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Chapter 29

Are soils the culprit? Linking natural and anthropogenic watershed processes to the degradation of the Chesapeake Bay

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Abstract

Natural weathering processes will tend to enrich the trace metal content of soils relative to the upper continental crust. Resultantly, the erosion of these soils will increase the loading of toxic trace metals to specific watersheds. The trace metal problems of the Chesapeake Bay have been well documented and it is clear that since the industrialization of the United States the flux of anthropogenic contaminants to the bay has steadily increased. However, recent work in the Patuxent River Basin suggests that much of the dissolved metal load is the result of desorption from suspended and bedload sediments and that current estimates of the trace element inputs from the sediment load are inadequate to evaluate their ultimate source. The questions that remain are, what portion of the toxic metal load being transported to the bay is the result of natural processes like chemical weathering and erosion and what portion of soil-derived metals are available to aquatic biota?

An investigation in the Patapsco River watershed, a subordinate drainage system within the Chesapeake Bay watershed, has determined that sediment being transported with in the Patapsco River watershed represents at least two sources. Soil-derived metals appear to dominate the suspended sediment flux during larger storm events for all analytes in this study. During smaller discharge storm events, there appears to be a Zn-enriched source that is a major component of the suspended sediments. This watershed signature is clearly different than the bulk trace metal signature in Baltimore Harbor and the Chesapeake Bay. Instead, the trace metal signature of Harbor sediments displays a pattern that requires an additional local trace metal source(s).

29.1. Introduction

Chesapeake Bay is one of the most studied bodies of water in the world. A primary focus of much of this research has been on the fate and transport of trace metals (e.g. copper, lead, zinc) deposited in the bay (Carpenter et al., 1975; Helz, 1976; Goldberg et al., 1978; Harris et al., 1980; Sinex and Helz, 1981; Nichols et al., 1982; Helz et al., 1985a,b; Kearney et al., 1985; Delfino and Otto, 1986; Marcus et al., 1993). A component of this trace metal problem, that to this point has not been adequately investigated, is the contribution of soil-derived trace metals to the bay. Natural weathering processes will tend to enrich the trace metal content of soils relative to the upper continental crust (Nesbitt and Young, 1982; Nesbitt and Young, 1984; Brimhall and Dietrich, 1987; Nesbitt and Young, 1989; Nesbitt et al., 1990; Maynard, 1992; McLennan, 1995; Nesbitt and Markovics, 1997; Gaillardet et al., 1999). Resultantly, the erosion of these soils will increase the loading of toxic trace metals to specific watersheds. With the increase in industrialization in the U.S. over the past 200 years came an increase in urbanization. The urbanization of large areas of the Chesapeake Bay watershed along with continued agricultural activities has dramatically affected land use and potentially enhanced erosion rates. The changing land use dynamics with in the Chesapeake Bay watershed have the potential to create non-equilibrium denudation conditions in the region. A non-equilibrium denudation region is one in which sediment yield is incongruous with the degree of weathering experienced by soils within the drainage area, which are the primary source of suspended sediment. Meaning, the rate of denudation and the weathering rate in a given region are not in equilibrium, as might be expected, and likely have been upset by anthropogenic influences (McLennan, 1993). These conditions will dramatically affect the flux of soil-derived trace metals being transported to the bay. Stated simply, the anthropogenic flux of trace metals to the bay may mirror and therefore be enhanced by an increase in the input of soil-derived trace metals as a result enhanced erosion brought about by the land use dynamics within the watershed.

The trace metal problems of the Chesapeake Bay have been well documented and it is clear that since the industrialization of the United States the flux of anthropogenic contaminants to the bay has steadily increased (Carpenter et al., 1975; Helz, 1976; Goldberg et al., 1978; Harris et al., 1980; Sinex and Helz, 1981; Nichols et al., 1982; Helz et al., 1985a,b; Kearney et al., 1985; Delfino and Otto, 1986, Marcus et al., 1993). However, recent work in the Patuxent River basin by Riedel et al. (2000) suggests that much of the dissolved metal load is the result of desorption from suspended and bedload sediments and that current estimates of the trace element inputs from the sediment load are inadequate to evaluate their ultimate source. The questions that remain are, what portion of the toxic metal load being transported to the bay is the result of natural processes like chemical weathering and erosion and what portion of soil-derived metals are available to aquatic biota?

The fate of the major elements (aluminum, calcium, sodium, potassium, iron, and magnesium) during weathering is fairly well understood (Nesbitt and Young, 1982; Nesbitt and Young, 1984; Nesbitt and Young, 1989; McLennan, 1995). In fact, the major element composition of soils is commonly used to determine changes in mineralogy and the degree of bedrock alteration associated with weathering and soil-forming processes (Nesbitt and Young, 1982; Nesbitt and Young, 1984; Brimhall and Dietrich, 1987; Nesbitt and Young, 1989; Nesbitt et al., 1990; Maynard, 1992; McLennan, 1995; Nesbitt and Markovics, 1997; Gaillardet et al., 1999). The fate of trace metals is much less understood. The same weathering processes that affect the major element composition of a soil profile and also affect the trace metal composition.

Trace metals can be enriched in soils over the parent material during chemical weathering. The extent of this enrichment can vary significantly based on the bedrock type and the weathering environment. Based on limited data, the trace metal compositions of bulk soils throughout Maryland rarely exceed regulatory limits (MDE, 2001). However, trace metals will tend to be concentrated in the clay size fraction of the soil (e.g., Lev, 2001). While the fine fraction is a minor component (typically <10%), it is more easily transported and the associated metals are typically more readily bio-available (i.e., not bound in the silicate structure). This, coupled with enhanced rates of erosion in both urban and rural settings sets up the possibility that the there is significant metal loading to tributaries of the Chesapeake Bay as a result of natural processes.

This investigation focuses on the Maryland West Shore watershed, known locally as the Patapsco-Back River system, one of the nine subordinate watersheds that feed the bay. In addition to its local significance, the Patapsco-Back River watershed incorporates a wide range of land use and includes the primary drinking water reservoirs for Baltimore County and the City of Baltimore. To investigate the extent of soil-derived trace metal loading in the Patapsco-Back River Watershed, representative soils (bulk and size fractions), suspended sediment and harbor and bay sediments were collected from sampling locations across the rural to urban gradient within the Patapsco-Back River watershed capturing the maximum number of potential sources of trace metals to the bay.

29.2. Sampling locations

The Patapsco-Back River watershed contains eight smaller watersheds including Baltimore Harbor (Fig. 29.1). Samples from this study were collected within four of the eight. These four were selected to maximize the range in bedrock type and land use. In addition, these watersheds drain directly into the main branch of the Patapsco River.

Suspended sediment samples from three separate storm events collected during the Summer and Fall of 2003 were analyzed and compared to integrated soil samples from the same locations and bottom sediments from three locations with in Baltimore Harbor and the Chesapeake Bay (Figs. 29.1 and 29.2). Storm events were sampled during this investigation in order to assess the geochemical characteristics of the sediment flux through the system as a result of storm transport. The watersheds sampled are profiled below with supporting data in Table 29.1.

