

Chapter 6

Environmental geochemistry of trace metal pollution in urban watersheds

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Abstract

Trace metal concentrations (notably lead, zinc, cadmium, chromium, and nickel) within urban watersheds on all continents remain higher than background levels primarily as the result of “non-point source” (i.e., diffuse) pollution. Metal contamination can be generated within a given urban watershed (*endogenous* pollution) or originate from and spread beyond its watershed boundaries (*exogenous* pollution). Zinc is likely the most prevalent urban metal contaminant today and the most important source of this trace metal is automotive tire wear. Other sources of urban metal pollution include road surfaces, roofs, paint, waste incineration, and untreated sewage effluent.

The largest flux of metals in most urban watersheds likely comes with the “first flush” (rising limb of the hydrograph). The dominant geochemical process controlling the fate of metals is adsorption in that most metal ions partition onto suspended sediment (operationally defined as particulate matter $>0.45\ \mu\text{m}$). The principal concern is that a large percentage of sediment-bound metal is “bioavailable” and therefore can be harmful to aquatic ecosystems (notably estuaries downstream of major urban centers) even at low concentrations.

The utilization of “cleaner” sampling methodologies and improved analytical capabilities indicate that metal concentrations in many urban and non-urban stream systems today are at low-trace levels (i.e., $<1\ \mu\text{g}\ \text{l}^{-1}$). Sediment core data from numerous urban lakes and reservoirs suggest that the Clean Water Act of 1972 and other environmental legislation resulted in reduced lead loading to our streams. Zinc concentrations, however, may be increasing as the result of increased urbanization and automotive traffic. Metal concentrations within sediment cores from many urban localities are

above environmental quality guidelines indicating that more work has to be done in reducing metal influx to our stream basins.

6.1. Introduction and Background

The horrendous occurrences of Itai–itai and Minamata diseases in Japan during the late 1950s and early 1960s made the modern world painfully aware of the health dangers posed by cadmium and methyl mercury pollution in natural waters. In high concentrations, heavy metals, including mercury, chromium, nickel, cadmium, and lead, can be toxic, carcinogenic, and mutagenic (Siegel, 2002). Lead has been implicated as an agent of mental retardation for two millennia (at least since Roman times) and chromium and cadmium are known to cause immunosuppressant effects in humans (McCabe, 1998). A few of the health problems as well as a few of the common sources of metals in drinking water are given in Table 6.1.

In addition to medical problems, elevated concentrations of trace metals entering streams and rivers from the urban environment may result in significant damage to ecosystems (Dunne and Leopold, 1978).

Table 6.1. US EPA National Primary Drinking Water Quality Standards (MCL), sources, and common medical effects for trace metals (from EPA, 2005)

Metal	MCL ($\mu\text{g l}^{-1}$) ^a	Potential health effects from water ingestion ^a	Common industrial or urban sources of contaminant in drinking water ^{a,b}
Cadmium	5	Kidney damage	Galvanized pipes, refineries, waste batteries and paints; anti-corrosive coatings, coal combustion
Chromium	100	Allergic dermatitis	Steel and pulp mills, erosion of natural deposits, steel alloys, plating operations, wood treatment
Copper	1300	Gastrointestinal distress, liver, kidney damage	Corrosion of household plumbing systems, paint pigments, alloys
Lead	15	Delays of physical and mental development, kidney damage, high blood pressure	Corrosion of household plumbing systems, anti-knock fuel agents, tetramethyl lead, lead–acid batteries, paint pigments, plastics, alloys, pipes

MCL, Maximum concentration limit.

^aEPA (2005).

^bSiegel (2002).

Cadmium concentrations as low $1\text{--}10\ \mu\text{g l}^{-1}$ can have lethal effects upon aquatic organisms (Eisler, 2000) and metal poisoning can occur via direct intake from water or indirectly from contaminated sediment or nutrients. Many of the so-called *urban metals* including lead, cadmium, zinc, and chromium are to some extent available to aquatic organisms. Microorganisms feeding off sediment have the ability to oxidize, reduce, methylate, or demethylate metals that affect their “bioavailability” for higher organisms (Amiard, 1992). In most modern urban environments, metal pollution likely poses a greater direct threat to ecosystems than it does to drinking water.

The Clean Water Act established in 1972 has greatly reduced the impact of metal pollution from industrial and municipal sources within urban watersheds in the United States. Similar environmental legislation during the past 30–40 years has had beneficial effects in many other nations as well. To cite a few examples of improving conditions, median concentrations of copper, cadmium, nickel, and zinc within the Hudson River estuary declined between 53% and 90% since the mid-1970s with the reduction of wastewater discharge (Sañudo-Wilhelmy and Gill, 1999). Lead importation to the Gulf of Mexico from the Mississippi River has declined by about 40% between 1974 and 1984 as a result of reduced lead consumption in gasoline within the United States (Treyfey et al., 1985). Nonetheless, urbanization and the advent of the *megalopolis* is a worldwide phenomenon and continues to produce higher-than-background metal loadings in river networks throughout the world. For example, concentrations of the “urban metals” including lead, cadmium, copper, and zinc vary by three orders of magnitude within the Seine River basin and are four times higher than upstream in the Paris region where they approach background levels (Horowitz et al., 1999). Furthermore, the exceptional metal contamination of the urbanized regions within the Seine basin remains high following 20 years of generally improved conditions (Meybeck et al., 2004).

Urban watersheds are complex systems that potentially sequester and remobilize both historical and contemporary metal pollutant inputs. Therefore, the long-standing health and environmental problems associated with trace metal pollution persist as a result of the contamination of sediment deposited within urban stream basins and estuaries downstream of our cities. Flood-plain soils and other urban sediment can remain polluted in a similar manner long after point-source pollution problems have been mitigated. In a recent study documenting this persistence, Filippelli et al. (2005) have measured lead concentrations between $200\ \text{mg kg}^{-1}$ and greater than $1000\ \text{mg kg}^{-1}$ within inner city soils of Indianapolis, Indiana and claim that 400,000 children within the

United States (mostly in the inner cities) have unsafe lead levels in their blood. Rice (1999) estimated that 49% of the stream sediments in U.S. urban settings are characterized by concentrations of trace metals that exceed levels at which adverse biological effects could occur in aquatic biota.

The problem of returning trace metal concentrations to *background levels* within urban watersheds is particularly difficult in that many of the remaining sources are diffuse (i.e., non-point sources). Our urban and suburban way of life is presently dependent upon automotive transportation, which with mining and waste incineration comprise the dominant sources of global metal contamination. Vink and Peters (2003), in a study of metal contamination within the Elbe River basin (which drains Berlin, Hamburg, Prague, and Leipzig), concluded that 84% of the input of lead and 64% of the input of mercury originate from diffuse sources and more metal is imported to this basin than is exported.

Although the literature is heavily weighted to studies of stream sediment within the United States, trace metal contamination is a global problem as documented by studies of urban watersheds in India (Singh, 2001), England (Dawson and Macklin, 1998), Sweden (Palm and Östlund, 1996), southern Africa (Zhai et al., 2003), Switzerland (von Gunten et al., 1997), Spain (de Miguel et al., 1998), Italy (Renoldi et al., 1997), Germany (Behrendt, 1993), and New Zealand (Abraham and Parker, 2002). These studies suggest that metal concentrations within urban stream sediment are elevated many times above “background” levels. For example, Lindström (2000) observed that cadmium, copper, mercury, and lead in the central areas of Stockholm are approximately five times above the surrounding regions. Widianarko et al. (2000) noted that while urban stream sediments in Semarang (Indonesia’s fifth largest city) are not universally contaminated; there are “hot spots” in which zinc, lead, and copper concentrations were hundreds of times above background levels.

