm 0.1	11 \pm 2	2.0 \pm 0.2	0.45 \pm 0.08	0.94 \pm 0.34
-47	1987.8	0.42 \pm 0.03	990 \pm 70	4.2 \pm 0.2	23 \pm 1	46 \pm 3	240 \pm 20	9 \pm 1	1.6 \pm 0.1	11 \pm 1	2.3 \pm 0.1	0.65 \pm 0.31	0.83 \pm 0.09
-53	1986.2	0.45 \pm 0.02	1220 \pm 90	4.8 \pm 0.2	38 \pm 3	56 \pm 2	370 \pm 30	10 \pm 1	2.0 \pm 0.2	11 \pm 1	1.6 \pm 0.1	0.74 \pm 0.06	1.39 \pm 0.76
-59	1984.7	0.47 \pm 0.03	1210 \pm 90	4.7 \pm 0.2	30 \pm 2	51 \pm 4	320 \pm 30	12 \pm 1	2.2 \pm 0.1	11 \pm 1	1.5 \pm 0.1	0.88 \pm 0.05	1.04 \pm 0.13
-82.5	1972	0.37 \pm 0.07	690 \pm 50	3.4 \pm 0.2	19 \pm 2	39 \pm 3	230 \pm 20	9 \pm 1	1.6 \pm 0.1	8 \pm 2	1.8 \pm 0.2	0.52 \pm 0.17	1.09 \pm 0.23
-122.5	1944.5	0.44 \pm 0.08	750 \pm 50	4.0 \pm 0.1	23 \pm 1	50 \pm 5	250 \pm 10	10 \pm 1	1.9 \pm 0.1	10 \pm 1	2.1 \pm 0.3	0.33 \pm 0.12	1.00 \pm 0.19
Chesapeake Bay Sites													
Susq. 8–10cm		0.94 \pm 0.17	2700 \pm 200	7.5 \pm 0.3	69 \pm 2	101 \pm 3	470 \pm 40	33 \pm 1	3.2 \pm 0.2	24 \pm 3	2.0 \pm 0.2	1.9 \pm 0.4	1.9 \pm 0.3
Susq. 28–30cm		0.37 \pm 0.07	1800 \pm 130	3.4 \pm 0.2	42 \pm 3	53 \pm 8	270 \pm 40	15 \pm 1	1.6 \pm 0.2	9 \pm 2	1.5 \pm 0.3	1.2 \pm 0.3	1.07 \pm 0.01
Susq. 44–46cm		0.56 \pm 0.07	1800 \pm 130	5.7 \pm 0.2	55 \pm 6	102 \pm 8	470 \pm 60	24 \pm 1	2.5 \pm 0.1	14 \pm 2	2.8 \pm 1.3	2.1 \pm 0.1	1.2 \pm 0.2
Fairharbor		0.36 \pm 0.08	110 \pm 10	2.4 \pm 0.3	4 \pm 1	17 \pm 4	140 \pm 10	9 \pm 2	1.5 \pm 0.1	9 \pm 2	13 \pm 2	0.44 \pm 0.05	10 \pm 1.5
B'More Harbor H		0.58 \pm 0.04	650 \pm 50	10 \pm 1	36 \pm 14	500 \pm 100	1800 \pm 400	17 \pm 1	4.2 \pm 0.4	18 \pm 1	8.5 \pm 1.4	2.5 \pm 1	9 \pm 7
B'More Harbor M		0.48 \pm 0.03	4800 \pm 400	7.4 \pm 0.3	21 \pm 2	1800 \pm 200	900 \pm 150	20 \pm 1	2.5 \pm 0.2	9 \pm 1	5.9 \pm 1	7.2 \pm 4	7.7 \pm 2
B'More Harbor N		0.54 \pm 0.07	860 \pm 60	6.8 \pm 0.6	30 \pm 4	730 \pm 80	1000 \pm 100	21 \pm 2	2.9 \pm 0.2	14 \pm 2	3.2 \pm 0.2	4.1 \pm 0.2	6.8 \pm 0.8
