9.03 Heavy Metals in the Environment—Historical Trends

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9.03.1 INTRODUCTION

9.03.1.1 Metals: Pb, Zn, Cd, Cr, Cu, Ni

These six metals, commonly classified as heavy metals, are a subset of a larger group of trace elements that occur in low concentration in the Earth's crust. These heavy metals were mined extensively for use in the twentieth century Industrial Society. Nriagu (1988a) estimated that between 0.5 (Cd) and 310 (Cu) million metric tons of these metals were mined and ultimately deposited in the biosphere. In many instances, the inputs of these metals from anthropogenic sources exceed the contributions from natural sources (weathering, volcanic eruptions, forest fires) by several times (Adriano, 1986). In this chapter, heavy metals (elements having densities greater than 5) and trace elements (elements present in the lithosphere in concentrations less than 0.1%) are considered synonymous.

It has been observed in the past that the rate of emission of these trace metals into the atmosphere is low due to their low volatility. However, with the advent of large-scale metal mining and smelting as well as fossil-fuel combustion in the twentieth century, the emission rate of these metals has increased dramatically. As most of these emissions are released into the atmosphere where the mammals live and breathe, we see a great increase in the occurrence of health problems such as lead (Pb) poisoning, cadmium (Cd) Itai-itai disease, chromium (Cr), and nickel (Ni) carcinogenesis.

In this chapter, the author has attempted to present a synopsis of the importance of these metals in the hydrocycle, their natural and anthropogenic emissions into the environment, their prevalent geochemical form incorporated into lacustrine sediments, and their time-trend distributions in watersheds that have been impacted by urbanization, mining and smelting, and other anthropogenic activities. These time trends are reconstructed from major–minor–trace–element distributions in age-dated sediment cores, mainly from reservoirs where the mass sedimentation rates (MSRs) are orders of magnitude greater than those in natural lakes, the consequences of which tend to preserve the heavy-metal signatures and minimize the metal diagenesis (Callender, 2000). This chapter focuses mainly on the heavy metals in the terrestrial and freshwater environments whilst the environmental chemistry of trace metals in the marine environment is discussed in Volume 6, Chapter 3 of the Treatise on Geochemistry.

The data presented in Tables 2–5 are updated as much as possible, with many of the references postdate the late 1980s. Notable exceptions are riverine particulate matter chemistry (Table 2), some references in Table 3, and references concerning the geochemical properties of the six heavy metals discussed in this chapter. There appears to be no recent publication that updates the worldwide average for riverine particulate matter trace metal chemistry (Martin and Whitfield, 1981; Martin and Windom, 1991). This is supported by the fact that two recent references (Li, 2000; Chester, 2000) concerning marine chemistry still refer to this 1981 publication. As for references in Table 3, there is a very limited data available concerning the pathways of heavy-metal transport to lakes. Some of the important works have been considered and reviewed in this chapter. In addition, the analytical chemistry of the sedimentary materials has changed little over the past 30 years until the advent and use of inductively coupled plasma/mass spectrometry (ICP/MS) in the late 1990s. Extensive works concerning the geochemical properties of heavy metals have been published during the past 40 years and to the author's knowledge these have survived the test of time.

9.03.1.2 Sources of Metals

There are a variety of natural and anthropogenic sources of these heavy metals (Pb, Zn, Cd, Cr, Cu, Ni) in the environment.

9.03.1.2.1 Natural

The principal natural source of heavy metals in the environment is from crustal material that is either weathered on (dissolved) and eroded from (particulate) the Earth's surface or injected into the Earth's atmosphere by volcanic activity. These two sources account for 80% of all the natural sources; forest fires and biogenic sources, account for 10% each (Nriagu, 1990b). Particles released by erosion appear in the atmosphere as windblown dust. In addition, some particles are released by vegetation. The natural emissions of the six heavy metals are 12,000 (Pb); 45,000 (Zn); 1,400 (Cd); 43,000 (Cr); 28,000 (Cu); and 29,000 (Ni) metric tons per year, respectively (Nriagu 1990b). Thus, we can conclude that an abundant quantity of metals are emitted into the atmosphere from natural sources. The quantity of anthropogenic emissions of these metals is given in the next section.

9.03.1.2.2 Anthropogenic

There are a multitude of anthropogenic emissions in the environment. The major source of these metals is from mining and smelting. Mining releases metals to the fluvial environment as tailings and to the atmosphere as metal-enriched dust whereas smelting releases metals to the atmosphere as a result of high-temperature refining processes. In the lead industry, Pb–Cu–Zn–Cd are released in substantial quantities; during Cu and Ni smelting, Co–Zn–Pb–Mn as well as Cu–Ni are released; and in the Zn industry, sizeable releases of Zn–Cd–Cu–Pb occur (Adriano, 1986). Table 1 shows that the world metal production during the 1970s and the 1980s has remained relatively constant except for Cr production that substantially increased during the 1980s due to the technological advances and increased importance (Faust and Aly, 1981).

Table 1 Global primary production and emissions of six heavy metals during the 1970s and the 1980s.

Metal	*Metal production*		*Emissions to air*		*Emissions to soil*	*Emissions to water*
	1970s	*1980s*	*1970s*	*1980s*	*1980s*	*1980s*
Pb	3,400	3,100	449	332	796	138
Zn	5,500	5,200	314	132	1,372	226
Cd	17	15	7.3	7.6	22	9.4
Cr	6,000	11,250	24	30	896	142
Cu	6,000	7,700	56	35	954	112
Ni	630	760	47	56	325	113

Source: Nriagu (1980a), Pacyna (1986), and Nriagu and Pacyna (1988).
All values are thousand metric tons.

Much of the demand for Cr was due to steel and iron manufacturing and the use of Cr in pressure-treated lumber (Alloway, 1995). Table 1 also shows that anthropogenic emissions to the atmosphere, to which mining and smelting are major contributors, are in the interval of two times (Cu, Ni), five times (Zn, Cd), and 33 times (Pb) greater than the natural emissions of metals to the atmosphere. Anthropogenic atmospheric emissions decreased substantially from the 1970s to the 1980s for Pb, Zn, and Cu (Table 1). On the other hand, Cd and Cr have remained the same and Ni emissions have increased in the 1980s. In addition, anthropogenic emissions of Cr are only about one-half of those from the natural sources. The major contributor of Cr to natural atmospheric emissions is windblown dust (Nriagu and Pacyna, 1988).

Other important sources of metals to the atmosphere include fossil-fuel combustion (primarily coal), municipal waste incineration, cement production, and phosphate mining (Nriagu and Pacyna, 1988). Important sources of metals to the terrestrial and aquatic environment include discharge of sewage sludges, use of commercial fertilizers and pesticides, animal waste and wastewater discharge (Nriagu and Pacyna, 1988). Table 1 shows that metal emissions to soil are several times those to air, suggesting that land disposal of mining wastes, chemical wastes, combustion slags, municipal wastes, and sewage sludges are the major contributors of these emissions. Emissions to water are only about twice those relative to air (except for Pb and Cd) suggesting that direct chemical and wastewater releases to the aquatic environment are the only additional inputs besides the atmospheric emissions (Table 1).

Table 2 gives a comparison of the six heavy-metal contents of a variety of natural earth materials that annually impact atmospheric, terrestrial, and aquatic environments. The primary data of metals are also normalized with respect to titanium (Ti). Titanium is a very conservative element that is associated with crustal rock sources. Normalization with respect to Ti compensates for the relative percentage of various diluents (non-crustal rock sources) and allows one to see more clearly metal enrichment due to anthropogenic inputs. For instance, in Table 2, recent lacustrine sediment is clearly enriched in metal content relative to pre-Industrial lacustrine sediment.

It is obvious that there is a progressive enrichment in the metal content of the earth materials as one migrates from the Earth's upper crust to the soils to river mud to lacustrine sediments, and finally to the river particulate matter. This is especially true for Zn and Cd. If we consider the recent lacustrine sediments, then Pb, Zn, Cd, and Cu are all highly enriched compared to the upper crust and soils. Chromium and Ni, on the other hand, are not especially enriched when compared to the crust and soils (Table 2). The metal content of the river particulate matter is also highly enriched in relation to the crust and soils. It is obvious that anthropogenic activities have a pronounced effect on the particulate matter chemistry of lakes and rivers. It is also obvious that much of the enriched portion of the riverine particulates are deposited near river mouths and in the coastal zone (continental shelf) as the Ti-normalized metals for estuarine sediments and hemipelagic mud are less enriched than riverine particulates but still enriched relative to the crust and soils. Table 2 also shows the effect of diagenetic remobilization and reprecipitation of ferromanganese oxides in surficial pelagic clays as both Cu and Ni (major accessory elements in ferromanganese nodules) are significantly enriched in these marine deposits relative to the precursor earth materials. Finally, Table 2 shows the effects of high-temperature combustion on the enrichment of metals in coals as they are concentrated in fly ash. This is especially true for Pb, Zn, Cr, Cu, and Ni.

9.03.1.3 Source and Pathways

The two main pathways for heavy metals to become incorporated into air–soil–sediment–water are transport by air (atmospheric) and

Table 2 Average concentration of six heavy metals in natural earth materials.

Material	*Pb* (ppm)	*Zn* (ppm)	*Cd* (ppm)	*Cr* (ppm)	*Cu* (ppm)	*Ni* (ppm)	*Ti* (wt.%)	*References*
Upper crust	17(52)	67(203)	0.1(0.30)	69(209)	39(118)	55(167)	0.33	Li (2000)
Average soils	26(68)	74(195)	0.1(0.26)	61(160)	23(60)	27(71)	0.38	Li (2000)
River mud	23(42)	78(142)	0.6(2.0)	85(155)	32(58)	32(58)	0.55	Govindaraju (1989)
Pre-industrial, baseline lacustrine sediment	22(69)	97(303)	0.3(0.55)	48(150)	34(106)	40(125)	0.32	Shafer and Armstrong (1991); Forstner (1981); Heit *et al.* (1984); Mudroch *et al.* (1988); Eisenreich (1980); Kemp *et al.* (1976, 1978); Wren *et al.* (1983); Wahlen and Thompson (1980)
Recent lacustrine sediment	102(316)	207(640)	2.2(6.8)	63(195)	60(186)	39(121)	0.32	Above references plus: Dominik *et al.* (1984); Rowell (1996); Mecray *et al.* (2001)
River particulate matter	68(120)	250(446)	1.2(2.1)	100(178)	100(178)	90(161)	0.56	Martin and Windom (1991); Martin and Whitfield (1981)
Estuarine sediment	54(108)	136(272)	1.2(2.4)	94(188)	52(104)	35(70)	0.50	Alexander *et al.* (1993); Coakley and Poulton (1993); Anikiyev *et al.* (1994); Hanson (1997)
Hemipelagic mud	23(49)	111(236)	0.2(0.44)	79(168)	43(91)	44(94)	0.47	Li (2000); Chester (2000)
Pelagic clay	80(174)	170(370)	0.4(0.9)	90(196)	250(543)	230(500)	0.46	Li (2000)
Coal	15(24)	53(84)	0.4(0.6)	27(43)	16(25)	17(27)	0.63	Tillman (1994); Adriano (1986)
Fly ash	43(70)	149(245)	0.5(0.8)	115(189)	56(92)	84(137)	0.61	Hower *et al.* (1999); Adriano (1986)

Values in parentheses are Ti-normalized.

water (fluvial). In the previous section it was shown that heavy-metal emissions to air and water (Table 1) are a significant percentage of the amounts of metals that are extracted from the Earth's crust by mining. Ores are refined by smelting thus releasing large amounts of metal waste to the environment (primary source). Relatively pure metals are incorporated into a multitude of technological products which, when discarded, produce a secondary, but important, source of metals to the environment. Metals are also incorporated naturally and technologically into foodstuffs which, when consumed and discarded by man, result in an important metal source to the aquatic environment (sewage wastewater), soils, and sediments (sewage sludge).

We can see from Table 3 that except for Pb in the terrestrial environment and Cd in the marine environment, metal transport to the lakes and to the oceans via water (fluvial) is many times greater (2–10) than that by air (atmospheric). This undoubtedly reflects the prevalence of wastewater discharges from sewage–municipal–industrial inputs that are so common in our industrialized society. The prevalence of Pb atmospheric emissions is probably due to the burning of leaded gasoline which was phased out in North America and Western Europe by the early 1990s but is still occurring in the Third World countries. Natural atmospheric emissions of Cd (volcanoes) are most likely the cause of substantial atmospheric Cd fluxes to the marine environment (Nriagu, 1990b).