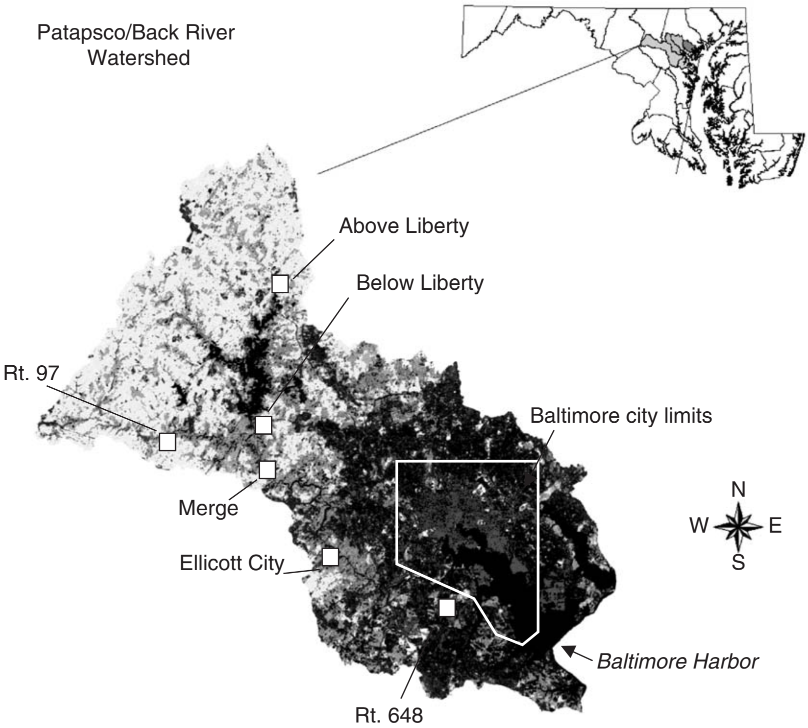

Figure 29.1. Location map with false color inset of the Patapsco-Back River Watershed. Light-colored areas are agricultural and dark-gray areas are sub-urban to urban. Sampling locations with in the watershed are indicated with a square.

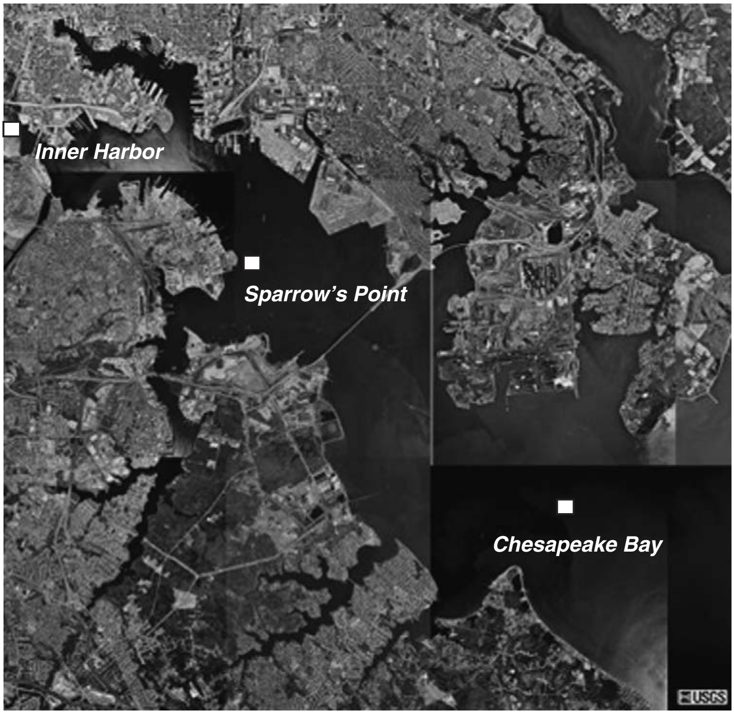

Figure 29.2. Satellite image of Baltimore Harbor and the Chesapeake Bay. Sample locations for this study are indicated with a white square.

Liberty Reservoir. The Liberty Reservoir watershed contains the North Branch of the Pataspco River that empties into and drains Liberty Reservoir, which is one of three major reservoirs that serve the greater Baltimore area. The North Brach was sampled above and below the reservoir (Fig. 29.1) in order to evaluate the impact the reservoir has on sediment transport in this part of the system. More than 80% of the land use in this watershed qualifies as agricultural or forested area with only 6.2% impervious surfaces. This is characteristic of the rural land use areas with in the Patapsco-Back River Watershed and is the rural end-member locale for this investigation.

Soils at the two sample sites have well developed A- and B-horizons and are forming on top of the Lower Pelitic Schist member of the Wissahickon Formation. The Wissahickon Formation is composed of intensively folded and cleaved muscovite-chlorite schist, chloritoid schist, and quartzite. The Lower Pelitic Schist member was formerly mapped

Table 29.1. Land use characteristics for the four subordinate watersheds of the Patapsco-Back River Watershed

Watershed	Characteristics	
Liberty Reservoir (101,404 acres)	Land use (%)	
	Urban	18.92
	Agricultural	48.02
	Forested	32.93
	Wetland	0.05
	Barren	0.08
	% impervous surface	6.3
	Population density (people/acre)	0.7
	Soil erodibility	0.28
	Historic wetland loss (acres)	3987
South Branch Patapsco (54,616 acres)	Land use (%)	
	Urban	18.26
	Agricultural	50.04
	Forested	31.52
	Wetland	0.00
	Barren	0.18
	% impervous surface	6
	Population density (people/acre)	0.79
	Soil erodibility	0.12
	Historic wetland loss (acres)	2745
Patapsco River Lower North Branch (75,513 acres)	Land use (%)	
	Urban	41.99
	Agricultural	12.67
	Forested	43.35
	Wetland	0.78
	Barren	1.21
	% impervous surface	21.9
	Population density (people/acre)	1.95
	Soil erodibility	0.31
	Historic wetland loss (acres)	8422
Baltimore Harbor (55,370 acres)	Land use (%)	
	Urban	75.79
	Agricultural	2.43
	Forested	20.08
	Wetland	1.00
	Barren	0.70
	% impervous surface	35.1
	Population density (people/acre)	3.55
	Soil erodibility	0.14
	Historic wetland loss (acres)	7681

as oligoclase facies of Wissahickon Formation and contains medium to coarse-grained biotite-oligoclase-muscovite-quartz schist with garnet, staurolite, and kyanite; fine- to medium-grained semipelitic schist; and fine-grained granular to weakly schistose psammitic granulite.

South Branch Patapsco. The South Branch watershed contains the second of the two main Patapsco tributaries to the west of Baltimore. The South Branch is roughly half the size of the Liberty Reservoir watershed with a similar land use distribution with a slightly smaller percent of impervious surfaces and a considerably lower soil erodibility factor of 0.12. There was one sampling station (Rt. 97) within this watershed located adjacent to secondary two lane state highway, route 97 (Fig. 29.1).

The soils at this location have the well developed A- and B-horizons. This location falls within the Boulder Gneiss which was formerly mapped as Sykesville and Laurel Formations. Characteristics of this formation include thick-bedded to massive, pebble- and boulder-bearing, arenaceous to pelitic metamorphic rock, typically a medium-grained, garnet-oligoclase-mica-quartz gneiss.

Patapsco River Lower North Branch. The Lower North Branch watershed referred to as the Merge area in this study is the second largest land area of the four watersheds in this study and is a transitional land use area best characterized as suburban. Roughly, 42% of the land use can be characterized as urban, slightly more, 43%, characterized as forested and almost 13% as agricultural. The percent impervious surface exhibits a dramatic increase in this area topping out at nearly 22%. There were two sampling locations within this watershed; the first, on the main branch of the Patapsco just below the merge between the North and South branches and the second, in a suburban area of Baltimore known as Ellicott City (Fig. 29.1).