PC368 0cm		0.43 \pm 0.08	520 \pm 40	3.9 \pm 0.1	13 \pm 1	18 \pm 3	75 \pm 10	15 \pm 1	1.6 \pm 0.2	9 \pm 1	1.8 \pm 0.3	0.07 \pm 0.01	0.17 \pm 0.05
PC423 57cm		0.59 \pm 0.15	510 \pm 40	4.1 \pm 0.2	15 \pm 1	18 \pm 1	84 \pm 7	16 \pm 2	1.7 \pm 0.2	14 \pm 3	4.1 \pm 0.7	0.07 \pm 0.03	0.19 \pm 0.04
PC484 114cm		0.44 \pm 0.12	510 \pm 40	3.7 \pm 0.1	13 \pm 1	14 \pm 1	77 \pm 2	15 \pm 1	1.5 \pm 0.1	10 \pm 2	1.8 \pm 0.2	0.11 \pm 0.09	0.11 \pm 0.05
Water-depth 3.4		0.46 \pm 0.05	3000 \pm 200	6.3 \pm 0.4	39 \pm 1	62 \pm 2	490 \pm 20	19 \pm 1	2.6 \pm 0.1	13 \pm 1	1.9 \pm 0.1	0.88 \pm 0.02	1.37 \pm 0.13
Water-depth 6.7		0.48 \pm 0.15	2200 \pm 200	5.7 \pm 1	48 \pm 8	80 \pm 20	500 \pm 100	19 \pm 4	2.5 \pm 0.6	14 \pm 4	2.4 \pm 0.5	1.7 \pm 0.4	0.94 \pm 0.32
Water-depth 26.2		0.42 \pm 0.09	1000 \pm 70	4.1 \pm 0.9	28 \pm 4	50 \pm 10	290 \pm 40	15 \pm 4	2.2 \pm 0.6	11 \pm 2	2.2 \pm 0.8	0.89 \pm 0.18	0.77 \pm 0.18
Depth (cm)	Year	In ($\mu\text{g/g}$)	Sn ($\mu\text{g/g}$)	Sb ($\mu\text{g/g}$)	Te ($\mu\text{g/g}$)	W ($\mu\text{g/g}$)	Re (ng/g) ^a	Tl ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Bi ($\mu\text{g/g}$)	U ($\mu\text{g/g}$)		
CORE 55													
-1	1978.6	0.18 \pm 0.03	4.6 \pm 0.8	0.93 \pm 0.19	0.08 \pm 0.02	1.45 \pm 0.34	8 \pm 3	0.87 \pm 0.17	45 \pm 7	0.37 \pm 0.08	5.9 \pm 2.2		
-9	1970	0.19 \pm 0.01	4.8 \pm 0.7	1.02 \pm 0.10	0.10 \pm 0.01	1.62 \pm 0.10	6 \pm 3	0.90 \pm 0.10	50 \pm 5	0.35 \pm 0.04	4.7 \pm 0.5		
-11	1967.8	0.23 \pm 0.02	5.9 \pm 0.2	1.17 \pm 0.04	0.13 \pm 0.01	1.82 \pm 0.29	20 \pm 9	0.88 \pm 0.08	56 \pm 3	0.42 \pm 0.02	4.2 \pm 0.8		
-13	1965.6	0.24 \pm 0.04	5.7 \pm 0.3	1.09 \pm 0.09	0.12 \pm 0.04	1.67 \pm 0.21	4 \pm 3	1.02 \pm 0.08	63 \pm 5	0.45 \pm 0.03	4.9 \pm 0.6		
-17	1964	0.24 \pm 0.04	6.2 \pm 1.2	1.18 \pm 0.13	0.13 \pm								