In this communication, we summarize our present understanding of the trace metal problem within urban watersheds by discussing the most common sources of metals, the dominant hydrogeochemical processes affecting the partitioning of metals between water and stream sediment, the developing methodologies used to measure and monitor trace metals, and historical trends for metals provided by sediment core data recovered from urban reservoirs. We focus primarily upon lead (Pb), zinc (Zn), and copper (Cu) in that these metals are readily associated with the urban environment and have been identified as priority pollutants in urban runoff (EPA, 1986). We also include some data for cadmium (Cd), nickel (Ni), vanadium (V), chromium (Cr), and cobalt (Co) in that these trace

elements are often coanalyzed and associated with the three major priority contaminants. Other metals, notably mercury (Hg), silver (Ag), aluminum (Al), barium (Ba), platinum (Pt), palladium (Pd), tin (Sb), and metalloids, such as arsenic (As) and selenium (Se), are potentially problematic contaminants within the urban environment but are not emphasized herein.

6.2. Sources and sinks of trace metals in the urban environment

All watersheds are potentially *open* systems in that metals can be transported from atmospheric, industrial, municipal, upstream riverine, and other sources such as mining operations that are not indigenous to the specific watershed under consideration (see Fig. 6.1). The urban watershed in turn has numerous sources of trace metals within its own boundaries that include automotive pollution, rooftops, galvanized pipe, paint, sewage effluent, industrial wastes, and contaminated soils (Table 6.1). Urban air is often contaminated to some degree with metals and both wet and dry deposition account for significant metal flux. Larger particulate

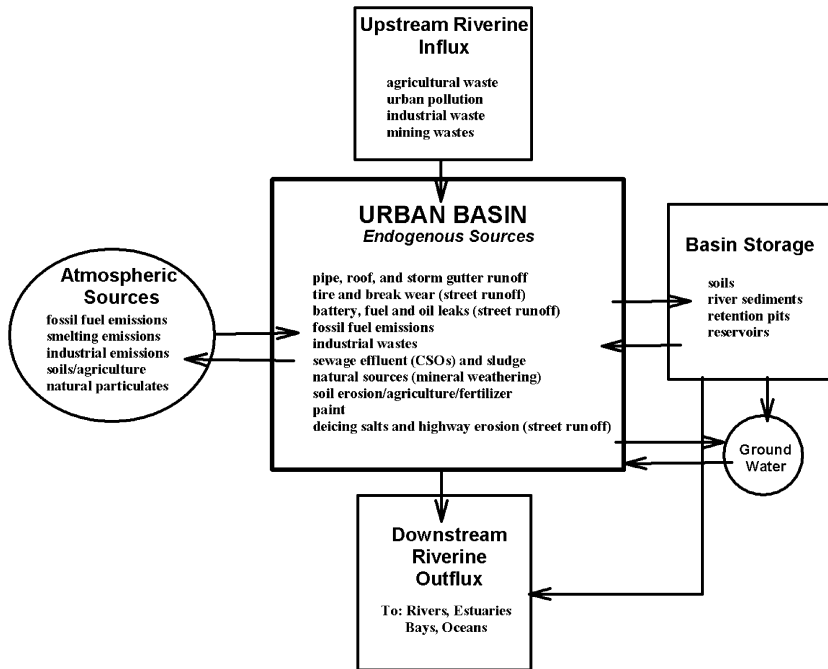


Figure 6.1. Common metal fluxes to and from upstream urban stream basins.

matter delivers most of the metals in dry precipitation or fallout (Sweet et al., 1998). Dusts emitted from the burning of fossil fuels in industrial regions are enriched in V, Ni, and Co (Norra and Stüben, 2004). Municipal waste incineration (Chillrud et al., 1999) along with fossil fuel emissions are potentially important sources of metal contamination within watersheds (*endogenous* pollution) and beyond the divides of urban watersheds (*exogenous* pollution).

Regional studies provide convincing evidence that the most salient feature of metal pollution is its diffuse (non-point source) nature. For example, in the vast Great Lakes Basin in Canada and the United States, urban metal pollution ranks second only behind agriculture as a non-point source of regional pollution (Marsalek, 1990). Aerosols in the Russian Arctic atmosphere are polluted with heavy metals originating from Europe, the Kola Peninsula, and North America (Shevchenko et al., 2003). Pb, Cu, and Zn concentrations within dry air were higher in Chicago than in the surrounding Lake Michigan region; however, Lake Michigan was strongly influenced by Chicago's metal emissions (Paode et al., 1998). Undisturbed urban soils in Madrid, Spain exceed background levels of Cu, Zn, and Pb by a factor of 2–4, likely due to the atmospheric fallout of metals from its own traffic (de Miguel et al., 1998). The extensive interstate highway system within the United States and similar road networks throughout much of the world serve not only as arteries for travel but also as conduits for automotive pollution. In short, the urban watershed should be viewed as both a source and a sink for metals and these metal contaminants are generated both endogenously and exogenously.

The urban watershed can store metals that have become sorbed to lake, reservoir, and stream basin sediment and soils. These watersheds can also export contaminated water and sediment downstream to estuaries, bays, and the oceans (Fig. 6.1). Groundwater–surfacewater interaction (both in terms of “gaining” and “losing” streams) is also a factor that in some cases need to be considered in understanding the total hydrogeochemical flux of metals within a watershed. We will now elaborate upon various sources of metal pollution, emphasizing automotive and roadway contamination in that these are often the most important non-point sources of trace metal pollution within the urban setting.

6.2.1. Natural sources of metals

As the term “trace metals” imply, natural concentrations of metals within the earth's crust and soils are relatively low, typically less than $100 \mu\text{g g}^{-1}$ (Li, 2000; Callender, 2004). Natural concentrations of V and Zn

approach $100 \mu\text{g g}^{-1}$ while Cd concentrations are lower than $1 \mu\text{g g}^{-1}$. Trace metal concentrations in river water reflect crustal concentrations and are often exceedingly low (typically $<1 \mu\text{g l}^{-1}$; Gaillardet et al., 2004; Table 6.2). In that many of the metals are *refractory* they are concentrated in mafic rocks (Li, 2000) and trace metals also tend to preferentially concentrate within shales (Wedepohl, 1991). Rock weathering and volcanic emissions account for an estimated 80% of the natural source of metals and are responsible for the release of between 1400 metric tonnes/year Cd and 45,000 metric tonnes/year Zn (Callender, 2004). In many locations, lithological factors pose only minor environmental controls in that the anthropomorphic flux of trace metals including Cd, Cu, Hg, Zn, and V exceed natural fluxes throughout the earth's surface by factors between 3 and 11 (Nriagu and Pacyna, 1988). However, lithological factors cannot be ignored, particularly in those watersheds where metal concentrations approach background levels.

6.2.2. Automotive sources of metals

In many urban areas, the industrial emission of atmospheric contaminants has been greatly reduced during the past three decades. In these regions the most significant source of metal pollution today is related to automotive use (Novotny and Olem, 1994 and references therein). Vehicular traffic generates waste products from exhaust emissions, lubrication fluid losses, tire wear, break pad linings, catalytic converters, deicing compounds, and road wear (Hares and Ward, 1999). The metals most commonly attributed to urban environments, and specifically to automobile pollution, are the priority pollutants Pb, Zn, and Cu; however, accumulations of Cd, Sb, Ba, Pt, and Pd have also been identified in sediment proximal to roadways (EPA, 1986). Zn flux is more significant than any of the other metals resulting from automotive wear and Pb is the dominant metal present within the automotive emissions (Legret and Pagotto, 1999; Table 6.3). There have been relatively few studies that have quantified inputs of metals from various sources within urban watersheds. However, in one such study Novotny and Olem (1994) estimate that ~45% of Pb in Milwaukee, Wisconsin watersheds originated from freeway and parking lot runoff and these sources account for approximately twice as much Pb as industrial, commercial, and residential runoff (Fig. 6.2).