9.03.2 OCCURRENCE, SPECIATION, AND PHASE ASSOCIATIONS

9.03.2.1 Geochemical Properties and Major Solute Species

9.03.2.1.1 Lead

Lead (atomic no. 82) is a bluish-white metal of bright luster, is soft, very malleable, ductile, and a poor conductor of electricity. Because of these properties and its low melting point (327 °C), and resistance to corrosion, Pb has been used in the manufacture of metal products for thousands of years. In fact, the ancient world technology for smelting Pb–Ag alloys from PbS ores was developed 5,000 years ago (Settle and Patterson, 1980). Lead has a density of 11.342 g cm^{-3}, hence finds extensive use as a shield for radiation; its atomic weight is 207.2. Lead has two oxidation states, +2 and +4. The tetravalent state is a powerful oxidizing agent but is not common in the Earth's surficial environment; the divalent state, on the other hand, is the most stable oxidation level and most Pb^{2+} salts with

Table 3 Relative percentage of atmospheric (%A) and fluvial (%F) inputs of six heavy metals to lakes, a coastal zone, and the ocean.

Lake/Ocean	*Metal*												*References*
	Pb		*Zn*		*Cd*		*Cr*		*Cu*		*Ni*		
	%A	*%F*	*%A*	*%F*	*%A*	*%F*	*%A*	*%F*	*%A*	*%F*	*%A*	*%F*	
Lake IJsselmeer	NA	NA	7	93	2	98	0.1	99.9	6	94	1	99	Salomons (1983)
Southern Lake Michigan	47	53	22	78	NA	NA	NA	NA	13	87	NA	NA	Dolske and Sievering (1979)
Lake Michigan	60	40	35	65	10	90	41	59	15	85	NA	NA	Eisenreich (1980)
Lake Erie	40	60	12	88	NA	NA	NA	NA	9	91	NA	NA	Nriagu *et al.* (1979)
South Atlantic Bight	2	98	1	99	41	59	NA	NA	7	93	9	91	Chester (2000)
Ocean	15	85	5	95	17	83	3	97	2	98	5	95	Chester (2000)

NA = not available.

naturally-occurring common anions are only slightly soluble. It is composed of four stable isotopes ($^{208}Pb = 52\%$) and several radioisotopes whose longest half-life is 15 Myr (Reimann and de Caritat, 1998). Lead belongs to group IVa of the periodic table which classifies it as a heavy metal whose geochemical affinity is chalcophilic (associated with sulfur).

In a simple freshwater system, exposed to atmospheric CO_2 and containing 10^{-3} M Cl^-, 10^{-4} M SO_4^{-2}, and 10^{-6} M HPO_4^{-2}, it is predicted that Pb will be complexed by the carbonate species $Pb(CO_3)_2^{-2}$ in the pH range of 6–8 (Hem and Durum, 1973). The complex $PbSO_4^0$ is stable below pH 6 (or in low sulfate waters Pb^{2+}) and the complex $Pb(OH)_2$ is stable above pH 8 (Hem, 1976). In oxygenated stream and lake environments the concentration of dissolved Pb is less than 1 $\mu g\ L^{-1}$ over the pH range of 6–8 (Reimann and de Caritat, 1998) while its average concentration in world river water is 0.08 $\mu g\ L^{-1}$ (Gaillardet *et al.*, 2003). The dissolved Pb concentration in ocean water (0.002 $\mu g\ L^{-1}$) is an order of magnitude lower than that in river water (Chester, 2000).

Adsorption and aggregation-complexation with organic matter appear to be the most important processes that transform dissolved Pb to particulate forms in freshwater systems. Krauskopf (1956) originally suggested that the concentration of Pb, as well as certain other trace metals, could be controlled by adsorption onto the ferric and manganese oxyhydroxides–clay mineral–organic matter. The extent of Pb adsorption onto hydrous Fe and Mn oxides is influenced by the physical characteristics of the adsorbent (specific surface, crystallinity, etc.) and the composition of the aqueous phase (pH, Eh, complexation, competing cations). In a recent study of Fe and Pb speciation, reactivity, and cycling in a lacustrine environment, Taillefert *et al.* (2000) determined that Pb is entrained during the formation of Fe-exocellular polymeric substances (EPS) that aggregate in a water column near the chemocline. It is not yet clear whether the metal is complexed to the EPS or adsorbed directly to the Fe oxide. However, extraction data from lake sediments suggest that the Pb–FeO_x phase is available to chemical attack (see below).

The average concentration of Pb in the lithosphere is about 14 $\mu g\ g^{-1}$ and the most abundant sources of the metal are the minerals galena (PbS), anglesite ($PbSO_4$), and cerussite ($PbCO_3$). The most important environmental sources for Pb are gasoline combustion (presently a minor source, but in the past 40 years a major contributor to Pb pollution), Cu–Zn–Pb smelting, battery factories, sewage sludge, coal combustion, and waste incineration.

9.03.2.1.2 Zinc

Zinc (atomic no. 30) is a bluish-white, relatively soft metal with a density of 7.133 g cm^{-3}. It has an atomic weight of 65.39, a melting point of 419.6 °C, and a boiling point of 907 °C. Zinc is divalent in all its compounds and is composed of five stable isotopes ($^{64}Zn = 49\%$) and a common radioisotope, ^{65}Zn, with a half-life of 245 days. It belongs to group IIb of the periodic table which classifies it as a heavy metal whose geochemical affinity is chalcophilic.

In freshwater, the uncomplexed Zn^{2+} ion dominates at an environmental pH below 8 whereas the uncharged $ZnCO_3^0$ ion is the main species at higher pH (Hem, 1972). Complexing of Zn with SO_4^{2-} becomes important at high sulfate concentrations or in acidic waters. Hydrolysis becomes significant at pH values greater than 7.5; hydroxy complexes of $ZnOH^-$ and $Zn(OH)_2^0$ do not exceed carbonate species at typical environmental concentrations of 15 $\mu g\ L^{-1}$ for world stream water (Reimann and de Caritat, 1998). More recent data of Gaillardet *et al.* (2003) places the concentration of dissolved Zn in average world river water at 0.60 $\mu g\ L^{-1}$. Significant complexing with organic ligands may occur in stream and lake waters with highly soluble organic carbon concentrations. The concentration of Zn in ocean water is 0.39 $\mu g\ L^{-1}$ (Chester, 2000), which is close to its value in world river water.

There are several factors that determine the relative abundance of dissolved and particulate Zn in natural aquatic systems. These include media pH, biogeochemical degradation processes that produce dominant complexing ligands, cation exchange and adsorption processes that control the chemical potential of solid substrates, and the presence of occluded oxyhydroxide compounds (Adriano, 1986). At pH values above 7, aqueous complexed Zn begins to partition to particulate Zn as a result of sorption onto iron oxyhydroxide. The clay mineral montmorillonite is particularly efficient in removing Zn from solution by adsorption (Krauskopf, 1956; Farrah and Pickering, 1977).

The average Zn content of the lithosphere is ~80 $\mu g\ g^{-1}$ and the most abundant sources of Zn are the ZnS minerals sphalerite and wurtzite and to a lesser extent smithsonite ($ZnCO_3$), willemite (Zn_2SiO_4), and zincite (ZnO) (Reimann and de Caritat, 1998). The smelting of nonferrous metals and the burning of fossil fuels and municipal wastes are the major Zn sources contributing to air pollution.

9.03.2.1.3 Cadmium

Cadmium has an atomic number of 48, an atomic weight of 112.40 consisting of eight stable isotopes ($^{112,114}Cd$ are most abundant), and a density of 8.65 g cm^{-3} (Nriagu, 1980a). In several aspects Cd is similar to Zn (it is a neighbor of Zn in the periodic table); in fact it is almost always associated with Zn in mineral deposits and other earth materials. Cadmium is a soft, silvery white, ductile metal with a faint bluish tinge. It has a melting point of 321 °C and a boiling point of 765 °C. It belongs to group IIb of elements in the periodic table and in aqueous solution has the stable 2+ oxidation state. Cadmium is a rare element (67th element in order of abundance) with a concentration of ~0.1 μg g^{-1} in the lithosphere and is strongly chalcophilic, like Zn.

In a natural, aerobic freshwater aquatic system with typical Cd–S–CO_2 concentrations (Hem, 1972), Cd^{2+} is the predominant species below pH 8, $CdCO_3^0$ is predominant from pH 8 to 10, and $Cd(OH)_2^0$ is dominant above pH 10. The solubility of Cd is minimum at pH 9.5 (Hem, 1972). The speciation of Cd is generally considered to be dominated by dissolved forms except in cases where the concentration of suspended particulate matter is high such as "muddy" rivers and reservoirs and near-bottom benthic boundary layers, and underlying bottom sediments in rivers and lakes (Li *et al.*, 1984). The distribution coefficient between the particulate and the dissolved Cd is remarkably consistent for a wide range of riverine and lacustrine situations (Lum, 1987). The sorption of Cd on particulate matter and bottom sediments is considered to be a major factor affecting its concentration in natural waters (Gardiner, 1974). Pickering (1980) has quantitatively evaluated the role clay minerals, humic substances, and hydrous metal oxides in Cd adsorption and concludes that some fraction of the particle-bound Cd is irreversibly held by the solid substrate. The concentration of dissolved Cd in average world river water is 0.08 μg L^{-1} (Gaillardet *et al.*, 2003). This concentration is identical to that of Cd in ocean water (0.079 μg L^{-1}; Chester, 2000).

9.03.2.1.4 Chromium

Chromium has an atomic number of 24, an atomic weight of 51.996 consisting of four stable isotopes ($^{52}Cr = 84\%$), and a density of 7.14 g cm^{-3} (Adriano, 1986). Crystalline Cr is steel-gray in color, lustrous, hard metal that has a melting point of 1,900 °C and a boiling point of 2,642 °C. It belongs to group VIb of the transition metals and in aqueous solution Cr exists primarily in the trivalent (+3) and hexavalent (+6) oxidation states. Chromium, as well as Zn, are the most abundant of the "heavy metals" with a concentration of about 69 μg g^{-1} in the lithosphere (Li, 2000).

In most natural waters at near neutral pH, Cr^{III} is the dominant form due to the very high redox potential for the couple Cr^{VI}/Cr^{III} (Rai *et al.*, 1989). Chromium(III) forms strong complexes with hydroxides. Rai *et al.* (1987) report that the dominant hydroxo species are $CrOH^{2+}$ at pH values 4–6, $Cr(OH)_3^0$ at pH values from 6 to 11.5, and $Cr(OH)_4^-$ at pH values above 11.5. The OH^- ligand was the only significant complexer of Cr^{III} in natural aqueous solutions that contain environmental concentrations of carbonate, sulfate, nitrate, and phosphate ions. The only oxidant in natural aquatic systems that has the potential to oxidize Cr^{III} to Cr^{VI} is manganese dioxide. This compound is common on Earth's surface and thus one can expect to find some Cr^{VI} ions in natural waters. The predominant Cr^{VI} species at environmental pH is CrO_4^{2-} (Hem, 1985). The principal Cr^{III} solid compound that is known to control the solubility of Cr^{III} in nature is $Cr(OH)_3^0$. However, Sass and Rai (1987) have shown that $Cr/Fe(OH)_3$ has an even lower solubility. This compound is a solid solution and thus its solubility is dependent on the mole fraction of Cr; the lower the mole fraction, the lower the solubility (Sass and Rai, 1987). Most Cr^{VI} solids are expected to be relatively soluble under environmental conditions. In the absence of solubility-controlling solids, Cr^{VI} aqueous concentrations under neutral pH conditions will primarily be controlled by adsorption/desorption reactions (Rai *et al.*, 1989). Under environmental conditions, iron oxides are the predominant adsorbents of chromate (Cr^{VI}) in acidic to neutral pH range and oxidizing environments. The Cr concentration in average world river water is 0.7 μg L^{-1} (Gaillardet *et al.*, 2003) and that in ocean water is 0.21 μg L^{-1} (Chester, 2000).

Chromium occurs in nature mainly in the mineral chromite; Cr also occurs in small quantities in many minerals in which it replaces Fe^{3+} and Al^{3+} (Faust and Aly, 1981). The metallurgy industry uses the highest quality chromite ore whilst the lower-grade ore is used for refractory bricks in melting furnaces. Major atmospheric emissions are from the chromium alloy and metal producing industries. Smaller emissions come from coal combustion and municipal incineration. In the aquatic environment, the major sources of Cr are electroplating and metal finishing industries. Hexavalent Cr^{VI} is a potent carcinogen and trivalent Cr^{III} is an essential trace element (Krishnamurthy and Wilkens, 1994).