Table 3 (continued)

Depth (cm)	Year	In (μg/g)	Sn (μg/g)	Sb (μg/g)	Te (μg/g)	W (μg/g)	Re (ng/g)*	Tl (μg/g)	Pb (μg/g)	Bi (μg/g)	U (μg/g)
–39	1989.8	0.17 ± 0.02	4.8 ± 0.5	0.88 ± 0.09	0.10 ± 0.01	1.39 ± 0.23	8 ± 2	0.78 ± 0.07	58 ± 8	0.36 ± 0.02	2.8 ± 0.5
–47	1987.8	0.19 ± 0.01	5.1 ± 0.3	1.15 ± 0.06	0.12 ± 0.01	1.36 ± 0.13	5.6 ± 0.3	0.81 ± 0.04	60 ± 7	0.38 ± 0.02	2.9 ± 0.2
–53	1986.2	0.21 ± 0.01	6.2 ± 0.6	1.49 ± 0.35	0.13 ± 0.01	1.53 ± 0.06	20 ± 10	0.92 ± 0.07	63 ± 4	0.48 ± 0.03	3.0 ± 0.1
–59	1984.7	0.24 ± 0.02	6.6 ± 0.5	1.32 ± 0.05	0.17 ± 0.01	1.62 ± 0.10	7 ± 1	0.82 ± 0.05	65 ± 6	0.43 ± 0.02	2.8 ± 0.2
–82.5	1972	0.16 ± 0.01	4.2 ± 0.4	0.78 ± 0.06	0.12 ± 0.01	1.11 ± 0.10	16 ± 3	0.66 ± 0.05	50 ± 2	0.31 ± 0.02	2.7 ± 0.2
–122.5	1944.5	0.23 ± 0.01	5.5 ± 0.3	1.03 ± 0.05	0.15 ± 0.01	1.19 ± 0.05	17 ± 7	0.76 ± 0.02	57 ± 5	0.37 ± 0.01	2.5 ± 0.1
<i>Chesapeake Bay Sites</i>											
Susq. 8–10cm		0.34 ± 0.05	9.3 ± 0.3	1.81 ± 0.10	0.11 ± 0.01	5.02 ± 0.39	4 ± 1	1.04 ± 0.04	76 ± 1	0.63 ± 0.06	4.8 ± 0.4
Susq 28–30cm		0.18 ± 0.02	5.0 ± 0.5	0.98 ± 0.12	0.04 ± 0.01	3.29 ± 0.74	2 ± 1	0.53 ± 0.05	44 ± 7	0.41 ± 0.08	3.2 ± 0.7
Susq. 44–46cm		0.34 ± 0.03	9.6 ± 1.3	2.09 ± 0.34	0.07 ± 0.01	4.00 ± 0.72	3 ± 1	0.88 ± 0.09	65 ± 5	0.77 ± 0.34	4.7 ± 0.3
Fairhaven		0.11 ± 0.02	1.9 ± 0.2	1.08 ± 0.2	0.13 ± 0.04	0.74 ± 0.11	15 ± 2	0.66 ± 0.14	10 ± 2	0.14 ± 0.01	9.7 ± 3.4
B'More Harbor H		1.7 ± 0.2	105 ± 18	10 ± 4	9 ± 2	3.72 ± 0.31	4 ± 2	0.78 ± 0.11	320 ± 30	1.54 ± 0.13	8.0 ± 0.7
B'More Harbor M		0.70 ± 0.09	37 ± 4	17 ± 3	75 ± 22	1.73 ± 0.13	2 ± 1	1.04 ± 0.08	640 ± 80	5.1 ± 1.2	6.1 ± 0.8
B'More Harbor N		0.72 ± 0.12	37 ± 2	8 ± 2	14 ± 2	3.36 ± 0.41	4 ± 1	0.96 ± 0.04	370 ± 30	1.44 ± 0.10	6.0 ± 0.7
PC368 0cm		0.13 ± 0.01	2.3 ± 0.3	0.44 ± 0.06	0.11 ± 0.07	0.95 ± 0.06	16 ± 7	0.48 ± 0.02	19 ± 2	0.26 ± 0.03	2.6 ± 0.4
PC423 57cm		0.15 ± 0.04	2.8 ± 0.6	0.57 ± 0.07	0.05 ± 0.02	1.34 ± 0.32	11 ± 1	0.53 ± 0.06	16 ± 1	0.22 ± 0.09	3.9 ± 0.8
PC484 114cm		0.16 ± 0.03	2.4 ± 0.3	0.43 ± 0.10	0.04 ± 0.01	0.92 ± 0.13	4 ± 2	0.46 ± 0.02	16 ± 2	0.21 ± 0.03	2.7 ± 0.4
Water-depth 3.4		0.29 ± 0.02	8.7 ± 1.8	2.1 ± 0.2	0.24 ± 0.01	2.67 ± 0.10	7 ± 2	0.73 ± 0.06	77 ± 2	0.55 ± 0.04	3.7 ± 0.2
Water-depth 6.7		0.33 ± 0.08	9.1 ± 2.1	2.0 ± 0.5	0.24 ± 0.06	2.38 ± 0.57	3 ± 1	0.81 ± 0.17	80 ± 20	0.59 ± 0.14	4.1 ± 1.0
Water-depth 26.2		0.22 ± 0.05	5.5 ± 1.3	1.2 ± 0.4	0.13 ± 0.04	1.51 ± 0.39	2 ± 1	0.68 ± 0.14	48 ± 6	0.35 ± 0.08	2.7 ± 0.5

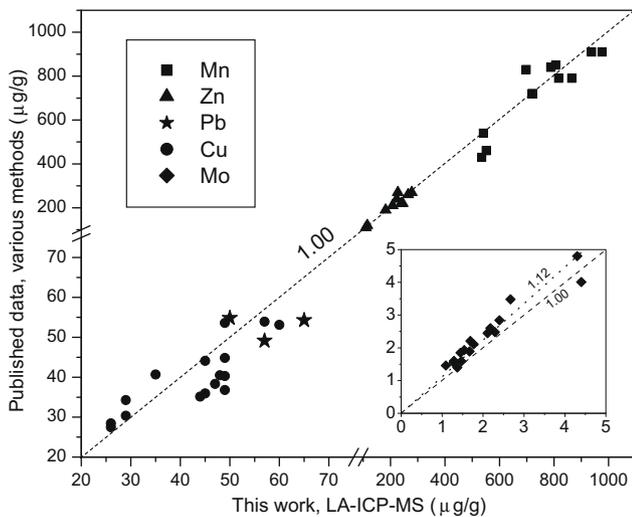


Fig. 3. Good agreement between independent determinations of five elements. Alternate methods: Mn and Zn, direct-current plasma emission spectroscopy; Pb, atomic absorption spectroscopy; Cu, flame atomic absorption spectroscopy; and Mo, isotope dilution ICP-MS. See text for sources of alternate method data.

An important implication of Fig. 3 is that our use of Mn as an internal standard is not generating systematic errors in the LA-ICP-MS data. Such errors would infect the LA-ICP-MS results for all elements in the figure. It would be improbable that such errors could be compensated by offsetting systematic errors in the various independent methods against which LA-ICP-MS results are compared in Fig. 3.