Several studies have correlated traffic density or fuel consumption with Zn and Pb sediment concentrations in urban areas (Novotny and Olem, 1994; Weisner et al., 1998; Callender and Rice, 2000). Topsoils immediately adjacent to highways with high-traffic densities are typically

Table 6.2. Trace metal concentrations in urban sediments and other sources

	Cu	V	Cd	Cr	Co	Ni	Pb	Zn	Reference
<i>Global reference materials</i>									
Upper crust ($\mu\text{g g}^{-1}$)	25	86	0.1	69	18	55	17	67	Li (2000) and Callender (2004)
Average soil ($\mu\text{g g}^{-1}$)	39	82	0.1	61	13	27	26	74	Li (2000) and Callender (2004)
Average shale ($\mu\text{g g}^{-1}$)	45	130	0.3	90	14	50	20	95	Li (2000)
River water ($\mu\text{g l}^{-1}$)	1.5	NR	0.08	0.7	NR	0.8	0.08	0.60	Gaillardet et al. (2003)
<i>Environmental quality guidelines ($\mu\text{g g}^{-1}$)</i>									
Agency or organization									
Georgia Environmental Protection Division ¹	100	100	NR	100	20	50	75	100	Leigh and Gamble (1997)
Canadian Environmental Quality Guideline ²	36	NR	NR	37	NR	NR	35	123	CCME (1995)
¹ Soil Criteria; ² Threshold Effect Levels, values greater than guideline indicate possible adverse effects on aquatic life; NR = not reported									
<i>Urban soils, suspended and Benthic sediments (from streams, lakes, canals, reservoirs; in $\mu\text{g g}^{-1}$)</i>									
Source of metal/study area									
Estuary sediment, Lower Hudson Valley, New York (average of 31 locations)	76	NR	1.2	NR	NR	NR	81	182	Feng et al. (1988)
Ala Wai Urban Canal sediment, Honolulu Hawaii (at depth of 49 cm below water)	16	245	1.1	398	55	282	276	456	De Carlo and Anthony (2002)
Suspended sediment, Yamuna River, Delhi, India (median values)	171	NR	3.0	303	18	69	37	232	Singh (2001)
Suspended sediments, River Manzanares, Madrid, Spain (mean "urban" samples, eight locations)	101	34	NR	48	6.4	22	146	294	de Miguel et al. (2004)

Stream-bed sediment from the US (median values for 540 sites)	27	NR	0.4	64	NR	27	27	110	Rice (1999)
Suspended sediment, Seine Mouth, downstream of Paris	130	NR	3.3	NR	NR	NR	147	510	Horowitz et al. (1999)
Suspended sediment, Seine background, upstream of Paris	20	NR	0.35	NR	NR	NR	19	60	Horowitz et al. (1999)
Roadside topsoil adjacent to highways in Osbgobo, Nigeria (mean values)	21.2	NR	0.60	NR	NR	8.4	68.7	42.4	Fakayode and Olu-Owolabi (2003)
Semerang Central Java, Indonesia (median values, 101 sites)	42	NR	NR	NR	NR	NR	18	105	Widianarko et al. (2000)
Gaborone, Boswana (average value of for nine sites in the city center)	36	NR	1.6	72	17	48	112	248	Zhai et al. (2003)
Post 1750 floodplain sediment, River Swale, northeastern England (mean concentrations)	18	NR	NR	33	NR	NR	1660	637	Hudson-Edwards et al. (1999)
Core from Burlington harbor, Vermont (maximum values)	110	NR	1.3	31	NR	NR	272	404	Mecray et al. (2001)
Stream and drainage system sediments, Ganga Plain, India, mean values, 1994	132	NR	1.5	2,685	55	102	197	857	Ansari et al. (1998)
<i>Urban stream water ($\mu\text{g l}^{-1}$)</i>									
River Thames estuary, England (1995)	10.7	NR	0.32	NR	NR	6.3	9.9	29.1	Power et al. (1999)
Peachtree Creek, urban Atlanta, storm runoff (median storm values)	1.9	0.9	NR	NR	NR	2.0	1.0	60	Rose et al. (2001)
Calder river in (urbanized stream in NE England, mean values)	5.8	NR	NR	4.82	1.86	7.6	1.25	35.9	Neal et al. (1996)
14 non-urbanized Wisconsin streams (mean concentrations)	0.6	NR	0.01	NR	NR	NR	0.08	0.46	Shafer et al. (1999)
Small urban watercourse, Dagenham, UK	11.3	NA	3.3	3.7	NR	70	7.7	65	Scholes et al. (1998)

Table 6.2. (Continued)

	Cu	V	Cd	Cr	Co	Ni	Pb	Zn	Reference
<i>Large river systems ($\mu\text{g l}^{-1}$)</i>									
Ottawa River, Canada	1.14	0.35	0.02	NR	0.07	0.83	0.11	3.53	Gaillardet et al. (2004)
Average of 21 Amazon River tributaries (sampled twice)	1.0	0.48	0.08	0.48	0.08	0.55	NA	1.2	Seyler and Boaventura (2003)
Average Mississippi River water	2.1	<3.0	<5.0	1.1	<0.5	1.8	<0.5	2.2	Horowitz et al. (2001b)
17 east coast rivers, United States (average values)	1.1	NR	0.01	NR	NR	NR	0.02	0.85	Windom et al. (1991)
Niger River, Africa	0.63	0.59	NR	0.45	0.04	0.29	0.04	0.89	Gaillardet et al. (2004)
Ohio River water, Olmstead, Illinois, 1990–1992	1.76	0.43	NR	NR	NR	1.21	11.74	0.33	Schiller (1997)
<i>Street or highway runoff ($\mu\text{g l}^{-1}$)</i>									
Svaneburg, Sweden, Highway E20 (summer)	13.3	NR	0.05	NR	1.4	NR	7.0	89.3	Bäckström et al. (2003)
Norsholm, Sweden, Highway E4 (winter)	126	NR	0.53	NR	13.3	NR	21.0	287	Bäckström et al. (2003)
Urban street runoff Atlanta, USA (median values)	16.9	3.2	NR	NR	NR	4.0	11.4	905	Rose et al. (2001)
Highway runoff, inflow to a biofiltration pond, London	274	29	14.1	105	6.7	93	81	208	Hares and Ward (1999)
IP 4 mountain highway runoff, Portugal (average values)	10.7	NR	NR	NR	NR	NR	10.8	172	Barbosa and Hvitved-Jacobsen (1999)

Table 6.3. Emission fluxes ($\text{kg km}^{-1} \text{year}^{-1}$) on roads, estimated by measuring mass fluxes of particles and metals over 10 months, for 1 km of road

Sources	Pb	Cu	Cd	Zn
<i>Vehicles</i>				
Tire wear	0.002	0.0006	0.0008	3.22
Brake linings	0.390	14.2	0.0003	2.17
Gasoline	13.0			
<i>Road</i>				
Safety barrier	0.002	0.0002	0.0002	0.95
Deicing agents	0.015	0.002	0.0007	0.002
<i>Vehicles</i>				
Leaded gasoline	200			
Unleaded gasoline	17			
Brake linings	3900	142,000	2.7	21,800
Tire rubber	6.3	1.8	2.6	10,250
<i>Road</i>				
Deicing agent	3.3	0.5	0.2	0.5

Note: Metal content (mg kg^{-1}) in vehicles and road materials (from Legret and Pagotto, 1999).

contaminated with metals (e.g., high Pb, Cd, Cu, Ni, and Zn concentrations adjacent to highways in Osobogo, Nigeria; [Fakoyde and Olu-Owolabi, 2003](#)). Lead contamination from street and roadside sources is of particular concern because Pb loads within surface water ranks second only to Zn ([Weisner et al., 1998](#)). [Kelly and Thornton \(1996\)](#) showed that Pb concentrations in roadside soils generally decrease exponentially with distance from the road. Elevated Pb concentrations are common in areas where traffic density is high and vehicles are required to start and stop regularly ([Lyons et al., 1990](#); [Kelly and Thornton, 1996](#)). [Shea et al. \(2004\)](#) found a convincing relationship between population and road densities and exchangeable Pb and Zn in stream sediment from the Atlanta, Georgia metropolitan region. However, there was far-less correlation between other trace metals and the degree of urbanization in the same basins. The maturation of global information system (GIS) analysis has added a needed spatial dimension for the correlation of trace metal distribution patterns with population and road density.