9.03.2.1.5 Copper

Copper has an atomic number of 29, an atomic weight of 63.546, consists of two stable isotopes ($^{63}Cu = 69.2\%$; $^{65}Cu = 30.8\%$), and has a density of 8.94 g cm^{-3} (Webelements, 2002). Metallic Cu compounds (sulfides) are typically brassy yellow in color while the carbonates are a variety of green- and yellow-colored. The metal is somewhat malleable with a melting point of 1,356 °C and a boiling point of 2,868 °C. It belongs to group Ib of the transition metals and in aqueous solution Cu exists primarily in the divalent oxidation state although some univalent complexes and compounds of Cu do occur in nature (Leckie and Davis, 1979). Copper is a moderately abundant heavy metal with a concentration in the lithosphere of about 39 μg g^{-1} (Li, 2000).

Chemical models for the speciation of Cu in freshwater (Millero, 1975) predict that free Cu^{2+}(aq) is less than 1% of the total dissolved Cu and that $Cu(CO_3)_2^{2-}$ and $CuCO_3^0$ are equally important for the average river water. Leckie and Davis (1979) showed that the $CuCO_3^0$ complex is the most important one near the neutral pH. At pH values above 8, the dihydroxo–Copper(II) complex predominates. The chemical form of Cu is critical to the behavior of the element in geochemical and biological processes (Leckie and Davis, 1979). Cupric Cu forms strong complexes with many organic compounds.

In the sedimentary cycle, Cu is associated with clay mineral fractions, especially those rich in coatings containing organic carbon and manganese oxides. In oxidizing environments ($Cu-H_2O-O_2-S-CO_2$ system), Cu is likely to be more soluble under acidic than under alkaline conditions (Garrels and Christ, 1965). The mineral malachite is favored at pH values above 7. Under reducing conditions, Cu solubility is greatly reduced and the predominant stable phase is cuprous sulfide (Cu_2S) (Leckie and Nelson, 1975). In natural aquatic systems, some of the Cu is dissolved in freshwater streams and lakes as carbonate and organic complexes; a larger fraction is associated with the solid phases. Much of the particulate Cu is fixed in the crystalline matrix of the particles (Gibbs, 1973). Some of the riverine reactive particulate Cu may be desorbed as the freshwater mixes with seawater. The biological cycle of Cu is superimposed on the geochemical cycle. Copper is an essential element for the growth of most of the aquatic organisms but is toxic at levels as low as 10 μg L^{-1} (Leckie and Davis, 1979). Copper has a greater affinity, than most of the other metals, for organic matter, organisms, and solid phases (Leckie and Davis, 1979) and the competition for Cu between the aqueous and the solid phases is very strong. Krauskopf (1956) noted that the concentration of copper in natural waters, 0.8–3.5 μg L^{-1} (Boyle, 1979), is far below the solubility of known solid phases. Davis *et al.* (1978) found that the adsorption behavior of Cu in natural systems is strongly dependent on the type and concentration of inorganic and organic ligands. Recent data of Gaillardet *et al.* (2003) places the concentration of dissolved Cu in average world river water at 1.5 μg L^{-1} and that in ocean water at 0.25 μg L^{-1} (Chester, 2000).

The most common Cu minerals, from which the element is refined into the metal, are Chalcocite (Cu_2S), Covellite (CuS), Chalcopyrite ($CuFeS_2$), Malachite and Azurite (carbonate compounds). It is not surprising that Cu is considered to have a chalcophillic geochemical affinity. In the past, the major source of Cu pollution was smelters that contributed vast quantities of Cu–S particulates to the atmosphere. Presently, the burning of fossil fuels and waste incineration are the major sources of Cu to the atmosphere and the application of sewage sludge, municipal composts, pig and poultry wastes are the primary sources of anthropogenic Cu contributed to the land surface (Alloway, 1995).

9.03.2.1.6 Nickel

Nickel has an atomic number of 28, an atomic weight of 58.71 consisting of five stable isotopes of which ^{58}Ni (67.9%) and ^{60}Ni (26.2%) are the most abundant, and a density of 8.9 g cm^{-3} (National Science Foundation, 1975). Nickel is a silvery white, malleable metal with a melting point of 1,455 °C and a boiling point of 2,732 °C. It has high ductility, good thermal conductivity, moderate strength and hardness, and can be fabricated easily by the procedures which are common to steel (Nriagu, 1980b). Nickel belongs to group VIIIa and is classified as a transition metal (the end of the first transition series) whose prevalent valence states are 0 and 2+. However, the majority of nickel compounds are of the Ni^{II} species.

Morel *et al.* (1973) showed that the free aquo species (Ni^{2+}) dominates at neutral pH (up to pH 9) in most aerobic natural waters; however, complexes of naturally occurring ligands are formed to a minor degree ($OH^- > SO_4^{2-} > Cl^- > NH_3$). Under anaerobic conditions that often occur in the bottom sediments of lakes and estuaries, sulfide controls the solubility of Ni. Under aerobic conditions, the solubility of Ni is controlled by either the co-precipitate $NiFe_2O_4$ (Hem, 1977) or $Ni(OH)_{2(s)}$ (Richter and Theis, 1980). The latter authors performed laboratory adsorption experiments for Ni in the presence of silica, goethite, and amorphous manganese oxide and found that manganese oxide removed 100% of the Ni over the pH range 3–10. The iron oxide began to adsorb Ni at pH 5.5, the oxide's zero point of charge. Hsu (1978) found that Ni was associated with both amorphous iron and manganese oxides that coated silica sand grains.

In 1977, Turekian noted that the calculated theoretical concentrations of Ni and other trace metals in seawater were in orders of magnitude higher than the measured values. Turekian (1977) hypothesized that the role of particulate matter was most important in sequestering reactive elements and transporting them from the continents to the ocean floor. For lakes, Allan (1975) demonstrated that atmospheric inputs were responsible for Ni concentrations in sediments from 65 lakes surrounding a nickel smelter. As Jenne (1968) and Turekian (1977) note, hydrous iron and manganese oxides have a large capacity for sorption or co-precipitation with trace metals such as Ni. These hydrous oxides exist as coatings on the particles, particularly clays, and can transport sequestered metals to great distances (Snodgrass, 1980). In the major rivers of the world, Ni transport is divided into the following phases (Snodgrass, 1980): 0.5% solution, 3.1% adsorbed, 47% as precipitated coating, 14.9% complexed by organic matter, and 34.4% crystalline material.

The concentration of Ni in the lithosphere is 55 $\mu g\ g^{-1}$ (Li, 2000) and the concentration of dissolved Ni in stream water is 2 $\mu g\ L^{-1}$ (Turekian, 1971). More recent data on the concentration of dissolved Ni in average world river water indicates the value to be 0.8 $\mu g\ L^{-1}$ (Gaillardet *et al.*, 2003) and the Ni concentration in ocean water to be 0.47 $\mu g\ L^{-1}$ (Chester, 2000). Natural emissions of Ni to the atmosphere are dominated by windblown dusts while anthropogenic sources that represent 65% of all emission sources are dominated by fossil-fuel combustion, waste incineration and nonferrous metal production (Nriagu, 1980b). Major uses of Ni include its metallurgical use as an alloy (stainless steel and corrosion-resistant alloys), plating and electroplating, as a major component of Ni–Cd batteries, and as a catalyst for hydrogenating vegetable oils (National Science Foundation, 1975).

9.03.2.2 Occurrence in Rocks, Soils, Sediments, Anthropogenic Materials

Table 4 presents the average concentration of six heavy metals (Pb, Zn, Cd, Cr, Cu, Ni) in a variety of earth materials, soils, sediments, and natural waters. For Pb it can be seen that the solid-phase concentration increases little along the transport gradient from the Earth's crust to world soils to lake sediments ($14 < 22 < 23\ \mu g\ g^{-1}$; Table 4). However, stream sediment and particularly riverine particulate matter is substantially enriched (50–68 $\mu g\ g^{-1}$) suggesting that anthropogenic inputs from the past use of leaded gasoline, the prevalent burning of fossil fuels and municipal waste, and land disposal of sewage sludge are mobilized from soils and become concentrated in transported particulate matter. The Pb content of soils in England and Wales (UK) is much higher (74 $\mu g\ g^{-1}$) than that (12 $\mu g\ g^{-1}$) found in remote soils of the USA (Alloway, 1995). This is due in part to the more densely populated regions of the UK that were sampled and the inclusion of metalliferous mining areas. Shallow marine sediments appear not to be

Table 4 Heavy metals in the Earth's crustal materials, soils, freshwater sediments, and marine sediments.

Material	*Pb*	*Zn*	*Cd*	*Cr*	*Cu*	*Ni*	*References*
Crust	14.8	65	0.10	126	25	56	Wedepohl (1995)
Granite	18, 17	40, 50	0.15, 0.13	20, 10	15, 20	8, 10	Adriano (1986); Drever (1988)
Basalt	8, 6	100, 105	0.2, 0.2	220, 170	90, 87	140, 130	"
Shale	23, 20	100, 95	1.4, 0.3	120, 90	50, 45	68, 68	"
Sandstone	10, 7	16, 16	<0.03,	35, 35	2, 2	2, 2	"
Limestone	9, 9	29, 20	0.05, 0.03	10, 11	4, 4	20, 20	"
Soils (general)	19	60	0.35	54	25	19	Adriano (1986)
Soils (World)	30	66	0.06	68	22	22	Kabata-Pendias (2000)
Soils, UK	74	97	0.8	41	23	25	Alloway (1995)
Soils, USA	12	57	0.27		30	24	"
Stream sediments	51 ± 28	132 ± 67	1.57 ± 1.27	67 ± 24	39 ± 13	44 ± 19	Various sources[a]
Lake sediment	22	97	0.6	48	34	40	Table 2
River particulates	68	250	1.2	100	100	90	"
Shallow marine sediment	23	111	0.2	79	43	44	Li (2000); Chester (2000)
Deep-sea clay	80	170	0.4	90	250	230	Li (2000)
Streams	1	30	0.01	1	7	2	Drever (1988)
Ocean	0.03	2	0.05	0.2	0.5	0.5	Drever (1988)

Units are $\mu g\ g^{-1}$ dry weight. Dissolved metal data for streams and ocean water are expressed in units $\mu g\ L^{-1}$.
[a] Various Sources: Dunnette (1992), Aston *et al.* (1974), Presley *et al.* (1980), Olade (1987), Mantei and Foster (1991), Zhang *et al.* (1994), Osintsev (1995), Chiffoleau *et al.* (1994), Borovec *et al.* (1993), Gocht *et al.* (2001).

enriched in Pb related to source materials (crustal rocks and world soils; Table 4) and deep-sea sediments appear to be the final repository of Pb that becomes concentrated in a variety of authigenic phases.

Zinc and Cd show a similar pattern with riverine particulate Zn (250 $\mu g\ g^{-1}$) greatly exceeding average Zn in terrestrial earth materials (68 ± 32 $\mu g\ g^{-1}$) and world soils (66 ± 17 $\mu g\ g^{-1}$), and particulate Cd (1.2 $\mu g\ g^{-1}$) greatly exceeding the terrestrial earth materials and soil concentrations (0.14 ± 0.08 and 0.23 ± 0.15 $\mu g\ g^{-1}$). As for Pb, UK soils are significantly greater in Zn and Cd concentrations relative to USA soils, a fact that reflects the urban and metalliferous character of the UK soils (Alloway, 1995). Stream–lake–shallow marine sediments are all more concentrated in Zn (113 ± 18 $\mu g\ g^{-1}$) than crustal rocks and soils (64 ± 3 $\mu g\ g^{-1}$). As in the case of Pb, deep-sea clays are the ultimate repository for Zn also.

Chromium has the highest concentration of all the six heavy metals in the Earth's crust (Table 4), mainly due to a very high concentration in basalt and shale. Average crustal rocks (72 ± 75 $\mu g\ g^{-1}$) are similar in Cr concentration to world soils (73 ± 19 $\mu g\ g^{-1}$) and the average Cr concentration in stream sediment–riverine particulates–lake sediment–shallow marine sediment (74 ± 22 $\mu g\ g^{-1}$). Only deep-sea clay is slightly enriched relative to all the other earth materials (Table 4). From these data it is apparent that natural Cr concentrations of various earth materials that constitute the weathering-transport continuum from continent to oceans have not been seriously altered by man's activities. As has been seen before, this is not the case for Pb, Zn, and Cd. These metals, along with Cu and Ni, are the backbone of the world's metallurgical industry and thus man's mining and smelting activities that have gone on for centuries have greatly altered the natural cycles.