To facilitate comparisons among the large number of element concentrations that have been determined in Chesapeake Bay sediments and related samples, we present analytical results graphically in terms of enrichment factors (EFs). Enrichment factors have the advantage of putting all elements on a common scale, representing the proportionate departure of each element in a sample from a reference composition.

Element concentrations are double-normalized when generating an EF. The first normalization is to a major component of the fine-grained fraction of the sediment. Iron or aluminum are common choices and have been shown to be equally suitable (Daskalakis and O'Connor, 1995). In this work, Fe is used for normalization; Al was not determined owing to analytical complications

arising from its high abundance. The purpose of this first normalization is to compensate for variable dilution of samples by sand-sized particles. Such large particles, typically of quartz, tend to dilute both Fe and trace elements but have much less effect on X/Fe ratios.

The second normalization is to the X/Fe ratio in a reference material:

$$EF = \frac{(X/Fe)_{\text{sample}}}{(X/Fe)_{\text{REF}}} \quad (4)$$

This second normalization is simply a scaling factor that makes EF = 1 for all elements if their X/Fe ratios are the same as in the reference material. As reference values, we will use average (X/Fe) ratios in the three oldest samples from Core 55 (94–96 cm, 96–98 cm and 100–102 cm). Sediments in these samples were deposited near the beginning of the 20th century. In Table 4, we give the reference concentrations for each element and compare them to the corresponding median values in fine-grained sediments or average shale.

For the most part, our reference composition, determined by our LA-ICP-MS method, resembles median values of fine-grained sediments. Exceptions include Mo and Cd, which are more abundant in our reference composition than in fine-grained sediments as determined by Hu and Gao (2008) but not relative to average

Table 4

Average element concentrations (μg/g) in the three deepest samples in core 55 and comparison to median values in shale. Median shale values are from Hu and Gao (2008) except those marked by an asterisk which are from Turekian and Wedepohl (1961).

Element	Deep core 55	Median shale	Element	Deep core 55	Median shale
Ti	4300	4375	Mo	1.4	0.48(2.6*)
V	117	110	Ag	0.082	0.07
Mn	505	620	Cd	0.3	0.063(13*)
Fe	40,100	42,000	In	0.15	0.073
Co	14	14	Sn	2.7	3.3
Ni	73	36(68*)	Sb	0.47	0.75
Cu	26	27	Te	0.032	0.039
Zn	98	71	W	1.6	2.22
Ga	15	20	Re	0.004	
Ge	1.9	1.9	Tl	0.59	0.84
As	13	4.4(13*)	Pb	20	19.3
Se	0.85	0.6	Bi	0.25	0.37
Nb	9.5	15	U	2.6	2.88

shale as determined by Turekian and Wedepohl (1961) (see parenthetical values in Table 4).

In Fig. 4, results are presented for Cu, Zn, Cd and Pb, the most commonly determined industrial pollutants. Four replicate analyses on different parts of each pressed sediment pellet are represented by small closed symbols; average values are represented by larger open symbols. Except in the case of Cd, the replicate determinations agree so well that most of the closed points lie within the open symbols. The vertical line in each graph denotes an enrichment factor of 1. After 1920, all four elements are enriched relative the early 20th century reference composition, but a slight decrease in enrichment seems to occur after 1980. The four elements in Fig. 4 are all enriched in Baltimore Harbor and the Susquehanna River, but not in the pre-European settlement samples of PC6. The considerable enrichment of these elements in the Harbor is most likely due to historical smelting operations in Baltimore (Mason et al., 2004). These elements have been found to be associated with smelting operations at other locations (Buchauer, 1973; Hong et al., 1996; Du et al., 2008). Additionally, Pb and Cd pigments would have been used in paint manufacturing, an important industry in Baltimore. Only Cd is strongly enriched in the Miocene Fairhaven sample. All the profiles shown in the graphs indicate that there is good agreement between cores 55 and RD.

Lead is a major indicator of anthropogenic influence in the Chesapeake Bay. The Pb profile presented here agrees with others from this region as well as others around the US and indicates that Pb concentrations began to decrease very soon after the decrease

in the use of leaded gasoline in the late 1970's (Edgington and Robbins, 1976; Lantzy and Mackenzie, 1979; Heit et al., 1981; Eisenreich et al., 1986; Alexander and Smith, 1988; Graney et al., 1995; Marcantonio et al., 2002; Lima et al., 2005).

In Fig. 5, results are presented for some rarely determined elements: In, Sn, Sb, Te and Bi. To our knowledge, these elements have never been determined previously in Chesapeake Bay sediments. Like the commonly determined pollutants, these elements all show enrichment after 1920 and a slight decrease after 1980. All of these elements, except Te, have been used increasingly in recent decades as substitutes for Pb because they are less toxic (Hou et al., 2005). These elements are strongly enriched in the Harbor and only mildly enriched in the Susquehanna sediments. As discussed below, all of these elements are potentially hazardous in the environment. Our results provide evidence that these elements are pollutants in Chesapeake Bay and their concentrations should be monitored along with the more commonly determined elements presented in Fig. 4.