The sample site below the confluence falls within the Lower Pelitic Schist member of the Wissahickon Formation. This member was formerly mapped as oligoclase facies and is described as medium- to coarse-grained biotite-oligoclase-muscovite-quartz schist with garnet, staurolite, and kyanite; fine- to medium-grained semipelitic schist; and fine-grained granular to weakly schistose psammitic granulite with psammitic beds. The Ellicott City location sits atop the Ellicott City Granodiorite. This unit ranges from biotite granodiorite along the body margin, to quartz monzonite in the core.

Baltimore Harbor. The urban areas directly adjacent to Baltimore's Inner Harbor are all part of the Baltimore Harbor watershed. This highly industrialized portion of the watershed (75.79% urban land use) is more than 35% impervious surface. The suspended sediment sampling location in this watershed was located just inside the Baltimore City limits on the main branch of the Patapsco River (Fig. 29.1). The two sampling locations within Baltimore Harbor also fall within the boundaries of this watershed. The sample site where suspended sediment and soils were collected sits atop the Potomac Group which is comprised of interbedded quartzose gravels; protoquartzitic to orthoquartzitic argillaceous sands; and white, dark gray and multicolored silts and clays, with a thickness of 0–800 feet, within this grouping are three formations, Raritan and Patapsco Formations, Arundel Clay, and the Patuxent Formation.

29.3. Field methods

29.3.1. Suspended sediment and soil sampling

Suspended sediment samples were collected with a depth-integrated sampler with Teflon spout. Approximately two liters of river water were collected during each sampling event. At the time of sampling, velocity measurements were recorded for each site following United States Geological Survey (USGS) methods for estimating discharge (Rantz, 1982). To collect a representative suspended sediment sample, at each site, the sampler was raised and lowered incrementally along a straight-line path across the width of the river. Each site's velocity measurements (Table 29.2) were integrated with their width and depth measurements to give an accurate reading of the discharge rates for each storm event sampled.

At each suspended sediment-sampling site, an area on the floodplain bank was cleared of grass and vegetation to expose 1 m of fresh soil. Approximately 1 kg of soil was collected from each 1-m profile and homogenized prior to analysis.

29.3.2. Bay sediment sampling

Three locations from within the Chesapeake Bay and the mouth of the Patapsco River in Baltimore's Inner Harbor were selected for grab sampling. These sites were selected due to their proximity to the Patapsco River delta (Fig. 29.2). To collect a representative sample at each site, a grab sampler was lowered three times at each sample location and approximately 1 kg of sediment was recovered. All bulk particulate organic matter (e.g. wood and leaf litter) collected from each site during the grab sampling processes was removed after the sample was dried for 72 h and was not included in the analysis.

29.4. Analytical methods

29.4.1. Grain size analysis

Soils that were collected were split for grain size and chemical analysis. Samples for chemical analysis were dried for 72 h, and then powdered to a uniform grain size using an agate mortar and pestle. Moist soil samples

Table 29.2. Storm water data for all events sampled. Sediment yield is presented as an instantaneous values rather than an average. The discharge and suspended sediment were collected at one time during the storm event therefore making the yield calculation valid for the time of sampling only

Sampling location	Date	Instantaneous discharge (ft.^{3} sec^{-1})	Suspended sediment (mg l^{-1})	Instantaneous sediment yield (t km^{-2})
Above Liberty Reservior	6.18.03	1977	24.5	0.29
	6.19.03	247	204.9	0.31
	8.7.03	72	5.4	0.002
	9.20.03	381	145.4	0.34
Below Liberty Reservior	6.18.03	525	5.6	0.02
	6.19.03	316	128.3	0.25
	8.7.03	84	12.5	0.01
	9.20.03	1901	2.4	0.03
Rt. 97	6.18.03	174	3.0	0.01
	6.19.03	469	272.4	1.48
	8.7.03	154	3.8	0.01
	9.20.03	1727	5.1	0.10
Merge	6.19.03	2524	1025.6	10.32
	8.7.03	600	2.5	0.01
Ellicott City	6.19.03	3124	963.0	25.42
	8.7.03	1495	146.7	1.85
	9.20.03	1242	385.1	4.04
Rt. 648	6.19.03	4798	633.7	25.69
	8.7.03	10514	25.1	2.23
	9.20.03	1788	130.0	1.96

were sealed within airtight zip bags, labeled, and stored at room temperature for grain size analysis. The moist soil was again split and half was passed through a 63-micron nylon sieve (silt-sized particles) and the remaining half through a 5-micron nylon sieve (clay-sized particles). Deionized water was used in the wet sieving for both the 63- and the 5-micron size fractions. Approximately 5 g of soil was placed on the sieve, and with the aid of deionized water, the soil was agitated within the sieve. What passed the sieve was collected, weighed, dried, and analyzed for trace metals using the methods described below.

29.4.2. Chemical analysis

Bulk samples, size fractions, and acid leachates were analyzed for trace metal concentrations using a Thermo Elemental (VG) PQExcell

Inductively Coupled Plasma-Mass Spectrometer in the Materials Research Laboratory at Towson University. 50 mg sample powder, crushed in an agate mortar and pestle, was weighed into a 30 ml acid cleaned screw top Savilex® Teflon® vial. For bulk metal concentrations, a 3:1 mix of ultrapure 7N HNO_3 and HF was added to each vial, the vial was sealed and placed on a hotplate at 170°C in a metal-free HEPA filtered clean hood overnight. After complete digestion was achieved samples were left uncapped on the hotplate and taken to dryness. Once completely dry, 3 ml of 2% HNO_3 spiked with a $1\,ng\,g^{-1}$ internal standards (indium and bismuth) was added to the sample and the vial was capped and returned to the hotplate. The sample remained on the hotplate until the remaining solution was clear. The dissolved sample was then transferred to a pre-weighed acid-cleaned 250 ml bottle. The sample was then diluted using the 2% HNO_3 $1\,ng\,g^{-1}$ internal standard solution. Sets of 10 samples were run with a procedural blank, a sample replicate and duplicate as well as at least 1 digestion of National Institute of Standards and Technology (NIST) Soil standard reference material (SRM) 2709. The precision of individual concentrations for all elements is better than 2% based on replicates and NIST standards in addition, recoveries for NIST SRM 2709 for all analytes were consistently between 85 and 105% and the detection limit for all elements measured was below 5 ppb.

Selected samples were split prior to digestion and 50 mg of the powdered sample was used to determine the acid leachable fraction of individual metals using 5 ml of 7N HNO_3. The samples were capped and let stand for 1 h. The leachate was then decanted, taken to dryness on a hotplate in a Teflon vial and prepared for trace element analysis by ICP-MS using the methods described above.

29.5. Results

Suspended sediments. Results are presented in Tables 29.2–29.8. In Table 29.2, the stream and suspended sediment data are presented by site location for each storm event sampled. The discharge and sediment yield calculations are instantaneous values rather than integrated averages since the stream data was collected near peak flow conditions for each storm event. As a result, these should be considered maximum values. Suspended sediment values for all sites and storm events range from a low of $2.4\,mg\,l^{-1}$ on September 20, 2003, at the BL site to a high of $1025.6\,mg\,l^{-1}$ on June 19, 2003, at the Merge sampling location (Table 29.2).