The Cu concentration of crustal rocks (32 ± 34 $\mu g\ g^{-1}$) is approximately equivalent to that for average soils (25 ± 4 $\mu g\ g^{-1}$). However, as the earth material is weathered and transported to streams–lakes–shallow marine sediments there is a minimal enrichment in Cu concentration (39 ≈ 34 ≈ 43 $\mu g\ g^{-1}$) (Table 4). And, as for Pb–Zn–Cd, riverine particulate matter is greatly enriched (100 $\mu g\ g^{-1}$) relative to the other sedimentary materials. While the Pb–Zn–Cd concentrations of deep-sea clay are enriched 1.5 times that of the continental sedimentary materials, Cu is enriched approximately five times. The substantial enrichment of Cu in oceanic pelagic clay relative to terrestrial earth materials is due to the presence of ubiquitous quantities of ferromanganese oxides in surficial ocean sediments (Drever, 1988).

The Ni concentration of crustal rocks (58 ± 53 $\mu g\ g^{-1}$) is substantially greater than the average world soils (23 ± 3 $\mu g\ g^{-1}$), but essentially equal to continental sedimentary materials (49 ± 13 $\mu g\ g^{-1}$). Riverine particulate matter (90 $\mu g\ g^{-1}$) is nearly twice the Ni concentration of these continental sedimentary materials and deep-sea clay is nearly three times (230 $\mu g\ g^{-1}$) that concentration. As noted for Cu, the substantial Ni enrichment of deep-sea clays is due to the presence of ferromanganese micronodules in the oxidized surficial sediment column (Drever, 1988).

Table 5 gives the average concentration of six heavy metals in anthropogenic by-products; that is, materials refined from natural materials such as fly ash from coal and smelting of metal ores or by-products from man's use such as sewage sludge and animal waste. It is evident that smelting of the metal ores is a major contributor to the environmental pollution caused by atmospheric transport of heavy metals (Table 5). However, fly ash emissions from coal-fired power plants is probably a more important source of atmospheric heavy-metal pollution due to the fact that these power plants are the main sources of electricity for much of the world's population. In addition, sewage sludge is a major contributor of heavy-metal pollution in soils as land disposal of human waste becomes the only practical solution. It is not surprising that riverine particulates are so enriched in Pb, Zn, Cd, Cu, and Ni as soils polluted with atmospheric emissions from mining and smelting activities, and those altered by the addition of sewage sludge are swept into streams and rivers that eventually empty into the ocean.

9.03.2.3 Geochemical Phase Associations in Soils and Sediments

Not all metals are equally reactive, toxic, or available to biota. The free ion form of the metal is thought to be the most available and toxic (Luoma, 1983). With regards to reactivity, it is generally thought that different metal ions display differing affinities for surface binding sites across the substrates (Warren and Haack, 2001). The speciation or dissolved forms of a metal in solution is of primary importance in determining the partitioning of the metal between the solid and solution phases. Mineral surfaces, especially those of Fe oxyhydroxides, have been studied well by aquatic chemists. This is due to their ubiquitous and abundant nature and their proven geochemical affinity (Honeyman and Santschi, 1988). Metals can be incorporated into solid minerals by a number of processes; nonspecific and specific adsorption, co-precipitation, and precipitation of discrete oxides and hydroxides (Warren and

Table 5 Average concentration of six heavy metals in anthropogenic by-products.

By-Product	*Pb*	*Zn*	*Cd*	*Cr*	*Cu*	*Ni*	*References*
Coal	15	53	0.4	27	16	17	Tillman (1994), Adriano (1986)
Fly ash	43	144	0.5	115	56	84	Hower *et al.*(1999), Adriano (1986)
Soils down-wind of smelters	28, 2200	61, 3000	25, 91		184	306	Adriano (1986), Alloway (1995)
Fertilizers	235	288, 371	32, 35	151, 60	18, 84	36, 20	”
Sewage sludge	1049, 820	3025, 2490	72, 18	1221, –	1085, –	319, –	”
Animal waste	45, 11	93, 130	0.36, 0.55	16, 30	20, 31	29, 19	Adriano (1986), Kabata-Pendias and Pendias (2001)

Units are μg g^{-1} dry weight.

Haack, 2001). Furthermore, Fe and Mn oxyhydroxides form surface coatings on other types of mineral surfaces such as clays, carbonates, and grains of feldspar and quartz. The three most common environmental solid substrates are Fe-oxides, Mn-oxides, and natural organic matter (NOM) (Warren and Haack, 2001).

Sediments are an important storage compartment for metals that are released to the water column in rivers, lakes, and oceans. Because of their ability to sequester metals, sediments can reflect water quality and record the effects of anthropogenic emissions (Forstner, 1990). Particles as substrates of pollutants originate from two sources; (a) particulate materials transported from the watershed that are mostly related to soils and (b) endogenic particulate materials formed within the water column. Since adsorption of metal pollutants onto air- and waterborne particles is the primary factor in determining the transport, deposition, reactivity, and potential toxicity of these metals, analytical techniques should be related to either the chemistry of the particle surface or to the metal species that is highly enriched on the particle surface (Forstner, 1990). In the absence of highly-sophisticated solid-state techniques, chemical methods have been devised to characterize the reactivity of metal-rich phases adsorbed to solid particle surfaces. Single leaching and combined sequential extraction schemes have been developed to estimate the relative phase associations of sedimentary metals in various aquatic environments (Pickering, 1981). The most widely applied extraction scheme was developed by Tessier *et al.* (1979) in which the extracted components were defined as exchangeable, carbonates, easily-reducible Mn oxides, moderately-reducible amorphous Fe oxides, sulfides and organic matter, and lithogenic material.

Partition studies on river sediments were first reported by Gibbs (1973) for suspended loads of the Amazon and Yukon rivers. Nickel was the main heavy metal bound to hydroxide coatings while a lithogenic crystalline phase concentrated the Cr and Cu. Salomons and Forstner (1980), in an extraction study of river sediments from different regions of the world, found that less polluted or unpolluted river systems exhibit an increase in the relative amount of the metals' lithogenic fraction and that the excess of metal contaminants released to the aquatic environment by man's activities exist in relatively unstable chemical associations such as exchangeable and reducible. With the exception of Cd and Mn, the amount of heavy metals in exchangeable positions is generally low (Salomons and Forstner, 1984). In addition to this, Zn is often concentrated in the easily reducible phase (amorphous Fe/Mn oxyhydroxides), and Fe–Pb–Cu–Cr are concentrated in the moderately reducible phase (crystalline Fe/Mn oxyhydroxides) (Salomons and Forstner, 1984). As can be seen later, for reservoir and lake sediments, Pb is almost completely extracted by the mildly acidic hydroxylamine hydrochloride but Zn is only partially extracted by this chemical that defines the easily-reducible phase.

In a series of landmark papers by Tessier and coworkers, the role of hydrous Fe/Mn oxides in controlling the heavy-metal concentrations in natural aquatic systems has been defined by careful field and laboratory studies by comparing with theory (Tessier *et al.*, 1985). They concluded that the adsorption of Cd, Cu, Ni, Pb, and Zn onto Fe-oxyhydroxides is an important mechanism in the lowering of heavy-metal concentrations in oxic pore waters of Canadian-Shield lakes. These heavy-metal concentrations were below the concentrations prescribed by equilibrium solubility models. In a more recent study, Tessier *et al.* (1989) concluded that Zn is sorbed onto Fe oxyhydroxides and that their field data fit reasonably well into a simple model of surface complexation. They also concluded that other substrates (Mn oxyhydroxides, organic matter, clays) can sorb Zn. Also, removal of Zn by phytoplankton has been shown to be an important mechanism for controlling the dissolved Zn concentrations in the eutrophic Lake Zurich (Sigg, 1987). Finally, Tessier *et al.* (1996) expanded their studies to include adsorbed organic matter. Their results strongly suggest that pH plays an important role in determining which types of particle surface binding sites predominate in the sorption of heavy metals in lakes. In circumneutral lakes metals are bound directly to hydroxyl groups of the Fe/Mn oxyhydroxides, and in acidic lakes metals are bound indirectly to these oxyhydroxides via adsorption of metals complexed by NOM.

Some words of caution should be included concerning these "solid speciation" sediment extraction techniques. Kersten and Forstner (1987) noted that "useful information on solid speciation influencing the mobility of contaminants in biogeochemically reactive sediments by the chemical leaching approach requires proper and careful handling of the anoxic sediment samples." Martin *et al.* (1987) showed that the specificity and reproducibility of the extraction method greatly depends on the chemical properties of the element and the chemical composition of the samples. They state that "these methods provide, at best, a gradient for the physicochemical association strength between trace elements and solid particles rather than their actual speciation." The problem of post-extraction readsorption of As, Cd, Ni, Pb, and Zn has been addressed by Belzile *et al.* (1989) who found that by using the "Tessier method" (Tessier *et al.*, 1979) on trace-element spiked natural sediments it is possible to recover the added trace elements within the limits of experimental error.

In a recent study of extraction of anthropogenic trace metals from sediments of US urban reservoirs, Conko and Callender (1999) showed that Pb had the highest anthropogenic content accounting for 80–90% of the total metal concentration. Three extractions were used: (i) easily-reducible 0.25 M Hydroxylamine HCL in 0.25 N HCl (Chao, 1984); (ii) weak-acid digest (Hornberger *et al.*, 1999); and (iii) Pb-isotope digest of 1 N HNO_3 + 1.75 N HCl (Graney *et al.*, 1995). Chao (1984) extraction, originally thought to extract only amorphous Mn oxyhydroxides, is now considered to be an acid-reducible extraction that solubilizes amorphous hydrous Fe and Mn oxides (Sutherland and Tack, 2000). Hornberger *et al.*'s (1999) weak-acid digest (0.6 N HCl) is thought to represent the bioavailable fraction of the metal (Hornberger *et al.*, 2000). Graney *et al.*'s (1995) HNO_3 + HCl acid digest is the most aggressive of the three extracts and has been shown to represent, using Pb isotopes, the anthropogenic fraction of Pb in lacustrine sediments. A plot of extractable Pb and total Pb for a 1997 sediment core from the suburban Lake Anne watershed in Reston, Virginia (Callender and Van Metre, 1997) is presented in Figure 1(a). It can be seen that between 85 and 95% of the total Pb is extracted by these chemicals. In general, the Chao extraction recovered 95% of the total Pb and since this technique is thought to specifically extract amorphous Fe and Mn oxyhydroxides, Conko and Callender (1999) postulated that most of the Pb is bound by these amorphous oxides. Figure 1(b) is a plot of various extractions and total Zn in the same Lake Anne core. Only 70% of the total Zn was extracted by any of the three techniques mentioned before; thus the remaining Zn must be associated with other sedimentary phases. Conko and Callender (1999) suggest Zn fixation by 2 : 1 clay minerals (i.e., montmorillonite), whereby sorbed Zn is fixed in the alumina octahedral layer, is an important phase (Pickering, 1981). An additional phase could be biotic structures that are postulated by Webb *et al.* (2000) as substrates where Zn occurs in intimate combination with Fe and P. While Lake Anne sediment is a typical siliclastic material, Lake Harding (located south of Atlanta, Georgia) sediment is reddish in color and consists of appreciably more iron and aluminum oxides. Much of the iron oxides are undoubtedly crystalline in character and may not be attacked by the mild extraction techniques listed above (especially the Chao extraction). Figure 2 shows a plot of the extractable and total Pb in a sediment core from Lake Harding. Contrary to the Lake Anne Pb data where 95% is extractable, only 75% of the total Pb in Lake Harding is extractable. The Chao easily-reducible

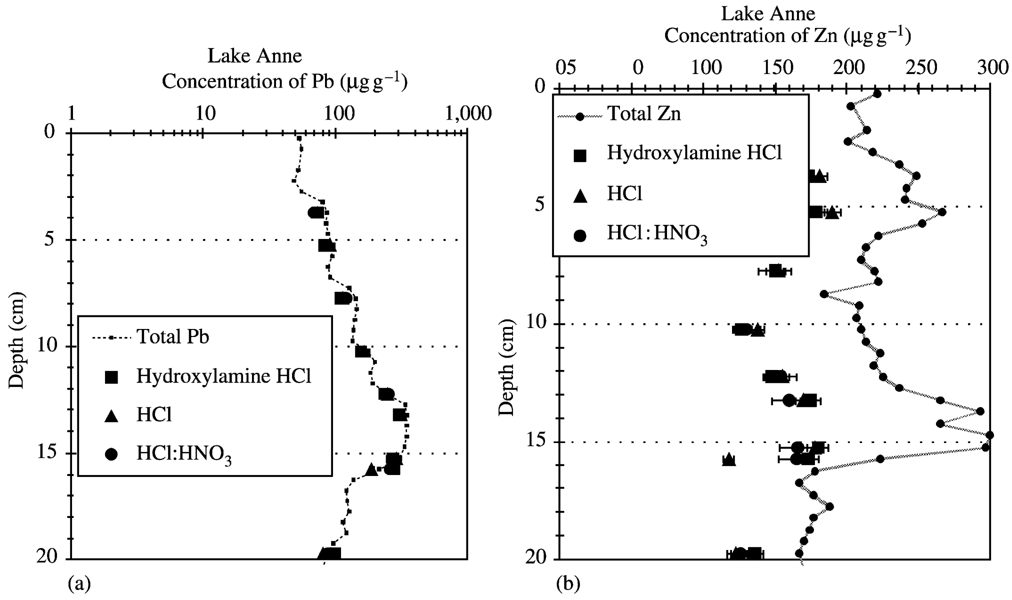


Figure 1 Temporal distribution of total and extractable lead (a) and zinc (b) in a sediment core from Lake Anne, Reston, Virginia, USA.

extraction yielded the lowest extraction efficiencies. It is clear from these data that the type and nature of phase components that comprise natural aquatic sediments are most important for understanding the efficiency of any extraction scheme. Very little is known about the relationship between easily-extracted phases removed by sequential extraction (Tessier *et al.*, 1979) and those liberated by single leaches. Sutherland (2002) compared the two approaches using soil and road deposited sediment in Honolulu, Hawaii. The results indicated that the dilute HCl leach was slightly more aggressive than the sequential procedure but that there was no significant difference between the Pb and Zn concentrations liberated by the two approaches. Further, the data also indicated that a dilute HCl leach was a valuable, rapid, cost-effective analytical tool for contamination assessment. The Hawaii data also indicated that between 75% and 80% of the total Pb is very labile and anthropogenically enhanced (Sutherland, 2002; Sutherland and Tack, 2000). On the other hand, while labile Zn comprises 75% of the total, it is equally distributed between acid extractable and reducible (Sutherland *et al.*, 2000). The extractable Pb data agrees well with the lacustrine Pb data presented in Figure 1(a). The single HCl leach method on Hawaii sediments (Sutherland, 2002) extracts about 50% of the total Zn; a figure even lower than the 70% for lake sediments. Unfortunately, no information was available concerning the phase distribution of Zn in these sediments.