Indium is produced during zinc ore processing and is used in a wide range of electronic industries such as semi-conductor and optoelectronic manufacturing (USGS, 2005). Indium is frequently associated with mineral deposits of Zn, Cu, Mn, Sn and Pb which points to its geochemical similarities to these elements (Poledniok, 2007). Indium has been found to be toxic to embryos in animal experiments (Nakajima et al., 2000; Hou et al., 2005).

Tin is mainly mined from cassiterite (SnO₂) deposits and has many uses in alloys, electrical/electronic applications as well as in glass-making (USGS, 2005). One particularly relevant modern

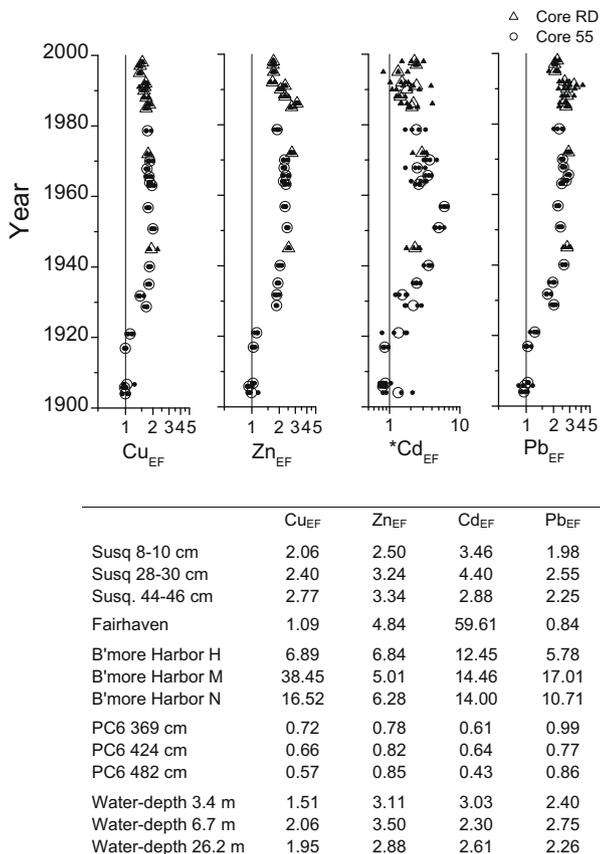


Fig. 4. Enrichment factors (Eq. (4)) for four commonly determined industrial pollutants: Cu, Zn, Cd, Pb. The table gives corresponding EF values for samples from potential sediment sources: Susq, Susquehanna River sediments from Conowingo Reservoir; Fairhaven, unlithified Miocene seacliff material that is undergoing wave erosion; B'more Harbor, sediments from Baltimore Harbor; PC6, deep samples from below the oak/ragweed pollen horizon that marks the onset of European land clearance. The Water-depth samples are surface sediments taken from shallow to deep water near the site of cores RD and 55. Sample localities are given in Fig. 1.

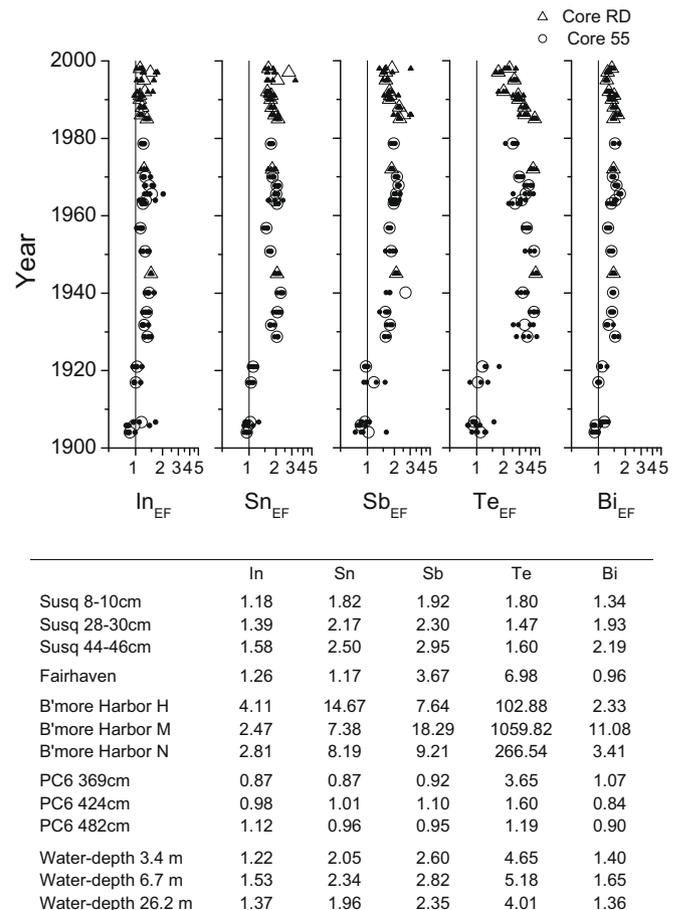


Fig. 5. Enrichment factors (Eq. (4)) for rarely determined industrial pollutants: In, Sn, Sb, Te, Bi. The table gives corresponding EF values for samples from potential sediment sources (see Fig. 4 for details).

source of Sn in the Chesapeake Bay is marine paint since organotin compounds are used as anti-fouling agents (Beaumont and Budd, 1984; Antizar-Ladislao, 2008). Historically, Sn was used in canning foods, a major industry in Baltimore after about 1860.