Trace metal discharges from gasoline combustion and other petroleum-related sources are, no doubt, important sources of metals; however, vehicle-related metal inputs are largely a product of wear, rather than derivatives of fuel combustion ([Sternbeck et al., 2002](#); [Harrison et al., 2003](#)). Tire erosion constitutes the most substantial source of

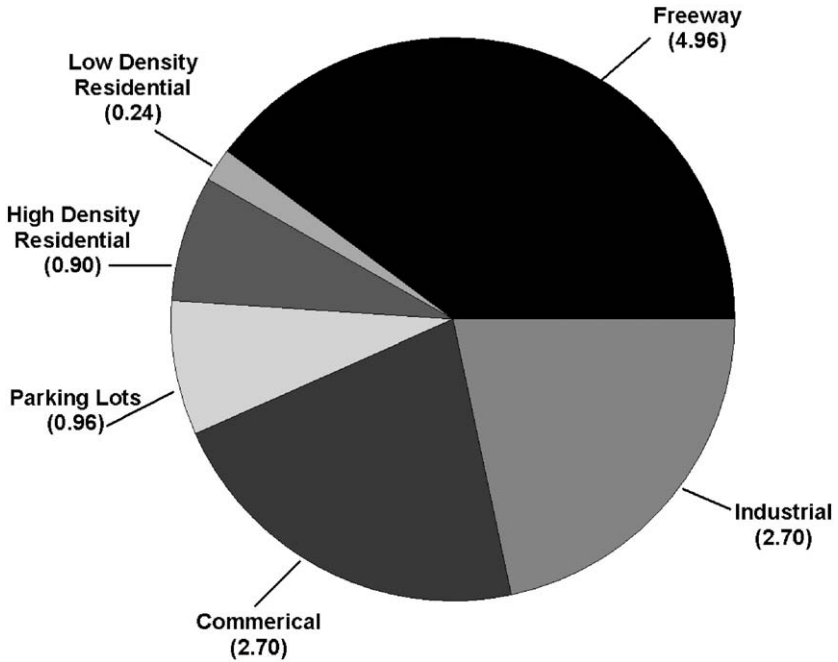


Figure 6.2. Lead sources to urban watersheds in Milwaukee, Wisconsin region. Numbers in parentheses indicate lead totals in kg/hectare/year (data from Novotny and Olem, 1994).

anthropogenic Zn in urban watersheds and also contributes smaller amounts of other trace metals including Cd, Co, Ni, Cu, and Pb (Adachi and Tainosho, 2004). Brake pad wear has been identified as a dominant source of Cu in urban runoff (Legret and Pagotto, 1999). In a study of urban pollution in the Santa Clara Valley region in California, brake pads accounted for 80% of Cu within the runoff discharged into the South San Francisco Bay (SCVURPPP, 1994). Legret and Pagotto (1999) estimated Cu emissions from brake linings between 20 and 47 mg/vehicle/km. Catalytic converters unquestionably have improved air quality; however, they are also sources of Pt and Pd in urban watersheds. Car batteries must also be considered as a potential source of Zn and Pb in the urban environment (Palm and Östlund, 1996).

Ranking only behind mining and waste incineration, tire wear is the third largest source of Zn to the environment (Callender, 2004). Automotive tires have a zinc content of approximately 1% (ZnO is added to tires as part of the “vulcanization” or hardening process) and an estimated 10,000 metric tonnes of Zn is released annually within the

United States. Typically, a tire will contain 25–40 g of Zn and wear at a rate of 0.05 g km^{-1} ; hence, there is a very strong correlation between traffic density and Zn accumulation in stream sediment within urban areas (Councell et al., 2004). Storage of used tires can also pose a potential hazard as a result of leaching (Smolders and Degryse, 2002).

Callender and Rice (2000) defined an “urban environmental gradient” where Zn and Pb concentrations in reservoir sediment collected within the Chattahoochee River basin varied directly with population density in the Atlanta, Georgia region. Filippelli et al. (2005) have identified a pronounced urban–suburban gradient for Pb brought about by the many decades of leaded gasoline use in the United States with the primary impact zones located in the inner cities. Automotive use, rather than population density, is likely a better indicator of metal flux as indicated by Zn concentrations in sediment from the Houston, Texas area. Sediment from this “automotive city” were eight times greater than more contaminated with Zn than similar sediment from other major cities such as Tokyo, Paris, Venice, and Hong Kong (Weisner et al., 1998).

The urban street surface is both a receptacle and means of conveyance for metals and other contaminants, notably motor oil, fuel, and their derivatives. Street runoff is often contaminated with organics resulting in high total organic carbon (TOC) and biological oxygen demand (BOD) levels in stream water. The initial portion of rain events (“first flush” phenomenon) can overload treatment systems with organic and metal contaminants from street runoff (Lazaro, 1990). For example, maximum concentrations of Cr, Pb, and Cu in road runoff from the Bayside Bridge in Tampa, Florida were 22, 440, and $1100 \mu\text{g l}^{-1}$, respectively (Forman et al., 2003). Concentrations of metals in *street* runoff are often many times greater than *stream* runoff during storm events. In a study within the Atlanta metropolitan region, Rose et al. (2001) found that median Zn concentrations in street runoff were ~15 times greater than within storm runoff in urbanized streams. Total metal loads (concentration \times discharge) are also greater in storm runoff as a result of the prolific discharge generated by impermeable roads.

Particulate matter on road surfaces can be an important source of metals. In cold climates such as Sweden’s, the export of metals from urban streams occurs mainly in the winter as the result of the erosion of roads by tire studs in combination with the use of deicing salts (Bäckström et al., 2003). The abrasion of asphalt that comes about as roads are eroded by vehicular traffic releases Ni and V to waterways (Ozaki et al., 2004). Most of the metals from the roads are derived from filler rock bound to the asphalt, rather than the asphalt itself (Lindgren, 1996). Metals that accumulate on road surfaces are most commonly

associated with relatively insoluble finer particulates (often iron oxides) (Wilber and Hunter, 1979) and therefore street sweeping can be ineffective in that it selectively removes mostly coarser particles (German and Svensson, 2002). Permeable pavement offers a viable alternative to impervious asphalt-based surfaces and has been shown to lower Cu and Zn concentrations in infiltration water as well as lower motor oil and diesel fuel in street runoff (Brattebo and Booth, 2003).