An important reason for testing "selective" leach procedures on sediments that are subjected

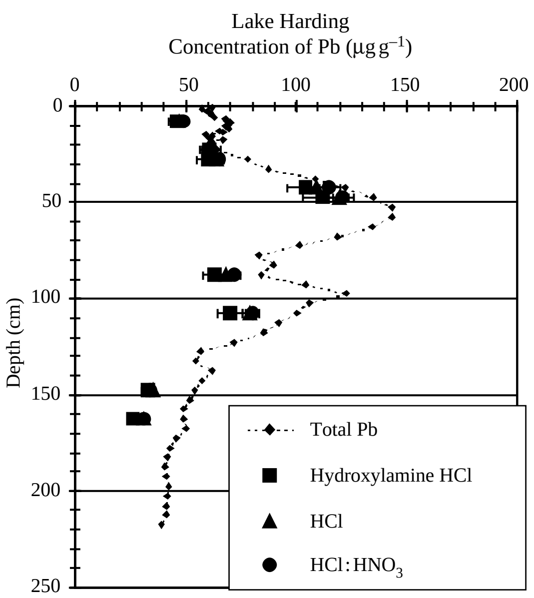


Figure 2 Temporal distribution of total and extractable lead in a sediment core from Lake Harding, Atlanta, Georgia, USA.

to anthropogenic influence is to determine whether such leaches can be used to measure the anthropogenic metal content of sedimentary materials. For Lake Anne sediment, Conko and Callender (1999) calculated the anthropogenic Pb and Zn content by subtracting the background metal concentrations from the total metal content. These were then compared to the "anthropogenic" leach concentrations. For both Pb and Zn, there was essentially no difference between the two procedures. These techniques were applied to several other lake sediments with similar successes suggesting that a mild acid leach might be used to estimate the labile, anthropogenic metal content of a variety of sedimentary materials.

Terrestrial materials (river sediments, lake sediments, and urban particulate matter) appear to have between 50% and 70% exchangeable Pb and Zn while marine sediments contain very little exchangeable metal but appreciably more reducible and much more residual Pb and Zn (Kersten and Forstner, 1995). This may not be too surprising as exchangeable metals are released once freshwater mixes with salt water and redistribution in the marine environment results in some precipitated phases (carbonates, Fe/Mn oxyhydroxides) and the relative increase in the lithogenic fraction. In future, the solid-phase identification techniques should be used to classify the sediments that are to be subjected to "selective" extraction techniques for the purpose of understanding the heavy metal phase associations.

9.03.3 ATMOSPHERIC EMISSIONS OF METALS AND GEOCHEMICAL CYCLES

Both natural and perturbed geochemical cycles include several subcycle elements, not the least of which is the emission of metals into the atmosphere. Atmospheric metals deposited on the land and ocean surface are a part of the runoff from land into the ocean and become incorporated in marine sediments. Thus, the two major pathways whereby heavy metals are injected into the natural geochemical cycles are atmospheric and fluvial. Considering the land surface, atmospheric emissions from stationary and mobile facilities and aqueous emissions from manufacturing and sewage disposal facilities are the primary sources of heavy metal contamination. As for the ocean, atmospheric deposition and continental runoff are the primary inputs. Duce *et al.* (1991) summarized the global inputs of metals to the ocean for the 1980s and these data are presented in Table 6. Riverine inputs are substantially greater than the atmospheric inputs, especially particulate riverine inputs that account for 95% of the total (Chester, 2000). For Pb and Zn, riverine inputs are 20 and 30 times greater than the corresponding atmospheric inputs. For Cd the factor is only 5, while for Cu and Ni the factors are 45 and 30, respectively. Global atmospheric inputs to land and ocean for the same time period are substantially greater (2–3 times, Table 6) than atmospheric deposition to the ocean. This is due to the presence of major pollution sources (mining, smelting, fossil-fuel combustion, waste incineration, manufacturing facilities) on the land masses. In fact, for Pb during the 1970s and 1980s, the use of leaded gasoline in vehicles resulted in the emission of four times the metal to the land surface compared to the ocean (Table 6).

Table 6 Global deposition of metals to the ocean for the 1980s.

Pb	*Zn*	*Cd*	*Cu*	*Ni*
Atmospheric				
90	137	3.1	34	25
Riverine				
1,602	3,906	15.3	1,510	1,411
World atmosphere				
342	177	8.9	63	86

Source: Duce *et al.* (1991).
All deposition values are thousand metric tons per year.

From the above data it is obvious that atmospheric emissions on land are a major source of heavy-metal contamination to our natural environment. In the following sections the focus will be on these emissions due to the fact that there are numerous data available to construct emission estimates (Nriagu and Pacyna, 1988) and that historical atmospheric emissions have been archived in continental ice accumulations (Greenland and Antarctica). The metal emission estimates of Nriagu and Pacyna (1988) are the most complete, and recent data are available for worldwide metal emissions.

9.03.3.1 Historical Heavy Metal Fluxes to the Atmosphere

Claire Patterson and his co-workers have pioneered the study of natural earth materials to uncover the "secrets of the ages". As early as 1963, Tatsumoto and Patterson (1963) related the high concentrations of Pb in surface seawater off Southern California to automotive aerosol fallout. In the United States it was found that Pb in gasoline was the largest single source of air pollution. Aerosols account for about one-third of the industrial Pb added to the oceans (Patterson *et al.*, 1976). Murozumi *et al.* (1969) provided a very convincing argument that airborne Pb particulates can be transported over vast distances in their classic study of the Greenland ice sheet. Their data indicated that before 1750 the concentration of Pb in the atmosphere began to increase above "natural" levels and that this was mainly due to the lead smelters, and that the sharp increase in the atmospheric Pb occurred around 1950 due to the burning of Pb alkyls in gasoline after 1940.

More recently, Claude Boutron and his co-workers in France have published high-quality data for Pb–Zn–Cd–Cu in Greenland snows (Boutron *et al.*, 1991; Hong *et al.*, 1994; Candelone *et al.*, 1995). Table 7 gives heavy metal deposition fluxes for the Summit Central Greenland Icesheet sampling locality. Lead increased dramatically between BP 7760 and AD 1773 (Industrial Revolution), and subsequently through 1850–1960 (Pb alkyl additives to automobile gasoline) (Nriagu, 1990a). Candelone *et al.* (1995) have successfully extended the uncontaminated metal record in ice from Central Greenland. Besides the above Pb record, for Zn, Cd, and Cu there is a clear increasing trend from 1773 to the 1970s (Table 7). However, between BP 7760 and AD 1773, there is essentially no change in metal flux. In fact, Zn decreased slightly; there is no change in Cd; and Cu increased slightly (Table 7). Over the past 200 years, Zn fluxes started to increase but it was not until 1900s that the increase became more rapid. On the other hand, for Cd and Cu, it was not until after the 1850s that their atmospheric concentrations and fluxes increased substantially (Candelone *et al.*, 1995). The maximum remote atmospheric concentrations of Zn occurred around 1960 while those for Cd and Cu occurred around 1970 (Candelone *et al.*, 1995). Finally, 1992 icesheet data indicate that the remote atmospheric Pb fluxes (Table 7) decreased by 6.5-fold in response to the banning of leaded gasoline throughout most of the world. Zinc and Cu decreased only 1.5 times while Cd decreased about 2.5 times (Table 7). These large increases in historical metal fluxes to the remote atmosphere are undoubtedly related to the major changes in the large scale anthropogenic emissions to the atmosphere in the northern hemisphere.

There is a wealth of data available on the world production of heavy metals during the past century or so (Nriagu, 1990b). Candelone *et al.* (1995) present historical Zn–Cd–Cu concentrations in snow/ice deposited at Summit, Central Greenland from 1773 to 1992. If one assumes that the 1773 concentrations are the result of natural atmospheric emissions, then the ratio of 1980s concentrations to 1773 concentrations are a measure of anthropogenic contamination of the remote atmosphere to that date. These ratios are 4, 7, and 3 for Zn, Cd, and Cu, respectively (figure 3 in Candelone *et al.*, 1995). Compare this to the 1983 total emissions divided by the natural emissions (Nriagu, 1990b). These values are 3.9, 6.4, and 2.3 for Zn, Cd, and Cu, respectively. It appears that historical changes in Zn–Cd–Cu deposition in the Greenland icesheet are consistent with the estimates of metal emissions to the global atmosphere (Candelone *et al.*, 1995). These emissions are primarily a result of smelting/refining, manufacturing processes, fossil-fuel combustion, and waste incineration (Nriagu, 1990b).

A similar analysis for Pb yields the following results: icesheet concentration ratio is about 15 and atmospheric emission ratio is about 20. While this is not too bad a comparison, it is not as good as for the other three metals (Zn–Cd–Cu). It is clear that most of the Pb increase in snow/ice samples from Greenland is due to the use of leaded gasoline after the 1950s (Murozumi *et al.*, 1969).

Going back to the Holocene era (BP 7760 years) where dated ice cores give metal concentrations that reflect a time when man's impact on the global environment was minimal, Candelone *et al.* (1995) measured Zn–Cd–Cu concentrations that were comparable to values for ice dated at AD 1773. Even by AD 1900 the concentrations of Zn and Cu were only 1.3 and 1.5 times those recorded for the AD 1773 date (Candelone *et al.*, 1995). Cadmium concentrations had increased more than four times during this period and Pb concentrations had increased nearly 10 times. In fact for Pb, the concentrations recorded in the icesheet have increased at least 30 times between BP 7760 and AD 1900. (Candelone *et al.*, 1995). It is obvious that much Pb was emitted to the atmosphere long before the Industrial Revolution and that some Cd was emitted during the early stages of the Industrial Revolution. It is possible that Cd was a by-product of the Pb mining and smelting during the Greco-Roman civilization (2500–BP 1700 years).

Table 7 Heavy metal deposition fluxes at Summit, Central Greenland.

Age	*Pb*	*Zn*	*Cd*	*Cu*
BP 7760	1.3	53	0.6	3.9
1773	18	37	0.6	5.0
1850	35	70	0.6	5.3
1960s–1970s	250	200	4.1	22
1992	39	120	1.8	17

Source: Candelone *et al.* (1995).
All values are in picograms per cm^2 per year.

9.03.3.2 Perturbed Heavy Metal Cycles

In this discussion of heavy metals, geochemical cycles are treated in a simple manner; emissions from land and oceans to the global atmosphere and subsequent deposition on the land and ocean surface, and runoff from the land to the ocean and eventual deposition in marine sediments. Only two components of this simple cycle will be discussed due to the availability of relatively accurate and complete data; deposition of metals from the atmosphere to the land and ocean surface, and continental runoff to the ocean.