Antimony has been used for centuries as a medicine and in cosmetics. It is used as a hardener in lead for storage batteries and in flame-retardant formulations (USGS, 2005). Antimony is one of the pollutants from coal-fired power plants (Klein et al., 1975) and despite its known toxicity, its geochemical behavior in sediments has not been extensively studied (Chen et al., 2003; Hou et al., 2005). One key finding is that it is associated with iron and manganese hydroxides and is thus released under reducing conditions in sediments (Chen et al., 2003). This is of particular importance in the Chesapeake Bay where seasonal anoxia occurs.

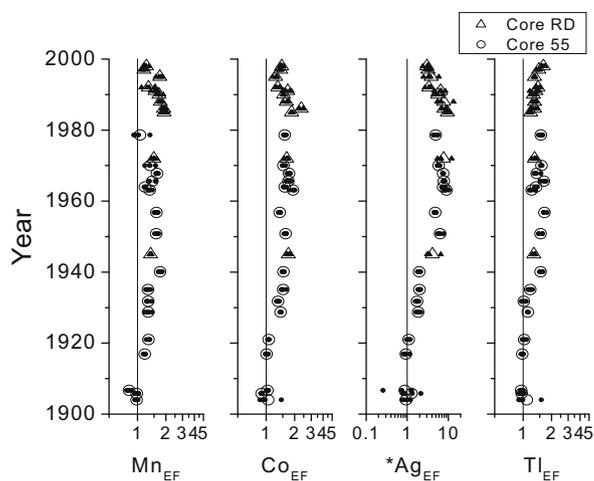
Tellurium is produced as a by-product of copper processing (USGS, 2005), a major industry in Baltimore from the early 19th to the middle 20th centuries. Tellurium is used in semiconductor materials, a wide range of electronics and metallurgy (D’Ulivo, 1997). Tellurium affects the nervous system and produces selenium-deficiency symptoms (Sadeh, 1987). Organisms transform inorganic Te to organotellurium compounds which are volatile and can be more easily released (Sadeh, 1987; D’Ulivo, 1997). Tellurium has not received as much attention as two of its periodic table neighbors As and Se, but our results show that it is among the most highly enriched elements in Chesapeake Bay sediments, so the origin of this contamination should be further investigated.

Bismuth is a by-product of lead-ore processing. It is used in solders, a variety of alloys, additives, medications and in atomic research (USGS, 2005). Like Sb, Bi is released during the combustion of fossil fuels (Karlsson et al., 2007). Very little environmental monitoring of bismuth has been done because its inorganic form exhibits low toxicity; however, organobismuth compounds such as triphenylbismuth are toxic (Arata et al., 2002; Dopp et al., 2004). Bismuth causes disorders of the kidneys, liver and nervous system (Winship, 1983; Dipalma, 1988; Hou et al., 2005).

In Fig. 6 results are presented for Mn, Co, Ag and Tl. Once more these elements follow the pattern of industrial pollutants and are enriched after 1920. It is somewhat surprising to find Mn included here. Profiles of Mn in sediments usually are controlled by diagenesis. However, in Chesapeake Bay, diagenetically active Mn tends to be refluxed out of the reduced, deep-channel sediments and deposited in shallower sediments that are exposed to toxic water throughout the year (Helz et al. 1985a). This effect can be seen in Fig. 6 in the data taken at three water depths; at the shallowest site, Mn is 3-fold enriched relative to our deep water reference composition. As a consequence of refluxing, deep channel sites accumulate Mn in forms that are less active diagenetically. Possibly, the modest Mn enrichment after 1920 in Fig. 6 reflects contamination of the Bay with diagenetically refractory Mn.

Silver is highly enriched in all the supplementary samples in Fig. 6 except PC6. Silver has been found to cycle with lead and copper in coastal waters (Sanudo-Wilhelmy and Flegal, 1992). Our results are consistent with these findings since Ag is enriched in the same samples and to a similar degree that Cu and Pb are. Notably, Tl is enriched only in the Fairhaven sample and seems to be depleted in Baltimore Harbor, so it is curious that Tl displays a profile that we associate with industrial contaminants; however, faintly.