6.2.3. Some other sources of metals in the urban environment

High-intensity rainfall can release Pb and other metals from painted wood and brick urban structures, particularly from older buildings (Davis and Burns, 1999). The most common source of Zn in urban structures is roofs, ranking only behind automobiles as a source of metal pollution in Stockholm, Sweden (Palm and Östlund, 1996). Metallic roofs and their drainage systems contribute Pb, Zn, Cu, Ni, Cd, Hg, Cr, and As to runoff and they are an important pathway from the atmosphere to water and soils (Förster, 1999; Davis et al., 2001). Roofs are both a temporary sink for atmospheric dusts and a source of urban metal pollution. Concentrations of Zn as high as $11900 \mu\text{g l}^{-1}$ were measured from the first flush emanating from galvanized roof surfaces (Good, 1993). Roof runoff accounted for an estimated 20% of Zn and Pb to watersheds in an Austin, Texas watershed and also contributed polyaromatic hydrocarbon (PAH) pollution (Van Metre and Mahler, 2003). Metal roofing materials constituted the main source of Cd, Pb, and Zn in an experimental catchment within the LeMarais basin in the center of Paris (Chebbo and Gromaire, 2004).

A principal source of metals in many urban locations is the illegal or accidental disposal of sewage wastes. In the river Manzanares watershed in Madrid, urban metals (Ag, Cr, Cu, Pb, and Zn) were enriched in sediment by factors of 200–400% as the result of uncontrolled sewage disposal (de Miguel et al., 2005). Sewage sludge is a potential source of metal and these composts were found to exceed “background” concentrations of Cu, Zn, and Pb by factors of 5–8 in Madrid (de Miguel et al., 2005). Sewage disposal problems and related metal contamination are not restricted to the expanding urban centers of the developing nations; however, untreated effluent is particularly problematic in these locations (e.g., the Ganga alluvial plain in north central India; Ansari et al., 1999). Numerous cities such as older sections of Atlanta convey both their street runoff and sewage through combined sewage overflow (CSO) systems that are unfortunately designed to pollute river basins during storm periods. CSOs in Paris convey a large urban metal (Cd, Cu, Pb, and

Zn) load with suspended sediment that rapidly settles in the Seine River channel. These metals are for the most part “bioavailable” and provide a chronic flux to the Seine basin downstream of Paris (Estébe et al., 1997).

6.2.4. Sinks

The sediment deposited in lakes, canals, reservoirs, and estuaries are local (and often only temporary) “sinks” for many of the contaminants present in urban effluents. Estuaries are the most problematic in that these are complex and dynamic natural features where metal-sensitive ecosystems have evolved. Concentrations of Pb, Cu, Zn, and Cd were enriched by factors of 3–25 in the tops of cores taken from the Tamaki estuary in the Auckland, New Zealand metropolitan region (Abraham and Parker, 2002). The Hudson River provides another well-studied example of how municipalities (New York City and other cities) can pollute an estuary with metals (e.g., Ag, Cu, and Pb) present in urban runoff and wastewater discharges (Feng et al., 1998). Estuary sediments record historical trends with respect to upstream urbanization and related pollution inputs. For example, sediment cores from the River Thames estuary downstream of London show a recent marked decline with respect to most of the urban metals (Cd, Cu, Hg, Ni, and Zn). This is partially the result of the reduction of sewage plant discharge into the river system from upstream municipalities, notably London and its surroundings (Power et al., 1999).

In one of the few quantitative studies of metal fluxes, watershed yields of various urban metals (notably Cd, Zn, and Pb) were found to represent only between 1% and 2% of the atmospheric input in the Tampa Bay region (Forman et al., 2003). This indicates that the watershed and bay were sinks for most of the metal input to this urban basin. Zn, Ni, Cu, and Cd readily form complexes with chlorides, sulfates, and organic matter, and are therefore relatively mobile and bioavailable within an estuary (Church and Scudlark, 1998). Most metals within the major Humber estuary in England are in the “acid soluble” particulate phase (i.e., can be removed in nitric acid; Neal et al., 1996) and are potentially exchangeable with water. In short, the estuary is the most important “sink” for metals generated by urban activities; however, estuary sediment often only provides a temporary repository for these contaminants. Metals within estuary sediment deposits are “bioavailable” to a variable degree and subject to remobilization within the water column, aquatic ecosystem, and food chain.

6.3. Methodological considerations

Improving methodologies for the sampling, storage, laboratory handling, and analysis of trace metals have greatly enhanced our ability to accurately assess the effects of urban pollution upon stream systems. However, as a result of these new “clean” techniques, a controversy has arisen regarding the validity of trace metal concentrations that were measured in river water decades ago. (The term *clean* usually refers to “metal-free” or an environment that is as free from contact with extraneous metals as possible.) Citing a representative example of recent research, clean room technology produced trace metal values from highway runoff in the Olentangy River near Columbus, Ohio that were $\sim 1/10$ of those previously reported (Gardner and Carey, 2004). In a landmark study involving one of the largest historical sets of water quality data within the United States (the United States Geological Survey’s “NASQAN” database), Windom et al. (1991) cast doubt upon the relatively high-stream water metal concentrations measured decades ago (refer also to Horowitz et al., 2001a). Shiller and Boyle (1985) reached similar conclusions regarding data from the 1960s and 1970s and noted that clean-techniques produced Zn concentrations in Mississippi River water that were often less than $1 \mu\text{g l}^{-1}$ as opposed to earlier studies in which Zn concentrations were as high as $30 \mu\text{g l}^{-1}$.

Today’s U.S. government (NASQAN) quality assurance/quality control (QA/QC) protocols call for field blanks, split samples (to be sent to different laboratories), sample replicates, “clean hands”, clean sampling equipment, and clean analytical facilities. Recent results have shown that metal concentrations (Pb, Co, V, and other metals) in major river systems within the United States are often below detection limits and in most cases certainly well below $1 \mu\text{g l}^{-1}$ (Horowitz et al., 2001b). In addition to improved sampling techniques, there has been a recent emphasis upon sampling stream water and stream sediment at multiple locations along a given stream transect (width- and depth-integrated sampling; Hart and Hines, 1995). Integrated sampling methods will be helpful in determining the effects of current velocity upon metal transport and will potentially provide a better estimate of total metal loads than single-point sampling.

Metal partitioning into the *dissolved*, *colloidal*, and *particulate* states in stream basins and estuaries poses a strong control upon metal concentrations both in solution and upon sediment. There is no universal agreement as to what “size” constitutes the upper and lower limits for these gradations although we often characterize metal distributions in the environment using these size classes. In a recent summary, Gaillardet

et al. (2004) characterize the *dissolved* state as below 1 nm, *colloids* are operationally defined as greater than 1 or several nanometers and less than 0.45–0.2 μm , and *particulates* or suspended matter as $>0.45 \mu\text{m}$. Horowitz et al. (1996) imply that the once-typical characterization of “dissolved metals” as those which pass through a 0.45 μm membrane is inadequate for determining metal concentrations because it does not accurately account for the significant loads of colloidal phase metals. The filtration of samples is an extremely important matter that will influence all subsequent characterization of metal distributions in natural systems. The most important consideration is the separation of colloidal material that involves removing material ~ 90 times finer than what is commonly removed using conventional filtering methods (Horowitz et al., 1996). Removing this colloidal material would involve the utilization of ultra-centrifugation techniques or the repeated filtering of samples in order to clog and thereby reduce the pore size of ordinary membranes (Shiller and Boyle, 1987).