Figure 3 presents these data for two simple scenarios: minimal human disturbances and maximum human disturbances. For the minimal human disturbances senario, it was assumed that deposition from the atmosphere was due to natural sources (Nriagu, 1990b) and that there was minimal anthropogenic impact on the Earth's surface. The continental runoff (riverine) data was taken from Bertine and Goldberg (1971) who calculated the amounts of metals entering into the world's oceans as a result of the weathering cycle. They accounted for both the dissolved and particulate phases by using the marine rates of sedimentation. It can be seen from Figure 3 that for Pb–Zn–Cr–Cu–Ni, continental runoff was 5–10 times greater than the natural atmospheric inputs. For Cd, the atmospheric fluxes are greater than the continental runoff suggesting that continental rocks are depleted in Cd or that there are poor quality Cd data for these two sources. The latter explanation seems to be the most likely.

For the maximum human disturbances scenario, riverine inputs were calculated with the data of Martin and Whitfield (1981). As can be seen from Table 2 in this chapter, Pb–Zn–Cd–Cu–Ni are strongly enriched (by man's activities) when compared to the average Earth's upper crust and soils and the Cr enrichment is found to be only somewhat enriched (Table 2). Atmospheric input data was computed as the average of global emissions data for the 1970s and 1980s (Garrels *et al.*, 1973; Lantzy and Mackenzie, 1979; Nriagu and Pacyna, 1988; and Duce *et al.*, 1991), and was assumed to be the time of maximum anthropogenic emissions to the atmosphere. For the maximum human disturbances scenario, riverine

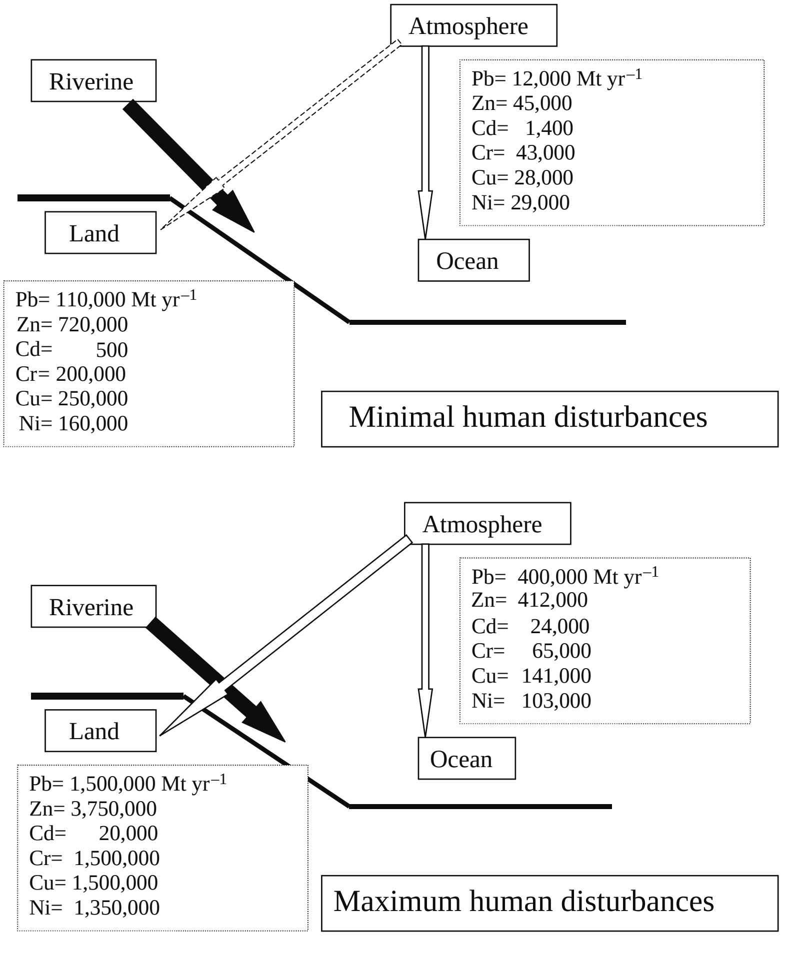


Figure 3 Schematic diagrams of perturbed heavy metal cycles representing prehistoric times of minimal human disturbances and modern times of maximum human disturbances. Data sources for minimum human disturbances: Nriagu (1990b), Bertine and Goldberg (1971). Data sources for maximum human disturbances: Martin and Whitfield (1981), Garrels *et al.* (1973), Lantzy and Mackenzie (1979), Nriagu and Pacyna (1988), Duce *et al.* (1991).

inputs are still larger than the atmospheric inputs except that Pb–Cr are only three times greater, Zn is six times greater, Cu is 10 times greater, Ni is 13 times greater, and Cd is about equal. These differences are undoubtedly due to the magnitude of different source functions.

A calculation of maximum/minimum ratio from the atmospheric input data in Figure 3 yields the following results: Pb = 33, Zn = 9, Cd = 17, Cr = 1.5, Cu = 5, Ni = 4. We know that the burning of leaded gasoline is responsible for the large increase of Pb. Enormous metal production of Zn and Cd ores as well as refuse incineration are responsible for the increases of these metals. In addition, marine aerosols are an important source of Cd (Li, 1981). Obviously, Cu–Ni production from ores increased during this period but not nearly as much as for Zn–Cd. Also, combustion of fossil fuels contributed somewhat to the increase of Cu and Ni. The main source of Cr is steel and iron manufacturing which appears to not be as important an impact on the atmospheric environment as sources for the other metals. The pollution sources of Cr are minimal as reflected in the balance between riverine input and marine sediment output (Li, 1981).

A similar calculation for the riverine inputs (Figure 3) yields the following results: Pb = 14, Zn = 5, Cd = 40, Cr = 7.5, Cu = 6, Ni = 8. With the exception of Pb and Cd, the increases for Zn–Cr–Cu–Ni are similar. Smelting wastes and coal fly ash releases are the common sources of these four metals. Gasoline residues are an obvious source of the Pb increases and urban refuse incineration is a major source of the Cd increase (Nriagu and Pacyna, 1988).

9.03.3.3 Global Emissions of Heavy Metals

Table 8 presents the data on the global emissions of heavy metals to the atmospheric and terrestrial environments for the 1970s and 1980s. The atmospheric and riverine input (weathering mobilization) data are the same as that used for the minimum and maximum human disturbances to the geochemical cycling of the heavy metals presented in the previous section. Total industrial discharges of heavy metals are the calculated discharges into soils and water minus the emissions to the atmosphere (Nriagu, 1990b). Only a fraction of the heavy-metal production from mines is released into the atmosphere in the same year (Nriagu, 1990b). For instance for Pb, in the year 1983, about 30% of the metal produced from mining is used for metal production, other sources, and is wasted as industrial discharges (Table 8): Zn 27%, Cd 190%, Cr 16%, Cu 14%, and Ni 57%. It is not surprising that the price of base metals fluctuate so widely in that there

Table 8 Global emissions of heavy metals to the atmosphere and terrestrial environment during 1970s and 1980s.

Element	*Atmospheric input*[a]	*Weathering mobilization*[b]	*Total industrial discharges*[c]	*Production from mines*[d]	*World Metal production* (Atmos.)[e]	*Other sources* (Atmos.)[f]	*Emissions H_2O, soil* (Atmos.)[g]	*Global natural emissions*[h]
Pb	400,000	295,000	565,000	3,077,000	83,800	292,000	875,000	12,000
Zn	412,000	1,390,000	1,427,000	6,040,000	125,800	67,000	2,083,000	45,000
Cd	24,000	15,000	24,000	19,000	8,500	3,500	43,000	1,400
Cr	65,000	1,180,000	1,010,000	6,800,000	28,500	25,000	1,397,000	43,000
Cu	141,000	635,000	1,048,000	8,114,000	35,400	15,500	1,428,000	28,000
Ni	103,000	540,000	356,000	778,000	15,900	71,000	614,000	29,000

Units are metric tons per year. Atmospheric Input (a) = World Metal Production (e) + Other Sources to the Atmosphere (f) + Natural Emissions to the Atmosphere (h). Pb: 400,000 = 388,000; Zn: 412,000? 238,000; Cd: 24,000 ≅ 13,400; Cr: 65,000 ≅ 96,500; Cu: 141,000 ≅ 79,000; Ni: 103,000 ≅ 116,000.
[a] Source: Lantzy and Mackenzie (1979), Garrels *et al.* (1973), Nriagu and Pacyna (1988), Duce *et al.* (1991). [b] Bertine and Goldberg (1971). [c,d,h] Nriagu (1990b). [e–g] Nriagu and Pacyna (1988).

appears to be a substantial excess of supply over demand (Table 8). This is not the case for Cd; the data presented in Table 8 suggest that there may be a deficit in the supply of Cd. It appears unlikely but it may be that there is a sufficient demand for Cd that can just about balance the mine production. Another explanation is that the estimate of Cd from industrial discharges might be in error. Other discrepancies in Cd estimates have also been noted and it is reasonable to think that since the concentrations of Cd are so low in natural earth materials, the analytical data may not be good.

In order to assess the internal consistency of the emissions, as shown in Table 8, a calculation was made whereby the mean atmospheric input was equated to the world metal production emitted to the atmosphere plus natural emissions and other sources to the atmosphere. With the exceptions of Cu and Zn, the quantities of emissions balance rather well. There is no obvious reason why Cu is out of balance by nearly a factor of 2 (atmospheric input > sources). For Zn, with an imbalance of 1.7 for atmospheric input > sources, there is an obvious problem with other sources in that the impact of rubber tire wear. This source term will be addressed in the next section. However, even with this term, the right side of the equation would increase to a maximum emissions figure of 300,000 t yr^{-1} (Table 8). It is possible that maximum Cu and Zn emissions to the atmosphere have been overestimated but there is no way to check this with the available data.

9.03.3.4 US Emissions of Heavy Metals

While there is a reasonable amount of data pertaining to global emissions of heavy metals during the last half of the twentieth century, there is a wealth of data available for emissions of heavy metals to the US atmosphere. Most of this has been calculated from USEPA and US Bureau of Mines materials production data combined with emission factors for a variety of source functions (Pacyna, 1986). In this section data plots will be presented to show the calculated emissions of several heavy metals to the US atmosphere over a decade of time. Some of the data, such as that for Pb, are from the published literature. On the other hand, much of the data for Zn has been calculated by the author and his colleagues and is presented for the first time.

9.03.3.4.1 Lead

With the scientific realization that Pb had contaminated the global atmosphere (Murozumi *et al.*, 1969), scientists set out to identify the major sources of this contamination. The late Claire Patterson, formerly of the California Institute of Technology, was the leader in this field. In an earlier paper concerning Pb contamination and its effect on human beings, Patterson (1965) wrote "the industrial use of lead is so massive today that the amount of lead mined and introduced into our relatively small urban environments each year is more than 100 times greater than the amount of natural lead leached each year from soils by streams and added to the oceans over the entire earth". This conclusion was reached by Chow and Patterson (1962) in their landmark study of Pb isotopes in pelagic sediments. This information, coupled with the well-known health impacts of Pb (USEPA, 2000a,b), arose the interest of toxicologists worldwide and prompted detailed studies of the cycling of this element in the environment. Ingested Pb (food, water, soil, and dust) damages organs, affects the brain and nerves, the heart and blood, and particularly affects young children and adults (USEPA, 2000a,b). With the use of leaded gasoline that began in the 1930s (Nriagu, 1990a), the public outcry about the outbreak of severe lead poisoning, and the drastic increase in the US in automobile miles traveled, the US Congress passed an amendment to the Clean Air Act (Callender and Van Metre, 1997) banning the use of leaded gasoline. The USEPA (2000a,b), in their most recent air pollutant emission trends report, showed that since 1973 the quantity of Pb emitted to the environment (Table 9) has decreased drastically from about 200,000 t to about 500 t in 1998. As a comparison, European Pb emissions for 1979/1980 were released at a rate of 80,800 t yr^{-1} (Pacyna and Lindgren, 1997) while those for the US were 66,600 tons per year (USEPA, 2000a,b).

Figure 4 presents the important EPA emissions data on a five-year time scale from 1970 to 1995. In the 1970s and 1980s, it is clear that leaded gasoline consumption was the overwhelming

Table 9 Total US emissions of lead (Pb) to the atmosphere.

Source category	*1970*	*1975*	*1980*	*1985*	*1990*	*1995*
Waste incineration	1,995	1,447	1,097	790	729	552
Fossil fuel combustion	9,269	9,385	3,899	469	454	446
Metals processing	21,971	9,000	2,745	1,902	1,968	1,864
Gasoline consumption	164,800	123,657	58,688	17,208	1,086	475

Source: USEPA (1998, 2000a,b).
Units are metric tons.

emitter of Pb to the environment with metal processing a far second. Presently, the total amount of Pb emitted to the environment is a paltry 2,500 t (USEPA, 2000a,b), with metal processing and waste disposal being the main emitters. While the US consumption of leaded gasoline has all but stopped, it is not the case for the rest of the world. As of 1993 when leaded gasoline consumption in North America (mostly Mexico) emitted 1,400 t of Pb to the atmosphere, the rest of the world emitted 69,000 tons of Pb to the atmosphere (Thomas, 1995).