In Fig. 7, results are presented for the redox-sensitive elements Mo, Re and U and the possible redox-sensitive element W. These elements are only modestly enriched, if at all, in the Susquehanna and Harbor sediments. In this respect, their distributions contrast with distributions of most of the other elements discussed up to this point. Mo, Re and U are all strongly enriched in the Miocene Fairhaven unit, which resembles black shales in composition. Erosion of the unlithified Fairhaven formation may have supplied enriched sediments to the PC-6 site prior to European settlement,



	Mn _{EF}	Co _{EF}	Ag _{EF}	Tl _{EF}
Susq 8-10cm	2.62	2.70	12.76	0.94
Susq 28-30cm	3.87	3.58	17.99	1.07
Susq. 44-46cm	2.35	2.83	18.15	1.06
Fairhaven	0.33	0.51	9.44	1.92
B'more Harbor H	0.45	1.00	11.81	0.50
B'more Harbor M	0.48	0.83	48.88	0.96
B'more Harbor N	0.96	1.32	30.34	0.96
PC6 369cm	1.00	0.97	0.89	0.85
PC6 424cm	0.92	1.03	0.85	0.88
PC6 482cm	1.01	1.04	1.45	0.85
Water-depth 3.4 m	3.50	1.82	6.70	0.79
Water-depth 6.7 m	2.87	2.48	15.42	0.96
Water-depth 26.2 m	1.81	2.00	10.22	1.13

Fig. 6. Enrichment factors (Eq. (4)) for elements which appear to be industrially enhanced but not from a Harbor source: Mn, Co, Ag, Tl. The table gives corresponding EF values for samples from potential sediment sources (see Fig. 4 for details).

accounting for the modest enrichment of those samples (Adelson et al. 2001).

Tungsten is directly below molybdenum in Group VIB and these two elements form analogous thio-compounds i.e. thiomolybdates and thiotungstates. Since Mo has been established as a redox-sensitive element due to the formation of particle-reactive thiomolybdates (Helz et al., 1996) we hypothesized that W would exhibit similar behavior. However, the profile presented here illustrates that W does not follow Mo. In fact, in the Susquehanna and depth-traverse sediments, W closely mirrors Mn (Bednar et al., 2008).

Rhenium is the least abundant of the elements determined in this survey (Table 4), and owing to analytical uncertainty its individual determinations (small, closed symbols) are the most scattered relative to mean values (open symbols). It is questionable whether useful historical information about Re deposition can be inferred from the data.

The Mo mean values also appear to be greatly scattered, but in contrast to Re, we believe that the Mo scatter reflects actual fluctuations in the Mo deposition rate, not analytical uncertainty. To illustrate this, in Fig. 8 we plot three independent determinations of Mo and corresponding determinations of Cu. We have connected the mean values of these independent determinations with line segments. It is apparent that the highly variable vertical Mo profile is affirmed by all three sets of data. This excludes analytical error as a source of the variation. Furthermore there is a marked contrast between the profiles of Mo and Cu. Whereas Cu, representative of industrial pollutants, rises to a steady level of enrichment between 1920 and 1980, Mo fluctuates between high and low enrichment in the same period. Adelson et al. (2001) have attributed this

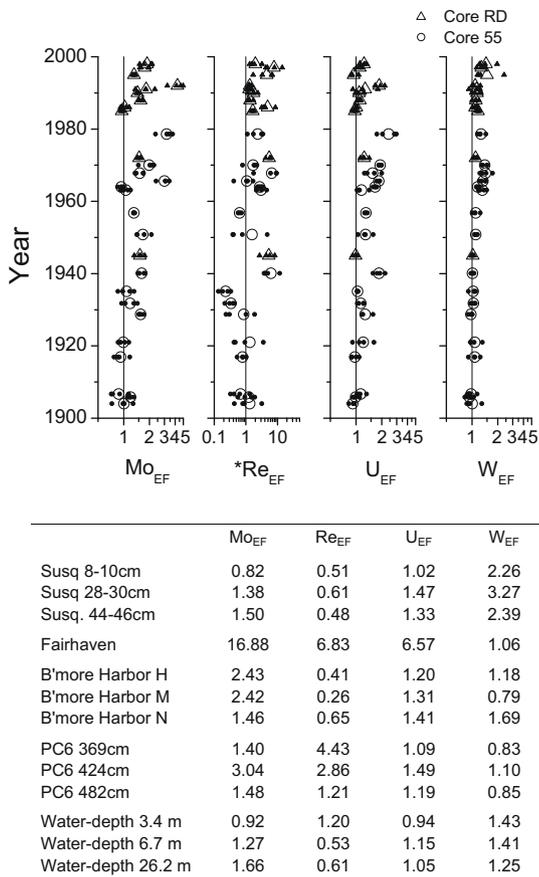


Fig. 7. Enrichment factors (Eq. (4)) for redox-sensitive elements: Mo, Re, U, (W). The table gives corresponding EF values for samples from potential sediment sources (see Fig. 4 for details).