Inductively coupled plasma emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS) are now the most commonly used analytical techniques for the measurement of trace metal concentrations in natural waters. ICP methodologies have largely supplanted (but not completely replaced) earlier atomic adsorption and emission techniques in that the concentrations of a suite of metals (~ 20), rather than a single metal, can be simultaneously determined at high excitation temperatures (7000–8000 K) within the plasma state (Ortega, 2002). Detection limits using conventional ICP-AES techniques are between 1 and 50 $\mu\text{g l}^{-1}$ while newer ICP-MS technologies (quadrupole and mass sector analyzers) can measure metal concentrations in the low ng l^{-1} and high pg l^{-1} range. Furthermore, the mass analyses for many of the metals are linear over many orders of magnitudes (Ortega, 2002). Anodic stripping voltammetry (ASV) methods can be used to analyze selected labile organic and inorganic metal–ligand complexes of environmentally important metals in natural waters (Salomons and Förstner, 1984); however, this is a seldom-used technique.

Horowitz (1997) cautions that our improved analytical techniques for measuring low concentrations of metals have dwarfed our ability to collect uncontaminated (i.e., “meaningful”) environmental samples. In summary, the recent advances with regard to analytical technology, filtering methodologies, and improved clean room and sampling techniques have brought the state-of-the-science to new levels within the last decade. These expanded methodologies based upon lower detection limits will continue to stimulate new research within the area of metal geochemistry in urban and natural watersheds. Lower detection limits

might also conceivably promulgate lower concentration limit standards for metals in drinking water.

6.4. Hydrological and geochemical processes

6.4.1. Storm runoff in the urban environment

A complex interactive set of hydrological and geochemical processes control the transport and fate of metals in urban and natural watersheds (Fig. 6.3). Probably, rainfall intensity is the most important hydrological factor determining metal concentrations and metals loads for any given period of sampling. High-intensity rainfall often flushes street wastes and fined grained sediment into streams and also directly transports metals from the atmosphere into watersheds; however, the control upon metal flux is often the amount of precipitation, rather than the metal concentration within wet precipitation (Sweet et al., 1998).

The most distinctive feature of urban surface water hydrology is the linear and grid-like drainage networks (both streets and storm water

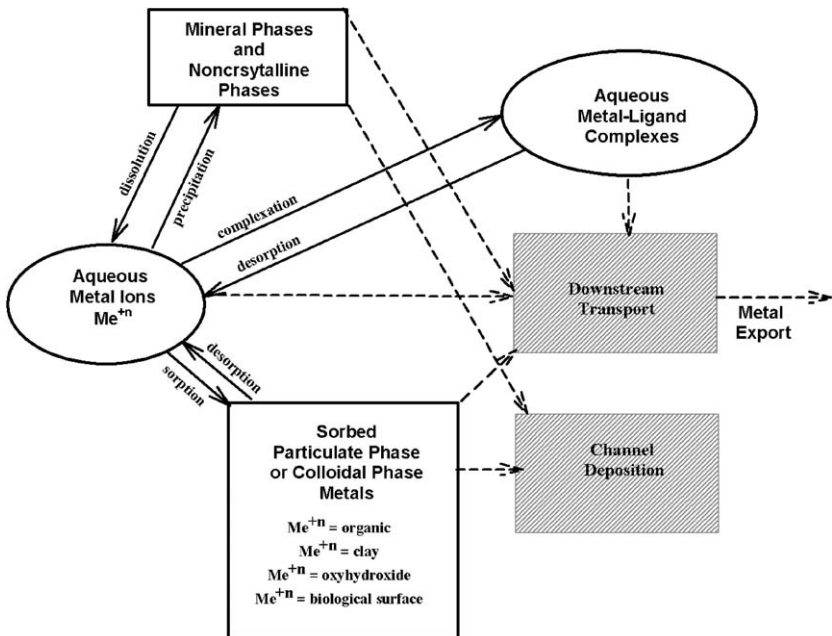


Figure 6.3. Some common geochemical processes (solid lines) and physical processes (dashed lines) affecting the fate of metals in stream water.

collection pipes) that result in higher peak flows and reduced lag time between rainfall and runoff (Lazaro, 1990). Relatively small changes in the percentage of impervious road cover will cause significant changes in the amount of runoff. For example, when the percentage of impervious street cover increases from 30% to 50%, the runoff coefficient (runoff/rainfall ratio) nearly doubles from 22% to 42% (Novotny and Olem, 1994). Higher metal concentrations and loads typically accompany the increased urban storm runoff. Generally, the highest concentrations of urban metals (notably Pb, Cu, and Zn) come with the first flush, coincident with the *rising limb* of the stream hydrograph (Rose et al., 2001; Blake et al., 2003). Mason et al. (1999) noted that the first flush of Cd, Cr, and Cu from rooftops quickly forms metal–ligand complexes that are often mobile in surface water.

6.4.2. Surface water–groundwater interactions and hydrograph “hysteresis”

Groundwater often dominates the *falling limb* of the hydrograph and in most cases is characterized by relatively low-metal concentrations. Therefore, the solute (metal)–discharge relationship in most urban basins will exhibit a *clockwise* hysteresis loop (Blake et al., 2003; Mishra et al., 2003) with higher-metal concentrations coincident with the earlier portion of the storm cycle or rising limb of the storm hydrograph (Fig. 6.4). There has been relatively little attention paid to metal concentrations in base flow (groundwater and soil water) which often is the dominant

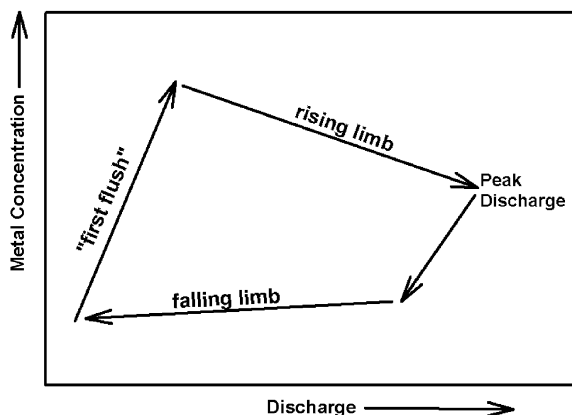


Figure 6.4. Metal concentration–discharge relationship for a typical urban stream showing clockwise hysteresis and “first flush” phenomenon.

year-round water resource in many stream basins in humid regions. Concentrations of common metals in groundwater are often exceedingly low (i.e., below detection limits) principally as the result of metal adsorption. Urban soils in which clay, iron oxyhydroxide and aluminum oxide coatings are abundant will provide the best sorbents for metals (see next section) and groundwater infiltrating through these soils should have the lowest metal concentrations. Metal concentrations within unpolluted base flow may in some cases provide a reference value for the contribution of lithological sources to total metal loads within a watershed.

Although there are relatively few sources for metal pollution within the subsurface, sewage effluent from leaky conveyance pipes often impact metal loading within urban basins. Counterclockwise hysteresis loops would most likely indicate that metal concentrations are higher within groundwater than in surface runoff and such a solute–discharge relationship would probably result from some subsurface source of metal pollution. The movement of stream water through pore waters adjacent to the stream and beneath the stream channel (i.e., the *hyporheic zone*) can result in the exchange of metals between stream water and sediment (Ren and Packman, 2004). Hyporheic exchange is a critical process, particularly in contaminated streams, in that under oxic conditions a significant fraction of exchangeable metals are bound to iron and manganese oxyhydroxides that precipitate in the near-stream zone (Fuller and Harvey, 2000).