Sediment yield. Instantaneous sediment yield (t km^{-2}) values generally increase from the rural portion of the watershed with a low of $0.002\,\text{t km}^{-2}$ on August 7, 2003, at the above liberty site to a high of $25.69\,\text{t km}^{-2}$ at the urban Rt. 648 location on June 19, 2003 (Table 29.2). While these instantaneous sediment yield values are maximum values some of the values are comparable to the average annual sediment yield of much larger river systems. This observation is considered in more detail within the discussion section of this paper.

Trace metal load. Instantaneous metal load (mg of element/storm sample) calculations are made for all metals in all storms using metal concentration suspended sediment data and are presented in Table 29.3. Zn and Mn consistently dominate the total measured metal load for all storms sampled.

Table 29.3. Instantaneous metal load calculations are reported in mg/sampling event. Land use averages for all storm events are also reported

Sampling location	Date	Suspended sediments					
		Cr	Mn	Ni	Cu	Zn	Pb
Above Liberty Reservior	6.18.03	112.0	2518.3	85.2	105.0	1373.6	12.6
	6.19.03	98.9	1227.0	43.7	32.2	327.9	1.4
	8.7.03	163.8	4757.8	93.4	89.3	1598.0	nd
	9.20.03	4.1	140.6	2.2	2.9	38.2	nd
Below Liberty Reservior	6.18.03	224.1	2688.3	148.0	102.6	1262.7	70.5
	6.19.03	15.7	59.4	6.6	2.7	35.3	2.8
	8.7.03	15.7	2243.7	117.4	64.4	1038.1	33.4
	9.20.03	127.2	3059.2	79.2	85.1	1612.0	nd
Rt. 97	6.18.03	332.6	5423.3	223.8	197.8	2188.9	115.6
	6.19.03	99.6	2014.0	51.8	49.1	228.6	1.5
	8.7.03	215.0	2243.7	117.4	64.4	1038.1	32.0
	9.20.03	193.1	3562.0	108.5	116.1	1322.0	nd
Merge	6.19.03	98.1	1697.0	48.2	49.2	166.6	43.3
	8.7.03	175.7	3584.2	97.7	74.3	2319.1	nd
Ellicott City	6.19.03	98.0	1566.0	47.4	47.2	160.7	43.3
	8.7.03	162.0	2713.0	68.5	55.7	371.7	6.8
	9.20.03	138.3	1941.0	61.0	47.7	242.1	5.9
Rt. 648	6.19.03	136.0	1794.0	66.1	59.7	255.5	1.5
	8.7.03	113.5	2005.2	50.7	59.9	549.3	64.7
	9.20.03	202.3	2689.0	87.1	80.6	446.7	64.2

Table 29.4. Chemical data for suspended sediments collected during storm events. All concentrations are reported in ug g^{-1} and RSDs are generally better than 2%

Sampling location	Date	Instantaneous metal load (mg/sampling event)					
		Cr	Mn	Ni	Cu	Zn	Pb
Above Liberty Reservior	6.18.03	2.7	61.6	2.1	2.6	33.6	0.3
	6.19.03	20.3	251.5	9.0	6.6	67.2	0.3
	8.7.03	0.9	25.7	0.5	0.5	8.6	nd
	9.20.03	0.6	20.4	0.3	0.4	5.6	nd
Below Liberty Reservior	6.18.03	1.3	15.1	0.8	0.6	7.1	0.4
	6.19.03	2.0	7.6	0.8	0.3	4.5	0.4
	8.7.03	0.2	28.0	1.5	0.8	12.9	0.4
	9.20.03	0.3	7.3	0.2	0.2	3.9	nd
Rural average		*3.5*	*52.2*	*1.9*	*1.5*	*17.9*	0.4
Rt. 97	6.18.03	1.0	16.3	0.7	0.6	6.6	0.3
	6.19.03	27.1	548.6	14.1	13.4	62.3	0.4
	8.7.03	0.8	8.5	0.4	0.2	3.9	0.1
	9.20.03	1.0	18.2	0.6	0.6	6.7	nd
Merge	6.19.03	100.6	1740.4	49.4	50.4	170.9	44.4
	8.7.03	0.4	9.0	0.2	0.2	5.8	nd
Transition average		*21.8*	*390.2*	*10.9*	*10.9*	*42.7*	11.3
Ellicott City	6.19.03	94.3	1508.0	45.7	45.5	154.7	41.6
	8.7.03	23.8	398.0	10.0	8.2	54.5	1.0
	9.20.03	53.3	747.5	23.5	18.4	93.2	2.3
Rt. 648	6.19.03	86.2	1136.9	41.9	37.8	161.9	1.0
	8.7.03	2.8	50.2	1.3	1.5	13.8	1.6
	9.20.03	26.3	349.6	11.3	10.5	58.1	8.3
Urban average		*47.8*	*698.4*	*22.3*	*20.3*	*89.4*	*9.3*

29.6. Trace metal concentrations

Cr, Mn, Ni, Cu, Zn, and Pb data for suspended sediments, soils (bulk and size fractions), bay sediments and 7N HNO_3 leachates on Bay samples and soil samples are presented in Tables 29.4–29.8. The results are presented below by sample type.

Suspended sediments. With the exception of two samples, Mn is present at levels between 1200 and 5400 ug g^{-1} for all locations and all storm events. Despite this range there is no overall pattern to this data. Chromium is generally high relative to the upper continental crust (i.e., 35 ug g^{-1}, Taylor and McLennan, 1985). Values are generally greater than 100 ug g^{-1} with a maximum value of 332.6 ug g^{-1} at the Rt. 97 location on June 18, 2003. Nickel and Copper are values are enriched relative to the upper continental crust. Nickel values range from a low

Table 29.5. Chemical data for soils and size fractions collected from the adjacent flood plain at each of the sample locations. All concentrations are reported in ug g^{-1} and RSDs are generally better than 2%

Sampling location		*Soils*					
		Cr	Mn	Ni	Cu	Zn	Pb
Above Liberty Reservior	Bulk	51.4	679.1	22.9	35.0	74.3	11.7
	< 63 µm	87.0	1479.0	51.5	75.3	198.8	62.0
	< 5 µm	84.6	1405.0	49.3	75.8	201.9	62.6
Below Liberty Reservior	Bulk	123.9	815.1	54.0	23.9	71.2	12.9
	< 63 µm	148.7	1381.0	106.3	54.2	141.6	56.1
	< 5 µm	185.9	1954.0	141.1	72.2	184.9	41.5
Rt. 97	Bulk	62.6	852.8	29.3	25.2	69.3	16.2
	< 63 µm	101.5	1704.0	51.3	48.1	138.3	65.8
	< 5 µm	110.1	1929.0	59.6	59.6	171.1	77.2
Merge	Bulk	85.9	785.0	30.8	25.0	77.6	22.2
	< 63 µm	94.8	1267.0	48.0	45.0	129.0	43.5
	< 5 µm	105.5	1509.0	60.4	54.1	173.6	59.5
Ellicott City	Bulk	121.5	676.8	41.0	22.1	74.4	22.3
	< 63 µm	152.9	1302.0	70.5	58.3	164.9	75.2
	< 5 µm	158.1	1416.0	87.5	69.0	211.7	93.5
Rt. 648	Bulk	92.3	412.7	41.6	27.3	96.1	64.7
	< 63 µm	144.9	513.0	81.0	71.5	216.1	192.7
	< 5 µm	115.2	453.2	57.5	46.8	166.5	82.4

of 2.2 ug g^{-1} at the Above Liberty Reservior site on September 20, 2003, to a high of 223.8 ug g^{-1} at the Rt. 97 site on June 18, 2003. Copper values range from a low of 2.7 ug g^{-1} at the Below Liberty Reservior site on June 19, 2003, to a high of 197.8 ug g^{-1} at the Rt. 97 site on June 18, 2003. Lead values are more variable for all samples collected. Zinc values for suspended sediment samples are considerably enriched relative to the upper continental crust for all samples except the June 19, 2003, and September 20, 2003, samples at the Below Liberty and Above Liberty sites, respectively.