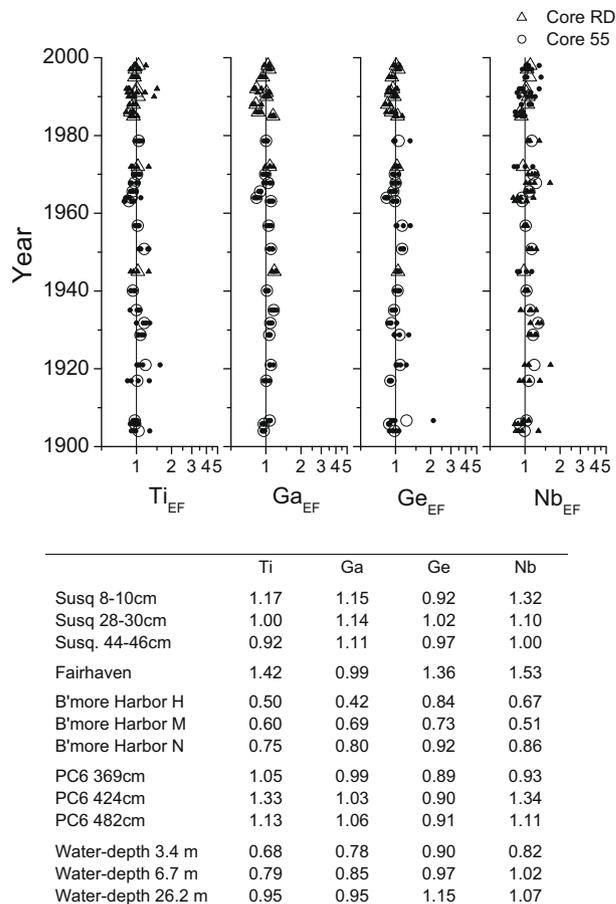


Fig. 9. Enrichment factors (Eq. (4)) for unperturbed elements: Ti, Ga, Ge, Nb. The table gives corresponding EF values for samples from potential sediment sources (see Fig. 4 for details).

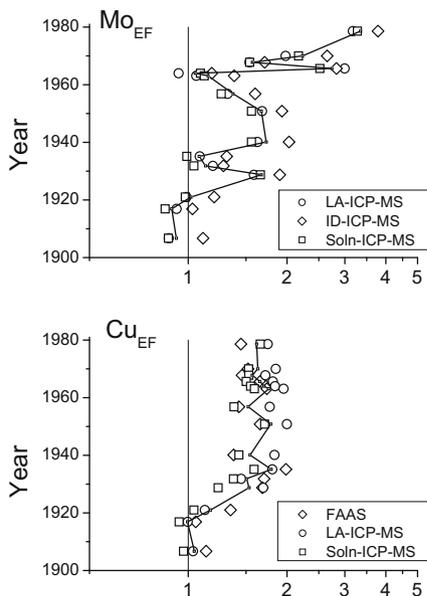


Fig. 8. Method comparison illustrating agreement between 3 independent determinations of Mo and Cu in the same samples. LA-ICP-MS (this work), ID-ICP-MS (Isotope Dilution ICP-MS Adelson et al. (2001)), Soln-ICP-MS (Solution ICP-MS analyses, this work), FAAS (Flame Atomic Absorption Spectroscopy Adelson et al. (2001)).

to fluctuations in redox conditions in Chesapeake Bay related to year-to-year variations in river flow. The pronounced minimum

in the Mo profile in the 1960's occurred during a period of multi-year drought. Drought deters seasonal anoxia and consequent Mo enrichment (Adelson et al., 2001).

Fig. 9 contains results for Ti, Ga, Ge and Nb. Except for Ti, these data are also believed to represent the first determinations of these elements in Chesapeake Bay. These elements display negligible temporal trends in their deposition history and are neither substantially enriched nor depleted relative to our reference composition. Geochemically, Nb tends to occur as a minor constituent in Ti minerals, so the similar behavior of these two elements is not surprising. Ga and Ge tend to associate with their more abundant cohorts in the periodic table, Al and Si, respectively.

4. Conclusions and perspectives

Excluding the redox-sensitive elements in Fig. 7, all the elements generally have EFs near one in the pre-European samples from PC-6. However, in the case of Fig. 4 (Cu, Zn, Cd and Pb), EFs are consistently less than one for the pre-European samples. Our early 20th century reference sediments (Table 3) may have been already somewhat enriched in these four elements relative to the pre-European sediments. This result would be consistent with derivation of these elements from smelting. The Baltimore Copper Smelting Company was formed around 1850, and for several decades, it and its allied companies operated within Baltimore the largest copper smelter in the United States.

Our work on trace element contaminants in Chesapeake Bay is continuing. It is already clear, though, that Laser Ablation ICP-MS is

going to be a very valuable tool in this effort. For many of the elements discussed here, no previous determinations have been made in Chesapeake Bay sediments and few determinations have been made in estuaries anywhere. This is one of the first demonstrations of LA-ICP-MS as a tool to perform a survey of anthropogenic impacts on modern sediments and suggests that the suite of elements monitored by environmental agencies should be broadened.

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