9.03.3.4.2 Zinc

The US atmospheric emissions data for Zn are somewhat sparse. Nriagu (1979) published data on the worldwide anthropogenic emission of Zn to the atmosphere during 1975 (Table 10). The author has taken this report as a model for the type of Zn emissions that appear to be important and has added several categories such as cement and fertilizer production and automobile rubber tire wear.

The reason why the emission data for Zn are sparse is that until recently it was thought that Zn was not harmful to the environment and that health risks were minimal compared to other heavy metals. Zinc is an essential micronutrient and plays a role in DNA polymerization (Sunda, 1991) and nervous system functions (Yasui *et al.*, 1996). Zinc is generally less toxic than other heavy metals (Nriagu, 1980a); however, it is known to cause a variety of

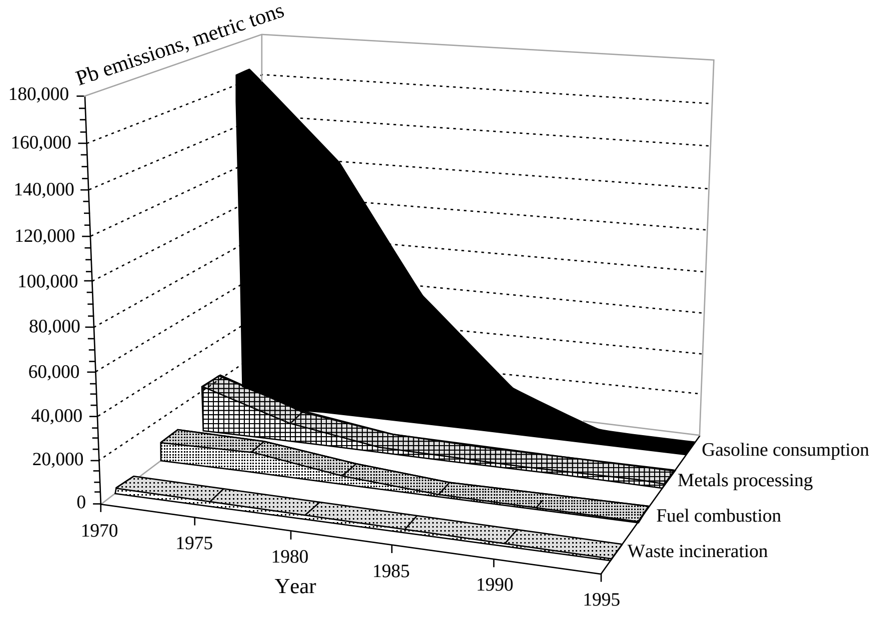


Figure 4 Three-dimensional plot of lead emissions to the US atmosphere for the period 1970–1995. Data from USEPA (2000a).

Table 10 Total US Emissions of zinc (Zn) to the atmosphere.

Source category	*1960*	*1965*	*1970*	*1975*	*1980*	*1985*	*1990*	*1995*
Cement production[a]	617	716	729	667	735	754	752	846
Fertilizer production[b]	1,000	1,000	1,054	1,329	1,632	1,525	1,390	1,365
Copper mining[c]	1,035	1,163	1,200	983	915	795	1,185	1,448
Iron and steel[d]	1,628	2,160	2,236	1,952	1,682	1,223	1,342	1,374
Fossil Fuel combustion[e]	1,532	1,719	2,141	1,878	1,916	1,984	1,658	1,298
Rubber tire wear[f]	3,747	4,901	5,503	5,044	5,983	7,258	8,329	8,847
Waste incineration[g]	6,367	7,280	5,920	5,006	3,232	5,659	7,298	7,941
Zinc mining[h]	101,500	126,280	111,440	55,580	47,600	36,540	36,820	32,480

Units are metric tons.
[a] Source: Nriagu and Pacyna (1988), http://minerals.usgs.gov/minerals/pubs/commodity/cement/stat/tbl1.txt. [b] Source: Nriagu and Pacyna (1988), http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/stat/tbl1.txt. [c] Source: Nriagu and Pacyna (1988), http://minerals.usgs.gov/minerals/pubs/commodity/of01-006/copper. [d] Source: Nriagu and Pacyna (1988), http://minerals.usgs.gov/minerals/pubs/commodity/of01-006/ironand steel [e] Source: Pacyna (1986), Statistical Abstracts of the United States (1998) (Coal and Oil production data). [f] Source: Councell *et al.* (2003). [g] Source: Pacyna (1986), USEPA (1998). [h] Source: Nriagu and Pacyna (1988)http://minerals.usgs.gov/minerals/pubs/commodity/of01-006/zinc.

acute and toxic effects in aquatic biota. Several studies have established links between human activities and environmental Zn enrichment (Pacyna, 1996).

Figure 5 is a plot of second tier Zn emissions to the atmosphere for the period 1960–1995 in five-year time intervals. The only important Zn emission category not included in Figure 5 is Zn mining. This is and has been the largest Zn emission category with 102,000 t in 1960 to 112,000 in 1970, declining to 48,000 in 1980, and stabilizing at about 32,000 t in the 1990s (Nriagu and Pacyna, 1988; www.minerals.usgs.gov). Obviously, emissions from Zn mining and smelting are the overwhelming sources. Total US Zn emissions for the 1980s amount to approximately 60,000 t yr^{-1} while European Zn emissions total 43,000 t yr^{-1} (Pacyna and Lindgren, 1997). Mining–smelting emissions overwhelm others that are important but it is difficult to plot these clearly on Figure 5 if Zn mining is also included.

Of the five Zn emission categories plotted in Figure 5, waste incineration and rubber tire wear are the most important. Note that in general these emissions have increased during the last 40 years such that the second-tier emissions total approximately one-half of the Zn mining–smelting emissions.

9.03.3.4.3 Cadmium

Cadmium has received a wide variety of uses in American industries with the largest being electroplating and battery manufacture. Its emission from natural sources (erosion and volcanic activity) are negligible. The dominant sources of Cd emissions to the atmosphere are primary metals smelting (Cu and Pb), secondary metals production, fossil-fuel combustion, waste incineration, iron and steel production, and rubber tire wear. Figure 6 is a plot of Cd emissions to the US atmosphere for five-year time periods from 1970 to 1990. Between 1970 and 1980, primary metals smelting was the primary source of Cd emissions to the atmosphere. Then fossil-fuel combustion became the primary emitter (60%) with Cu–Pb smelting accounting for much of the remainder (30%) (Wilber *et al.*, 1992). These emissions were concentrated in the central part of the US (Wilber *et al.*, 1992). By 1990, fossil fuel emissions decreased significantly, a fact that is probably related to the increased efficiency of stack emission controls; and secondary metal production became the major source of Cd to the US atmosphere (Figure 6). In the 1980s, Cd emissions to the US atmosphere amounted to 650 t yr^{-1} (Table 11). European emissions were nearly double this amount, i.e., 1,150 t yr^{-1} (Pacyna and Lindgren, 1997).

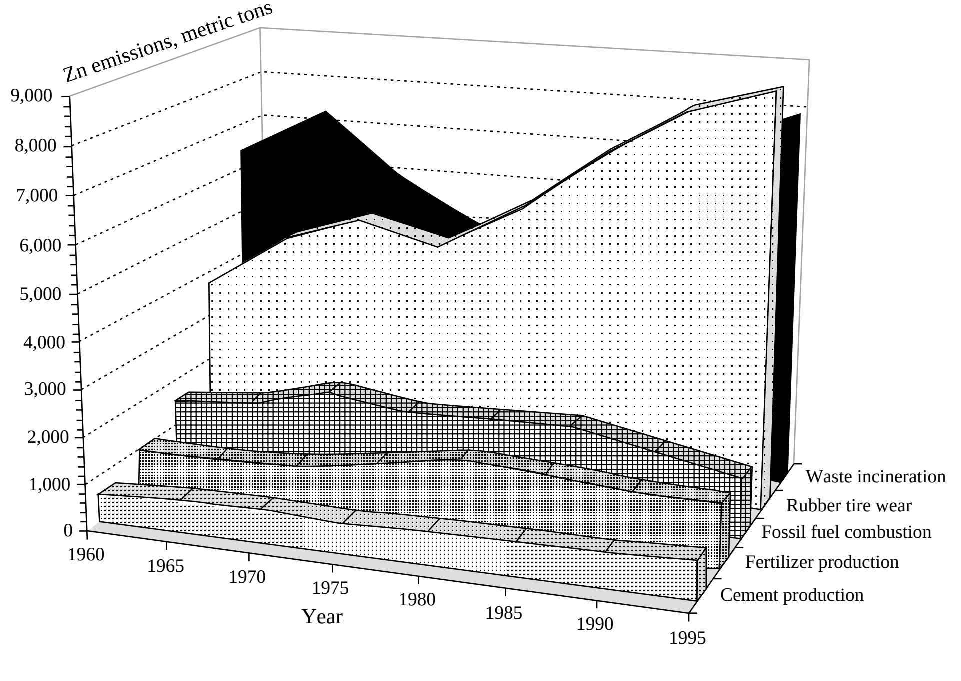


Figure 5 Three-dimensional plot of second tier zinc emissions to the US atmosphere for the period 1960–1995. Data from Councell *et al.* (2003), Nriagu and Pacyna (1988), minerals.usgs.gov/minerals/pubs/commodity/cement/stat/tbl1.txt, minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/stat/tbl1.txt, Pacyna (1986), USEPA (1998), Statistical Abstracts of the United States (1998), author's calculations.

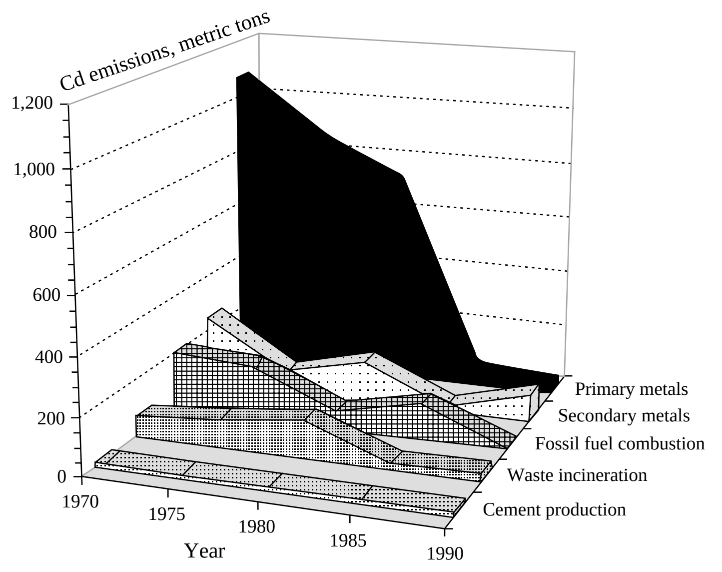


Figure 6 Three-dimensional plot of cadmium emissions to the US atmosphere for the period 1970–1990. (sources Davis and Associates, 1970; USEPA, 1975a,b, 1976, 1978; Wilber *et al.*, 1992).

Table 11 Total U.S. emissions of cadmium (Cd) to the atmosphere.

Source category	*1970*[a]	*1975*[b]	*1980*[c]	*1985*[d]	*1990*[e]
Rubber tire wear	6	6	5	5	5
Cement production	14	13	14	14	15
Waste incineration	72	97	131	21	28
Fossil fuel combustion	200	186	60	121	7
Secondary metals	245	75	143	15	96
Primary metals	1,075	860	728	54	32

Units are metric tons.
[a] Source: Davis and Associates (1970). [b] Source: USEPA (1975a,b, 1976). [c] Source: USEPA (1978). [d] Source: Wilber *et al.* (1992). [e] Source: USEPA (2000b).

9.03.4 HISTORICAL METAL TRENDS RECONSTRUCTED FROM SEDIMENT CORES

9.03.4.1 Paleolimnological Approach

Many governmental agencies collect the data routinely for the assessment of the quality of rivers, streams, lakes, and coastal oceans. Water-quality monitoring involves temporal sampling of water resources that are affected by natural random events, seasonal phenomena, and anthropogenic forces. Testing water quality, monitoring data at regular intervals has become a common feature and an important exercise for water managers who are interested in checking whether the investment of large sums of money has improved the water quality of various water resources during the past 30 years. In addition, trends available by such monitoring can provide a warning of degradation of water quality.