Bulk soils and size fractions. Mn values for bulk soil samples are very similar to upper continental crust values. The grain size fractions are enriched to similar levels (i.e., 2–3 times the bulk soil value) relative to the bulk soils. Chromium in the bulk soils is enriched by up to 3.5 times values for the upper continental crust and up to 5.3 times in the grain size separates. Nickel in the bulk soils is enriched relative to crustal values at most of the locations with the lowest concentration of 22.9 ug g^{-1} at the AL site and the highest value of 54 ug g^{-1} at the Below Liberty site. The grain size fractions are enriched relative to the upper continental crust and the bulk soil at all locations. Copper in bulk soils, unlike Nickel, is

Table 29.6. Acid extractable metals data for soils and size fractions collected from the adjacent flood plain at each of the sample locations. All concentrations are reported in ug g^{-1} and RSDs are generally better than 2%

Sampling location		7N HNO_3 extractable from soils					
		Cr	Mn	Ni	Cu	Zn	Pb
Above Liberty Reservior	Bulk	5.2	123.0	4.8	7.2	19.2	4.4
	<63 μm	19.2	473.7	15.8	23.0	62.7	15.8
	<5 μm	18.6	520.2	15.0	26.7	75.0	19.8
Below Liberty Reservior	Bulk	16.8	111.0	9.8	4.4	14.0	3.0
	<63 μm	52.5	541.5	39.3	21.6	56.3	19.0
	<5 μm	43.5	527.9	35.7	18.6	49.3	18.2
Rt. 97	Bulk	11.8	255.5	8.0	7.0	23.2	5.0
	<63 μm	22.6	548.3	15.4	15.0	44.7	16.2
	<5 μm	14.8	474.9	12.6	13.4	40.9	16.0
Merge	Bulk	12.8	167.1	7.4	6.8	22.4	5.0
	<63 μm	13.0	258.7	9.8	9.4	28.5	8.4
	<5 μm	19.2	523.6	13.6	16.8	58.3	15.0
Ellicott City	Bulk	20.0	190.8	11.8	10.2	25.9	8.6
	<63 μm	14.6	181.8	8.8	8.0	26.7	11.0
	<5 μm	37.7	394.6	20.0	16.2	56.3	23.0
Rt. 648	Bulk	14.6	78.8	8.8	6.0	22.2	10.0
	<63 μm	32.3	171.5	21.0	16.4	57.3	46.1
	<5 μm	46.3	219.0	27.3	23.4	89.8	39.3

only significantly enriched above crustal values at the Above Liberty site. The copper concentrations in the grain size fractions exhibit a behavior similar to the other metals described and are generally enriched relative to bulk soils and the upper continental crust by as much as three times. Zinc and Pb are not generally enriched in the bulk soils with the exception of the Rt. 648 site which has Zn and Pb concentrations of 96.1 ug g^{-1} and 64.7 ug g^{-1}, respectively. The grain size fractions are generally 2–3 times greater than the bulk soils and upper continental crust concentrations at all sites.

All soil samples and grain size fractions were treated with 7N HNO_3 and the leachates were analyzed for the analytes of interest. This extraction is meant to represent a maximum value for the potentially bioavailable fraction. All samples of bulk soil and associated size fractions yield metals at the ug g^{-1} level when treated using the acid extraction method described above. The clay-sized fraction from the Rt. 648 soil sample yields the highest fraction of extractable metals at greater than 40% for all analytes with a high of 54% extractable Zn.

Bay sediments. Surface sediment samples collected from three locations in Baltimore's Inner Harbor and the Chesapeake Bay were analyzed for

Table 29.7. Acid extractable fractions available from soils and size fractions. All concentrations were normalized to individual values for total digestion

Sampling location		Acid extractable fraction from soils					
		Cr	Mn	Ni	Cu	Zn	Pb
Above Liberty Reservior	Bulk	0.10	0.18	0.21	0.21	0.26	0.37
	<63 μm	0.22	0.32	0.31	0.30	0.32	0.25
	<5 μm	0.22	0.37	0.30	0.35	0.37	0.32
Below Liberty Reservior	Bulk	0.14	0.14	0.18	0.18	0.20	0.23
	<63 μm	0.35	0.39	0.37	0.40	0.40	0.34
	<5 μm	0.23	0.27	0.25	0.26	0.27	0.44
Rt. 97	Bulk	0.19	0.30	0.27	0.28	0.33	0.31
	<63 μm	0.22	0.32	0.30	0.31	0.32	0.25
	<5 μm	0.13	0.25	0.21	0.22	0.24	0.21
Merge	Bulk	0.15	0.21	0.24	0.27	0.29	0.23
	<63 μm	0.14	0.20	0.20	0.21	0.22	0.19
	<5 μm	0.18	0.35	0.22	0.31	0.34	0.25
Ellicott City	Bulk	0.16	0.28	0.29	0.46	0.35	0.39
	<63 μm	0.10	0.14	0.12	0.14	0.16	0.15
	<5 μm	0.24	0.28	0.23	0.23	0.27	0.25
Rt. 648	Bulk	0.16	0.19	0.21	0.22	0.23	0.15
	<63 μm	0.22	0.33	0.26	0.23	0.27	0.24
	<5 μm	0.40	0.48	0.48	0.50	0.54	0.48

Table 29.8. Chemical data for Baltimore Harbor and Chesapeake Bay sediments. All concentrations are reported in ug g^{-1} and RSDs are generally better than 2%. Acid extractable concentrations were normalized to individual values for total digestion to determine the acid extractable fraction

Sampling location		Harbor and Bay Sediments					
		Cr	Mn	Ni	Cu	Zn	Pb
Inner Harbor	Bulk	172.3	535.4	56.1	106.0	274.6	89.7
	7N HNO_3 extractable	37.0	402.7	14.2	16.6	109.9	19.8
	Acid extractable fraction	0.215	0.752	0.254	0.156	0.400	0.220
Sparrow's Point	Bulk	402.9	879.2	54.7	152.1	665.3	154.0
	7N HNO_3 extractable	33.2	112.6	14.3	28.2	76.2	20.8
	Acid extractable fraction	0.082	0.128	0.261	0.185	0.114	0.135
Chesapeake Bay	Bulk	151.1	1378.0	48.9	56.3	366.0	72.1
	7N HNO_3 extractable	25.7	60.4	3.8	10.6	50.3	11.3
	Acid extractable fraction	0.170	0.044	0.077	0.189	0.138	0.157

their bulk and acid extractable trace metal concentrations. Bulk trace metal concentrations from all Bay sediment samples are generally higher than bulk soil concentrations. Zinc in particular, ranges from 274 to 665 ugg^{-1} and falls between the ranges for bulk soils and suspended