6.4.3. Metal–ligand complexation

The simplest of the many chemical partitioning processes that occur in stream water (Fig. 6.3) is the formation of metal–ligand complexes. The most common organic ligands are phenols and carboxylic groups that are derived from the breakdown of humic substances. Organic-metal complexes are often chemically unstable and can break down in sunlight (Martino et al., 2003). The complexation of metals within naturally occurring organic matter is kinetically controlled by the metal-to-ligand ratio, the ionic potential (charge/ionic radius) of the metal and the ligand field stabilization energy of the metal within the complex (Fasfous et al., 2004). Typically chloride, sulfate and bicarbonate are the dominant inorganic ligands in most natural waters. Many of the trace metals form fairly stable complexes with oxygen and hydroxide ligands; common inorganic ionic complexes that form at near neutral pH under these oxidizing conditions include CuOH^+ , CuCl^+ , CuHCO_3^+ , Zn(OH)_2^0 , PbSO_4^0 and PbOH^+ (van Loon and Duffy, 2000). To illustrate the relative significance of inorganic complexes, Hermann et al. (1994) found

that greater than 70% of the Pb from roof runoff was bound in complex form (PbSO_4^0 and PbOH^+) while 30–80% of Cu and virtually all Cd were in free-ion form. The portion of the total metal load that is partitioned into complexes cannot precipitate to form solids; however, the formation of metal–ligand complexes may significantly enhance the adsorption of some trace metals onto iron oxyhydroxide surfaces (Davis and Leckie, 1978).

6.4.4. Partitioning with colloidal matter

Much of the aqueous trace metal load is associated with *colloidal* matter, which has a very large surface area and hence has a high affinity for trace metals. The colloidal state is between the particulate and dissolved states and has been operationally defined as between 0.006 and 0.2 μm (Hart and Hines, 1995) or 0.001–0.2 μm (Gaillardet et al., 2004). Most organic colloids are made up of humic and fulvic substances and the inorganic colloids are typically oxyhydroxides of aluminum, iron, and manganese. At the pH of most natural waters, colloids are negatively charged and hence have an electrostatic attraction for trace metals and positively charged metal complexes. Cr, Pb, Zn, Cd, Cu, and Pb are either divalent or trivalent and therefore at a pH of 6 or above should be nearly 100% partitioned onto negatively charge colloidal (or particulate) surfaces (Gaillardet et al., 2004). To determine the proportion of the metal bound to colloids, ultracentrifugation or multiple filtration methods must be employed (refer to previous discussion). Grout et al. (1999), using ultracentrifugation techniques, found that ~43% of the total Cr and ~29% of the total Zn were colloidal in urban storm water runoff from the Houston, Texas area.

6.4.5. Chemical precipitation and redox considerations

In most cases, the pH of stream water is a master variable controlling both the adsorption of metals onto colloidal and particulate surfaces and the precipitation of metals. In stream water, Cu, Zn, Pb, and Cd are all “alkaline” type metals that precipitate with increasing pH (Salomons and Förstner, 1984). However, the precipitation of trace metals to form crystalline solids is often only a minor geochemical process in that metal concentrations in most river systems are usually exceedingly low and therefore surface waters remain grossly under saturated with respect to most metallic mineral phases. The oxidation state of stream water is another key variable controlling the precipitation of metals. Typically, the non-stagnant river water is oxic; however, in some urban streams

(e.g., the River Meuse in the Netherlands (Van Den Berg et al., 1999)) the water–sediment interface is anoxic due to high-organic loads. Under these “micro-reducing” conditions, metals can precipitate to form sulfide minerals and then possibly become remobilized as reduced sediments subsequently dissolve under oxidizing conditions (von Gunten et al., 1991).

The single most important control upon the oxidation state of most urban streams is the degree to which they are polluted and thereby electrochemically reduced with organic matter from sewage effluent and other sources. Sunlight also plays a role in controlling metal concentrations in that it catalyzes photosynthetically enhanced redox reactions (Scott et al., 2002). In a study of the non-urbanized Clark Fork River in southwestern Montana, Brick and Moore (1996) found that metal (Fe and Al) and trace metal concentrations increased by factors of two or three at night (i.e., “diel variation”) when the absence of photosynthesis dictates that dissolved oxygen concentrations and pH are at a minimum and CO₂ is at a maximum. Probably, the most important redox consideration involves the precipitation of iron oxyhydroxides (which occurs at relatively high-redox potentials) in that these phases provide the primary surface area for metal adsorption. Metals can be released to water when the oxyhydroxides dissolve under reducing conditions, such as those that can occur on lake bottoms or in stagnant streams, mires, and bogs (Shiller, 1997).

6.4.6. Adsorption

The most important mechanism of metal transport within most river systems is adsorption upon suspended sediment or particulates. The diffusion of trace metals within microporous amorphous iron and aluminum oxyhydroxides and oxides is another physiochemical mechanism for sequestering metals; however, it would be difficult to distinguish from adsorption. Greater than 70% of the Cu, Zn, Cr, and Ni within many of the major river systems throughout the United States are transported in association with suspended sediment (Horowitz et al., 2001b). Adsorption is the major reason why metal concentrations in relatively uncontaminated rivers such as the Amazon are often less than 1 µg l⁻¹ (Seyler and Boaventura, 2003). In highly polluted waters such as the Guadaira River (southwest Spain), Pb, Zn, Cr, Cu, and Cd are 50–7500 times more concentrated in sediment than in river water (Gonzalez et al., 2000). Marine sediments contain very little exchangeable metals; however, 50–70% of the Pb and Zn in terrestrial sediments are exchangeable (Callender, 2004).

One of the most commonly referenced schemes for the extraction of metals from sediment was devised by Tessier et al. (1979) in order to

differentiate the “exchangeable” fraction of the total metals from that associated with carbonates, organic matter, Mn and Fe oxides, and sulfides. Some other investigators (e.g., [Shea, 2003](#)) simply approximate “exchangeable” or “adsorbed” metals as those liberated in contact with strong ultra-clean nitric acid (i.e., at $\text{pH} < 2-3$). The utilization of different treatment techniques to quantify sorbed metal concentrations makes it extremely difficult to meaningfully compare the results between different studies and different study basins.

Nonetheless, *partition coefficients* (K values) where K is the equilibrium ratio of particulate metal concentrations to dissolved metal concentrations) for metals onto natural particulate matter in rivers throughout the world are similar and are in the range of 10^4-10^5 ([Sigg, 1998](#)). Sediment grain size is the primary factor controlling the adsorption of metals ([Horowitz and Elrick, 1987](#)) in that surface area increases within decreasing grain size and adsorption is proportional to surface area. The electrostatic affinity of a surface for a given metal varies primarily as a function of the metal’s ionic potential. However, trace metals, regardless of their size and charge are almost always preferentially concentrated within the $< 63 \mu\text{m}$ or $125 \mu\text{m}$ size fraction ([Horowitz and Elrick, 1987](#)).

Sediments are not merely “passive recipients” of metals; rather they act as “biogeochemical reactors” where numerous processes including redox-mediated microbiological transformations occur ([Van Cappellen and Wang, 1995](#)). In most cases, adsorbed metals are considered to be “bio-available” and hence can potentially work their way up the food chain. However, biological activity is probably not as an important control upon trace metal concentrations in natural waters as adsorption ([Hart and Hines, 1995](#)). Probably all particulate matter including bacterial surfaces, clay minerals, organic substances, crystalline mineral phases, and amorphous iron oxyhydroxides can adsorb metals to some degree, depending upon their specific surface area and surface charge. Iron oxyhydroxides have received the greatest attention in that they are ubiquitous in oxic waters and often mask the effects of other sorbents such as the clay minerals that they coat. Naturally occurring aluminum oxides in soils and stream sediments also are effective sorbents of trace metals.