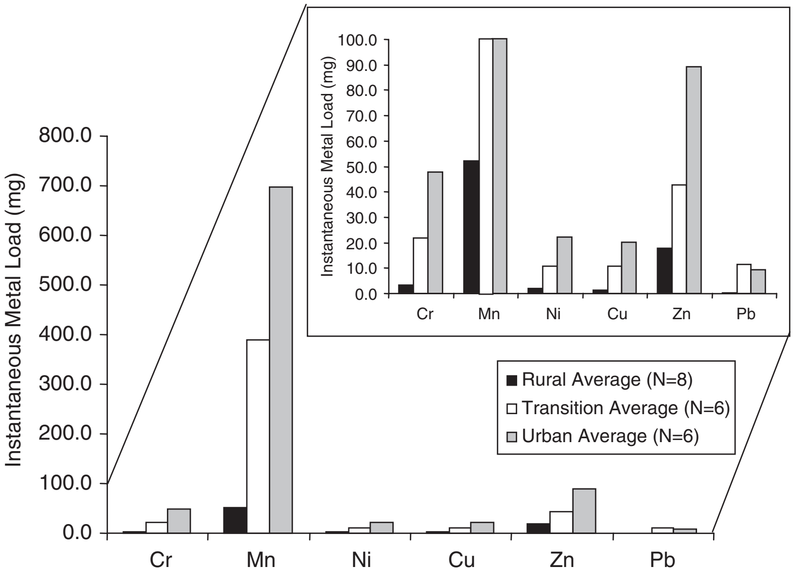

Figure 29.3. Instantaneous metal load values were grouped according to land use and the average values for all elements are plotted by land use. The inset highlights the differences for all elements except Mn. Zn and Mn are the most abundant trace metals for all land uses. Urban sampling sites are making a larger contribution to the total metal load than any of the other land use designations.

sediments. Bulk bay sediments are more comparable to the clay-sized fraction of soil samples although still relatively enriched. With the exception of 75% extractable Mn and 40% extractable Zn at the Inner Harbor sampling location all other extractable metal concentrations from bay sediments are uniformly below 25%.

29.7. Discussion

There are three distinct trends in the data described above. The chemical data suggest a multi-source system comprised of both natural and anthropogenic trace metal sources to both the Patapsco River and the Inner Harbor. The stream data and trace metal load calculations portray a storm water dominated system characterized by disproportionately high-sediment yield through out the Patapsco River watershed, a trace metal flux that is directly related to discharge and a increasing trace metal load during storm events from rural to urban land use zones within the watershed. These relationships are evident in Figs. 29.3, 29.4 and 29.5. In Fig. 29.3, the instantaneous metal load is clearly related to the land use characteristics in the local catchment (see Table 29.1). This suggests, especially for Zn and Mn, that the flux of metal to the Chesapeake Bay is dominated by input from the urbanized portion of the watershed.

In Fig. 29.4, trace metal concentrations are plotted versus suspended sediment concentration for all storm events sampled at all locations. Using Zn as an example, as the amount of sediment being transported during a storm event increases, the Zn concentration decreases. As Zn values decrease, they trend toward values similar to the upper continental crust and Patapsco watershed soils. Therefore, storm events generating larger sediment yields will tend to exhibit a soil-derived trace metal signature while the smaller events trend toward higher, non-soil derived, Zn values indicating the importance of a secondary Zn-enriched non-point source. Despite higher overall concentrations of Zn in the smaller storm events (low yield–low discharge), the low concentration (high yield–high discharge) events are delivering the largest total load of Zn to the bay (Table 29.3 and Fig. 29.5a). In addition, it appears that with increasing storm intensity the trace metal character of the suspended sediment load trends toward the range of concentrations typical for bulk soils within the Patapsco watershed (Fig. 29.5b).

There are two likely scenarios that can account for the elevated Zn concentrations in the suspended sediment of the smaller storm events. The first is that the fine fraction of the soil being eroded and transported through the Patapsco river system is enriched in Zn due to chemical weathering processes. Smaller storm events with lower velocity discharge will tend to carry a smaller average grain size. The fine fraction of all the soils sampled are enriched relative to the bulk soil suggesting that they are a viable source; however, the suspended sediment Zn concentrations are greatly in excess of even the most elevated values in the fine soil fraction (Fig. 29.4). The second scenario is that there is a ubiquitous metal-enriched anthropogenic source of Zn to the Patapsco river system that dominates smaller low-sediment yield events but is diluted by soil-derived metals during larger events when there is more sediment being transported through the system. A plausible non-point source of Zn within the watershed is roadway dust.

In an developed setting, such as the urban portion of the Patapsco Watershed, roadway-derived contaminants have recently been identified as a significant component of urban dust (Kupiainen and Tervahattu, 2005; Omstedt et al., 2005; Samara and Voutsa, 2005). In several Scandinavian and European cities, urban dust in the 2.5–10 μm size range (PM_{10}) is primarily composed of non-tailpipe, roadway-derived particles.

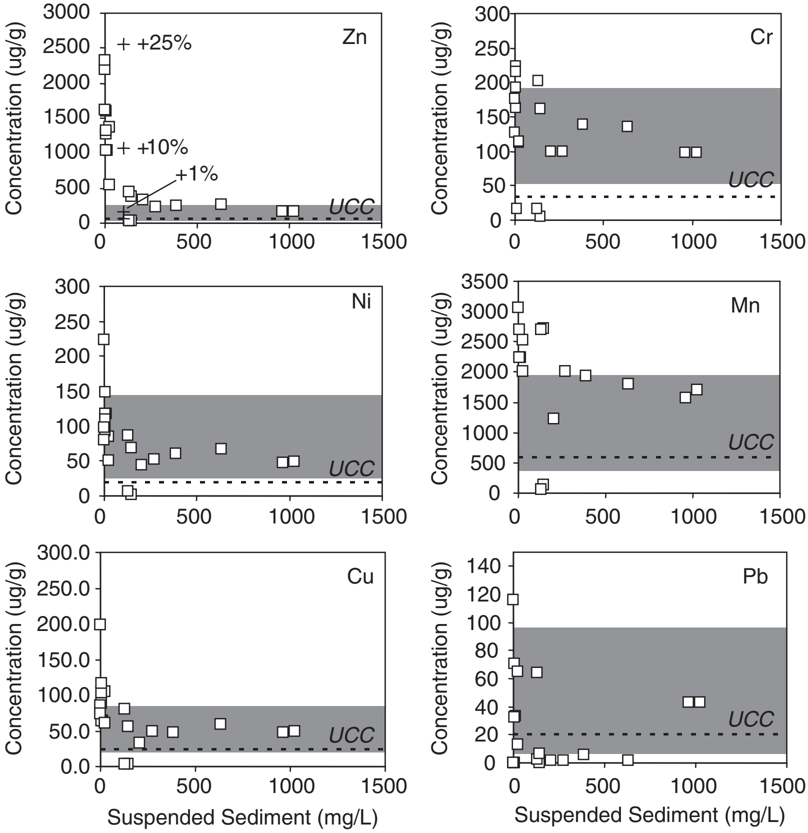

Figure 29.4. Plots of trace metal concentrations in suspended sediments versus suspended sediment concentrations. All metal values are in $\mu g\,g^{-1}$, suspended sediment values are in $mg\,l^{-1}$. The dashed line in each plot represents the average value in the upper continental crust (UCC) as reported in Taylor and McLennan (1985). The gray field in each plot represents the range in concentrations found in the fine soil fraction. The + marks in the Zn plot represent a mixing model between the UCC and tire-derived Zn. The percentages are the total Zn contribution from tires.