The chemisorption of metals upon oxyhydroxide surfaces is dependent upon numerous factors including the ionic potential and concentration of the metal, solution pH, the type and concentration of sorbent, ligand concentrations ([Benjamin and Leckie, 1981](#)), and redox conditions. At relatively low concentrations there might not be significant competition among the metals for exchange sites on hydrous ferric oxides

(Swallow et al., 1980); however, the major cations (notably Ca^{2+} and Mg^{2+}) in stream water will successfully compete with trace metals for these sites. The amorphous iron oxyhydroxide surface is composed of many groups of binding sites and the strength of bonding may vary by an order of magnitude or more (Benjamin and Leckie, 1981). The more electronegative metals form the strongest covalent bonds with oxygen atoms on mineral surfaces and therefore Cu and Zn tend to be more effectively bound than Co and Pb (McBride, 1994). The same metal can bond to multiple sites to form *monodentate*, *bidentate*, or *polydentate* bonds, all with different free energies or strengths (Davis and Leckie, 1978). Interestingly, the adsorption of metals tend to form *binuclear complexes* which increases the stability of the oxyhydroxides, thereby lowering their solubility and the solubility of adsorbed metals (Bondietti et al., 1993).

Probably, the most important environmental factor controlling metal adsorption onto the oxyhydroxide surface is the pH of stream water. In all cases, Pb, Cu, Zn, and Cd adsorption decreases with decreasing pH (Benjamin and Leckie, 1981), and at a $\text{pH} < 4.5$ Cu, Pb, Ni, Zn, Cd, and Cr are effectively desorbed from oxyhydroxide and ferrihydrite surfaces (Schultz et al., 1987). Conversely, as the pH of the solution approaches neutral, the percentage of metals (Pb, Cu, Zn, and Cd) that are sorbed sharply increases as shown by the “adsorption edges” in Fig. 6.5 (Benjamin and Leckie, 1981). Urban streams often maintain near neutral

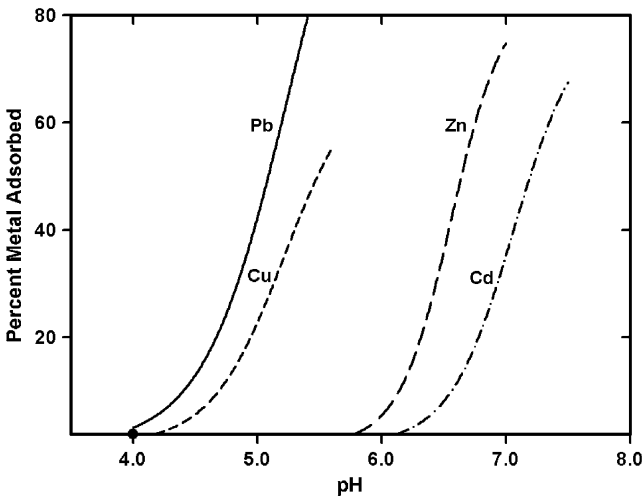


Figure 6.5. Metal adsorption as a function of pH for four common trace metals. These plots are known as “adsorption edges” (after Benjamin and Leckie, 1981).

pH values and adsorption of metals onto iron oxyhydroxides (and clay minerals making up the suspended sediment) is a very important factor in keeping the concentration of metal contaminants within stream water in the low parts per billion range or less. Development and construction activities within urban watersheds often supply streams with large quantities of fine-grained suspended sediment (i.e., turbidity), which provide abundant surface area for the adsorption of trace metals. Fast-acting adsorption processes may be an important factor in explaining why metal concentrations in urban stream runoff are often so much lower than metal concentrations in street runoff.

Bacterial surface coatings typically have a negative charge and therefore represent potential binding sites for metals and positively charged complexes. *Escherichia coli*, a common microbe in sewage waste, has a remarkable affinity for metals and the biofilms that form stable coats on algae, fungi, and bacteria are also potentially important metal sorbents (Schultze-Lam et al., 1995). Metals bind to numerous anthropogenic compounds such as NTA in detergents, phosphates (in detergents and fertilizers), and EDTA (in cleaning agents) (van Loon and Duffy, 2000); many of which are present in urban stream water.

The most important of the organic sorbents are the humic and phenolic compounds found in naturally occurring organic matter (NOM) and are widely distributed in aquatic systems (Kerndorff and Schnitzer, 1980). Sorption of trace metals on organic substances (either colloidal or particulate) varies directly with pH, similar to the relationship between metals and inorganic surface coatings. At $\text{pH} > 6$, more than 40% of the Ni, Zn, Cr, Cu, Pb, and Hg were found under laboratory conditions to be sorbed upon humic acids (Kerndorff and Schnitzer, 1980). Organic acids not only provide direct surface sites for sorption but also enhance the sorption of Cu^{+2} on ferric oxyhydroxide suspensions and shift the “adsorption edge” to lower pH values (Ali and Dzombak, 1996).

6.5. Summary of metal pollution trends

Core analysis of lake and flood plain sediment provides convincing evidence that the anthropogenic input of metals to stream systems did not begin within the modern industrial and urbanized era. The lead isotope record in high latitude Swedish lake sediment reveals a 3000-year history of pollution input and a prominent peak during the medieval period between AD 900 and 1600 (Brännvall et al., 1999). The Rio Tinto estuary in southwestern Spain was mined for perhaps 5000 years and has been heavily polluted by V, Zn, Ni, Co, and Cu since pre-Roman times.

Metal concentrations at this site are to this day 3–6 orders or magnitude greater than contaminant levels found in most other watersheds (Davis et al., 2000). Lake cores in northeastern England flood plain sediment reveal similar high levels of Pb and Zn ($> 500,000 \mu\text{g kg}^{-1}$) since AD 1750 as a result of mining in the Yorkshire district (Hudson-Edwards et al., 1999).

In recent decades, the flux of many trace metals into surface waters has apparently declined as the result of conservation, replacement, and improved disposal technologies (van der Voet et al., 2000). Interpreting recent historical trends from archival water data is problematic due to the inaccurate measurements made prior to the advent of the cleaner sampling methods used today (see proceeding section). Nonetheless, sediment core data suggest that metal concentrations (notably Cu, Cr, Pb, and Ag) within urban streams have generally declined during the past two decades in many locations on different continents (von Gunten et al., 1997; Power et al., 1999; Mecray, 2001).

Lead concentrations in the recent sedimentary record for 30 U.S. reservoirs (many of which are urban) have undergone the most unequivocal decline while Cu and Ni trends are much more ambiguous (Callender, 2004). Lead concentrations in sediment have declined the most notably since the 1970s peak. This is the result of both reduced automotive emissions and better sewage treatment disposal within the United States and elsewhere. Core analysis from lakes in Boston and Forth Worth, Texas indicates that pesticides, PCBs, and PAHs have declined somewhat with Pb during the past three decades (Van Metre and Mahler, 2004). Unfortunately, Zn concentrations during this period of time have increased in numerous reservoir cores as the result of diffuse non-point source urban contamination (mostly tire wear). Despite reductions in contaminant inputs, concentrations of metals in numerous lakes within densely populated urban watersheds remain greater than sediment quality guidelines (Callender, 2004; Van Metre and Mahler, 2004).

6.6. Concluding statement

The prevalence of Pb in gasoline used in many developing countries, the continued high rates of atmospheric release of metals from mining and industrial sources, increasing automobile traffic with the concomitant paving of urban watershed surfaces strongly suggest that metal pollution will continue to be part of the “urban hydrology problem”. The reduction of point source pollution has undoubtedly lowered metal loading within urbanized and undeveloped watersheds within the United States and

elsewhere. However, non-point source pollution, particularly that associated with automotive traffic continues to present a risk to urban streams and major estuary ecosystems downstream of our cities. Even if all sources of metal pollution were eliminated today, past inputs of metals can become remobilized through natural chemical and physical weathering processes. Hence, efforts to lower metal loads including conservation, reduction of automotive traffic, improvement of wastewater treatment and conveyance infrastructure, design of phreatophyte remediation schemes, and construction of artificial wetlands or other buffers should be encouraged.

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