A large portion of the roadway particulate load is thought to be geological material (Kupiainen and Tervahattu, 2005). Recent sampling of roadway dust from within the Chesapeake Bay watershed confirms this assertion and documents the relatively low-trace metal load associated with this fraction of the dust (Camponelli et al., 2005). This work also documents the presence of a trace metal enriched (specifically Zn and Cu) component in the roadway dust. One of the major components of roadway dust is thought to be fine rubber fragments derived from tire wear

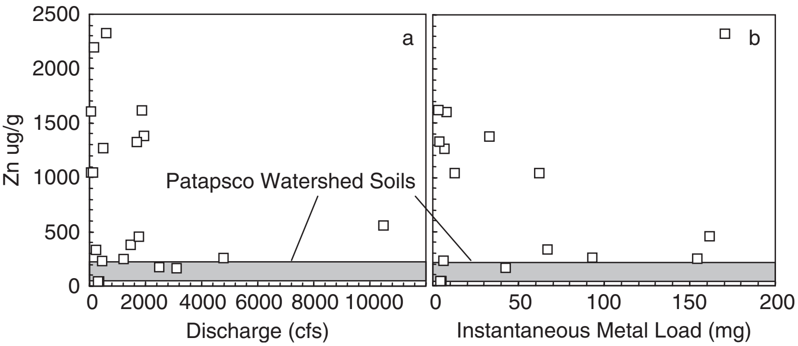

Figure 29.5. (a) Zinc concentrations for suspended sediments are plotted versus discharge. The gray field represents the range of Zn measured in bulk soils analyzed during this investigation. As discharge increases, the Zn concentration of the suspended sediment flux decreases toward soil Zn range indicating the importance of soil-derived Zn in during larger storm events. (b) Zn concentration for suspended sediments is plotted versus instantaneous metal load values calculated for each storm event. There is an inverse trend between Zn concentration of the suspended sediment and the metal load for each event. As in (a) larger storm events have lower overall Zn concentrations in the particulate load; however, the total Zn load is greater. These diagrams suggest that soil-derived Zn is the primary component in the metal load to the Chesapeake Bay.

(Councell et al., 2004). The presence of tire particles in roadway dust from with in the Chesapeake Bay Watershed has been confirmed by Camponelli et al. (2005). These particles tend to be enriched in metals such as Pb, Cd, Cr, Ni, V, Cu, Mn, and Zn and may represent a significant nonpoint source of metals to roadside environments (Samara and Vousta, 2005; Kupiainen and Tervahattu, 2005 and references therein).

In the case of Zn, tire particles have been documented to contain up to wt.% Zn and are widely distributed on roadway surfaces (Councell et al., 2004). In Fig. 29.4, we present a model for the addition tire-derived Zn to naturally derived suspended sediments. Starting at an upper crustal composition similar to Patapsco soils, the proportion of tire-derived Zn in the suspended sediments is incrementally increased (1%, 10%, and 25%). Based on this simple two-component mixing model, there may be as much as 10% tire-derived Zn in the suspended sediments during the low-sediment yield discharge events (Fig. 29.4). This model is complicated by the fact that there may be other minor roadway-derived sources of Zn in addition to tires and therefore represents a maximum value for tire-derived Zn.

All other metals analyzed exhibit a pattern similar to that of Zn when plotted versus suspended sediment concentrations indicative of storm water controlled grain size effect (Fig. 29.4). However, with the exception of Cu and Mn, the fine fraction of the soils generally overlap the highest metal concentrations in the suspended sediments suggesting that these metals are primarily soil derived within the watershed and by extrapolation, the harbor and the bay. This does not hold up when examining Baltimore Harbor and Chesapeake Bay sediment samples from this study and previous work (Sinex and Helz, 1981; McGee et al., 1999). In Fig. 29.6, harbor, bay and suspended sediment samples from this study and work by Sinex and Helz (1981) and McGee et al. (1999) are plotted in Zn versus Cr concentration space. Also plotted is the upper continental

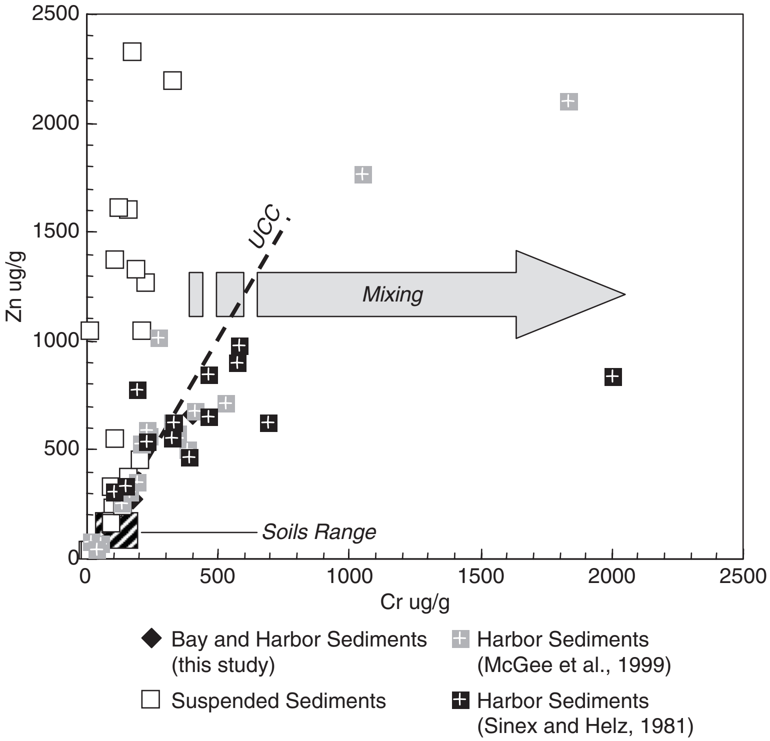

Figure 29.6. Zinc versus Cr concentrations are plotted for suspended sediment from this study (white square), harbor and bay sediments from this study (black diamond) and harbor sediments from two previous investigations (black and gray with white plus). Also plotted for reference in an UCC line that represents the ratio of Zn/Cr in the crust. If soils are the primary source of these metals the point would lie on or near the line. The gray arrow represents a general mixing pathway between the suspended sediments entering Baltimore Harbor from the Patapsco and local point sources adjacent to the Harbor. With no local source addition Harbor sediments should look very similar to the suspended sediment input from the Patapsco River.

crust (UCC) line used previously. If the metals in the Harbor and Bay sediments are soil derived we would expect these samples to lie along the upper continental crust line and within the soils range. If either metal is enriched via an anthropogenic source, the sample(s) would lie off the line in the direction of the enriched source. Based on the chemical characteristics of suspended sediments within the watershed, harbor and bay sediments should be enriched in Zn and essentially crustal with respect to Cr concentrations. This is clearly not the case in for the harbor and bay sediments plotted in Fig. 29.6. The Zn and Cr ratio for the bay sediments from this study and those from Sinex and Helz (1981) and McGee et al. (1999) appear to have a crustal ratio but plot well out of the soils range. This does not appear to be in agreement with the predictions made when considering the chemical composition of the suspended sediments entering the bay. The expectation would be for enriched Zn, but Cr this is comparable to the soils range defined in this study.

The discrepancy between the trace element characteristics of Patapsco River suspended sediments entering Baltimore Harbor and bottom sediments within the Harbor can be explained with a simple two-component mixing model. If the concentration of suspended sediments within the Patapsco River is set as one end member, the Harbor sediments likely represent an intermediate composition between the suspended sediments and a local point source within the Harbor. It is also possible that there is some contribution to Harbor sediments by transported or dredged sediments; however, this does not change the basic premise that there are at least two significant trace metal sources to Baltimore Harbor, suspended sediment and at least one local source. A generalized mixing pathway is plotted in Fig. 29.6. The process of trace metal addition in the Harbor is most clearly demonstrated in Fig. 29.6 with the addition of a Cr-enriched source to watershed-derived Zn-enriched sediments. The suspended sediment concentrations can therefore be considered a lower limit for recently deposited Baltimore Harbor sediments. If average Harbor sediments (McGee et al., 1999) are normalized to average Patapsco suspended sediments (this study) a signature for the non-watershed trace metal source(s) can be discerned. In Fig. 29.7, Cr, Cu, and Pb are enriched by as much as a factor of 2 over Patapsco-derived suspended sediments while Mn, Ni, and Zn are comparable in Harbor and suspended sediments. While these signatures are based on a small number of samples the relative pattern of enrichment in the Harbor is clear.

Regardless of the ultimate source of trace metals to the Harbor, the mobility of these metals remains a question. In an effort to begin to evaluate the availability of the analytes in this investigation bulk soils, size fractions and harbor and bay sediments were treated with 7N HNO_3.

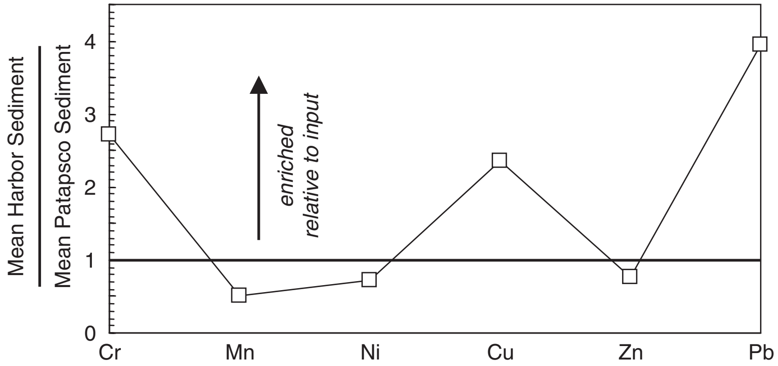

Figure 29.7. Plot of mean Baltimore Harbor sediment concentrations normalized to mean Patapsco suspended sediment input. If the primary source of trace metals to the Harbor is the suspended sediments from the Patapsco River the ratio of Harbor sediment/suspended sediment will be 1. Mn, Ni, and Zn are similar in the suspended sediments and Harbor sediments, while, Cr, Cu, and Pb are highly enriched in the Harbor relative to the suspended sediment input.

While this is an aggressive treatment of these sediments and soils, it will provide an estimate of the upper limit for extractable metals. In Fig. 29.7, average extracted metal patterns are plotted for bulk soils, size fractions and harbor and bay sediments. On average between 20% and 35% of the metals bound in soils are acid extractable. Excluding Mn and Zn, metals bound in harbor and bay sediments are less available at <20% and generally uniform. Zn and Mn are more available in harbor and bay sediments at 21% and 30%, respectively and are enriched within the Patapsco River watershed relative to soils and the upper continental crust (Fig. 29.8). In addition, these metals do not appear to have a significant local source in the Harbor (Fig. 29.7) that may suggest that the watershed trace metal sources may be more reactive than harbor and bay sources. Suspended sediments were not treated due to limited sample size.

29.8. Summary and conclusions

In summary, sediment being transported within the Patapsco River watershed represents at least two distinct trace metal sources. Soil-derived metals appear to dominate the suspended sediment during larger storm events for all analytes in this study. During smaller discharge storm events, there appears to be a Zn-enriched source that is a major

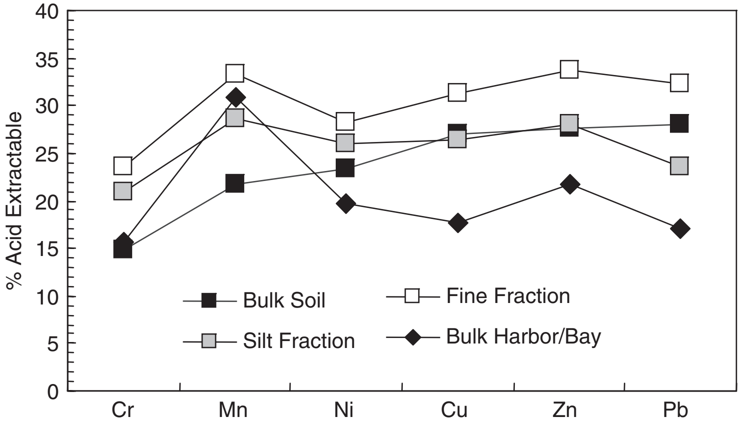

Figure 29.8. Plot of average % acid extractable metals for bulk, silt and the fine fraction of soils from the study area and bulk harbor and bay samples from this study. Trace metals in the soils and hence much of the suspended sediment load are more available than metals bound in harbor and bay sediments.

component of suspended sediment flux. This combined watershed signature is clearly different than the bulk trace metal signature in Baltimore Harbor and the Chesapeake Bay. Instead, the trace metal signature of harbor sediments displays a pattern that requires an additional local trace metal source(s). The local source is enriched in Cr, Cu, and Pb relative to the Patapsco input and is apparently less reactive than the trace metal bearing phases in the suspended sediment load.

One of the primary research questions in this investigation is the importance of soil-derived trace metals to the total flux of trace metals to the Chesapeake Bay. The results of this study point to a storm water controlled system of sediment and therefore trace metal flux. High-discharge storm events carry soil-derived suspended sediments with relatively low-metal concentrations but deliver the greatest metal load to the bay. Smaller storm events in the Patapsco are dominated by a Zn-enriched anthropogenic non-point source that is likely derived from roadway dust. While this non-point source is certainly present during the lager discharge events, its trace metal signature is overwhelmed by the soil signature. By evaluating the background trace metal signature of the sediment flux through the Patapsco River watershed it is possible to identify watershed-derived sources and local point sources to Baltimore Harbor. This is an important step toward characterizing the trace metal flux to the Chesapeake Bay.

There are several more general conclusions that can be drawn from this investigation:

(1) The trace metal concentration of suspended sediments in a mixed land use watershed, typical of the Chesapeake Bay watershed as a whole, do not correlate with the transported trace metal load;
(2) In a mixed land use watershed, soil sources will dominate the trace metal load and therefore the total flux of metals during large storm events;
(3) Urban regions in a mixed watershed will contribute the majority of the trace metal load during most storm water discharge events.

These more broad statements will be useful for future investigations in the Chesapeake Bay watershed and other large at risk regional catchments. The notion that the trace metal concentration of the suspended sediment load may not accurately reflect the total trace metal flux through a system is potentially the most important finding from this investigation.

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