Historical water quality databases suffer from many limitations such as lack of sufficient data, changing sampling and analytical methods, changing detection limits, missing values and values below the analytical reporting level. With regard to trace metal data, the problem is even more difficult in that many metals occur at environmental concentrations so low (parts per billion or less) that current (up until the early 1990s) routine analytical methodology was unable to detect ambient concentrations with adequate sensitivity and precision. Even the best statistical techniques, when applied to questionable data, can produce misleading results. For example, Pb in the Trinity River, south of Dallas, TX, USA. Abundant dissolved Pb data for the period 1977–1992 (Van Metre and Callender, 1996) indicate that there were no trends in Pb; in fact, the concentrations were scattered from 0 to 5 ppb. On the other hand, Pb in sediment cores from Lake Livingston, downstream from the Trinity River sampling station, showed a decline in Pb concentration from 1970 to 1993 (Van Metre and Callender, 1996). Thus, from the core data, one can conclude that there is a declining trend in Pb in the Trinity River.

For these very reasons, the US Congress supported the US Geological Survey's National Water Quality Assessment Program with its goals to describe the status and trends in water quality of our Nation's surface and groundwater, and to provide an understanding of the natural and human factors that affect the observed conditions and trends. The US public is eager to know whether the water quality of US rivers and lakes has benefited from the expenditure of billions of dollars since the passage of the Clean Air and Clean Water Acts in the 1970s.

An alternate approach to statistical analyses of historical water-quality data is to use metal distributions in dated sediment cores to assess the past trends in anthropogenic hydrophobic constituents that impact watersheds (paleolimnological approach). It is well known that marine and lacustrine sediments often record natural and anthropogenic events that occur in drainage basins, local and regional air masses, or are forced upon the aquatic system (Valette-Silver, 1993). A good example of the former is the increase in erosional inputs to lakes in response to anthropogenic activities in the drainage basin (Brush, 1984). Atmospheric pollution resulting from the cultural and industrial activities (Chow *et al.*, 1973) is a compelling example of the latter. Thus, aquatic sediments are archives of natural and anthropogenic change. This is especially true for hydrophobic constituents such as heavy metals.

Because of their large adsorption capacity, fine-grained sediments are a major repository for the contaminants and a record of the temporal changes in contamination. Thus, sediments can be used for historical reconstruction. To guarantee a reliable age dating, and, therefore, to be useful in the historical reconstruction, the core sediment must be undisturbed, fine-grained, and collected in an area with a relatively fast sedimentation rate. These conditions are often found in lakes where studies in the 1970s by Kemp *et al.* (1974) and Forstner (1976) used lake sediments to understand the pollution history of several Laurentian Great Lakes and some European lakes. However, there is a serious limitation in using sediment cores from many natural lakes in that the sedimentation rate is generally too slow in providing the proper time resolution to discern modern pollution trends. Lacustrine sediments usually accumulate at rates less than 1 cm yr^{-1} (Krishnaswami and Lal, 1978) and often at rates less than 0.3 cm yr^{-1} (Johnson, 1984). Thus, there may be sufficient time for early diagenesis, such as microbiologically-mediated reactions, to occur. On the other hand, in lacustrine environments where sediments accumulate at rates exceeding 1 and may exceed 5–10 cm yr^{-1} (Ritchie *et al.*, 1973), such as in surface-water reservoirs, rapid sedimentation exerts a pronounced influence on sedimentary diagenesis.

A brief discussion of sedimentary diagenesis is warranted as post-depositional chemical, and physical stability is probably the most important factor in preserving heavy-metal signatures that may be recorded in aquatic sediments. For sediments to provide a historical record of pollution, the pollutant must have an affinity for the sedimentary particles. It is well known that most of the metals, and certainly the heavy metals discussed in this chapter, are hydrophobic in nature and allow partition to the solid phase. Once deposited in the sediment, the pollutants should not undergo chemical mobilization within the sediment column nor should the sediment column be disturbed by physical and biological processes.

Natural lacustrine and estuarine sediments whose accumulation rates are low, generally below 0.25 cm yr^{-1}, often do not satisfy the above requirements. The biophysical term bioturbation refers to surficial sediments mixed by the actions of deposit feeders, irrigation tube dwellers, and head-down feeders (Boudreau, 1999). In general, these bioturbation processes do not occur in reservoirs where sediment accumulation rates exceed 1 and often 5 cm yr^{-1} (Callender, 2000). At these rates, the sediment influx at the water–sediment interface is too great for benthic organisms to establish themselves.

On the other hand, geochemical mobility affects every sedimentary environment; varying in degree, from slowly accumulating natural lacustrine and estuarine sediments to rapidly accumulating reservoir sediments. The major authigenic solid substrates for adsorption and co-precipitation of heavy metals in aquatic sediments are the hydrous oxides of iron (Fe) and manganese (Mn) (Santschi *et al.*, 1990). These primary metal oxides sorb/co-precipitate Pb–Cr–Cu (Fe oxyhydroxides) and Zn–Cd–Pb (Mn oxyhydroxides) (Santschi *et al.*, 1990). Manganese oxides begin to dissolve in mildly oxidizing sediments while Fe oxides are reduced in anoxic sediments (Salomons and Forstner, 1984). In the mildly oxidizing zone, Mn^{2+} diffuses upward and precipitates as Mn oxide in the stronger oxidizing part of the sediment column. At greater sediment depths, Fe oxide reduction to Fe^{2+} begins and ferrous iron diffuses upward and precipitates as Fe oxide in the mildly oxidizing part of the sediment sequence (Salomons and Forstner, 1984).

An example from a slowly-accumulating (0.01–0.1 cm yr^{-1}) sediment profile in a freshwater lake in Scotland (Williams, 1992) should suffice to illustrate the formation of diagenetic metal profiles. Early diagenetic processes, such as those described before, have promoted extensive metal enrichment immediately beneath the water–sediment interface. The oxic conditions, near the water–sediment interface, that promote metal precipitation and enrichment (Mn, Fe, Pb, Zn, Cu, Ni) are entirely confined to strata of post-industrial age (Williams, 1992).

Callender (2000) extensively studied the geochemical effects of rapid sedimentation in aquatic systems and postulated that rapid sedimentation exerts a pronounced influence on early sedimentary diagenesis. The following are two case studies that illustrate this point. The Cheyenne River Embayment of Lake Oahe, one of the several impoundments on the upper Missouri River, accumulates sediment at an average rate of 9 cm yr^{-1} (Callender and Robbins, 1993). Three interstitial-water Fe profiles from the same site taken over a three-year period (August 1985, August 1986, June 1987), when superimposed on the same depth axis, show the effects of interannual variations in sediment inputs such that in 1986 a rapid input of oxidized material suppressed the dissolved Fe concentration to less than 0.1 mg L^{-1} to a depth of 8 cm. In 1985 when there was a drought and sediment inputs were reduced substantially, near-surface sediment became nearly anoxic and the interstitial Fe concentration rose to a very high 26 mg L^{-1} (Callender, 2000). In Pueblo Reservoir on the upper Arkansas River in central Colorado, cores of bottom sediments showed distinct reddish-brown layers that indicate rapid transport and sedimentation of Fe-rich colloids formed by the discharge of acid-mine waters from abandoned mines upstream (Callender, 2000). The amorphous sedimentary Fe profile from a sediment core near the river mouth shows two peaks at depths that correspond to the dates of heavy metal releases from the mines. Although the amorphous Fe oxyhydroxide concentrations are only 10% of the total Fe concentrations, they are adequate to adsorb Pb (Fergusson, 1990) and produce the anthropogenic Pb concentrations found in the core (Callender, 2000). Copper and Zn show similar distributions in this core whose sedimentation rate is 5 cm yr^{-1}.

In these examples as well as for most aquatic sediments, the principal diagenetic reactions that occur in these sediments are aerobic respiration and the reduction of Mn and Fe oxides. Under the slower sedimentation conditions in natural lakes and estuaries, there is sufficient time (years) for particulate organic matter to decompose and create a diagenetic environment where metal oxides may not be stable. When faster sedimentation prevails, such as in reservoirs, there is less time (months) for bacteria to perform their metabolic functions due to the fact that the organisms do not occupy a sediment layer for any length of time before a new sediment is added (Callender, 2000). Also, sedimentary organic matter in reservoir sediments is considerably more recalcitrant than that in natural lacustrine and estuarine sediments as reservoirs receive more terrestrial organic matter (Callender, 2000).

The author hopes that this discussion of sedimentary diagenesis, as it applies to heavy-metal signatures in natural lacustrine and reservoir sediments, will help the reader interpret the results presented in the following sections on reconstructed metal trends from age-dated reservoir sediment cores.

The approach that Callender and Van Metre (1997) have taken is to select primarily reservoir lakes that integrate a generally sizeable drainage basin that is impacted by a unique landuse such as agriculture, mining, stack emissions, suburban "sprawl", or urban development with some commercial and light industrial activity. Sediment cores are taken to sample the post-impoundment section as much as possible and to penetrate the pre-impoundment material. Core sampling is accomplished with a variety of coring tools (box cores, push cores, piston cores) in order to recover a relatively undisturbed sediment section. The recovered sediment is sampled on approximately an annual sediment thickness and samples are preserved (chilled, then frozen) for future analytical determinations. In the laboratory, sediment samples are weighed, frozen, freeze-dried, weighed again, and ground to a fine powder. Elemental concentrations are determined on concentrated acid digests (nitric and hydrofluoric in microwave pressure vessels) by inductively coupled plasma-atomic emission spectrometry (ICP/AES) or by graphite furnace atomic adsorption spectrometry (GF/AAS).

For reservoirs to be a good medium for detecting the trends in heavy metals, several conditions need to be satisfied. First, the site sampled should be continuously depositional over the life of the reservoir. This condition is most easily satisfied by sampling in the deeper, lacustrine region of the reservoir where sedimentation is slower but more uniform and the sediments predominantly consist of silty clay material. The second condition is that the sediments sampled should not be subject to significant physical and chemical diagenesis; that is, mobilization of chemical constituents after deposition. Callender (2000) has written an extensive paper indicating that rapid sedimentation promotes minimal diagenesis and preserves historical metal signatures. The third condition is that the chemical quality of reservoir bottom sediments should be related to the water quality of the influent river and that the influent water quality be representative of the drainage basin.

9.03.4.2 Age Dating

In general, reservoir sediments can be dated by several techniques. In one technique, the sediment surface is dated by the time of coring while in the other the date is derived from a visual inspection of the cored sediment column which often penetrates the pre-impoundment surface. The primary age dating tool for reservoir sediments is by counting the radioactive isotope ^{137}Cs which has a half-life period of 30 years (Robbins and Edgington, 1975; McCall *et al.*, 1984). The ^{137}Cs activity of freeze-dried sediment samples is measured by counting the gamma activity in fixed geometry with a high-resolution, intrinsic germanium detector gamma-spectrometer (Callender and Robbins, 1993). Depending on the penetration depth of the core and the age of the reservoir, ^{137}Cs can provide one or two date markers and can be used to evaluate the relative amount of postdepositional mixing or sediment disturbance (Van Metre *et al.*, 1997). The peak ^{137}Cs activity in the sediment core is assigned a date of 1964, consistent with the peak in atmospheric fallout levels of ^{137}Cs for 1963–1964. In reservoirs constructed prior to or around 1950, the first occurrence of ^{137}Cs, if it did not appear to have been effected by postdepositional sediment mixing, was assigned a date of 1953 which is consistent with the generally accepted date of 1952 for the first large-scale atmospheric testing of nuclear weapons by the US in Nevada (Beck *et al.*, 1990). This is also the date of the first globally-detectable levels of ^{137}Cs in the atmosphere. In some cases dates for samples between the known date-depth markers were assigned using constant mass accumulation rates (MARs), and in other cases the MARs were varied.

In natural lacustrine and slowly-accumulating reservoir sediments, core dating with the isotope ^{210}Pb has been used extensively (Schell and Barner, 1986). Appleby and Oldfield (1983) found that the constant rate of ^{210}Pb supply model (CRS) provides a reasonably accurate sedimentation chronology. The basic assumption of the CRS model is that the rate of supply of excess ^{210}Pb to the lake is constant. This model, thus, assumes that the erosive processes in the catchment are steady and give rise to a constant rate of sediment accumulation (MAR) (Appleby and Oldfield, 1983). In practice, for reservoirs, this assumption is rarely met because, for example, an increase in the MAR caused by land disturbances, such as those associated with the urban development, transports additional surficial soils and sediments to the lake. This additional erosion increases the MAR and also increases the rate of supply of ^{210}Pb to the lake. In general, because excess ^{210}Pb is an atmospheric fallout radionuclide, the model works better in low sedimentation rate, atmospherically dominated lakes with undisturbed watersheds, than in high sedimentation rate, fluvially dominated urban lakes and reservoirs.

Another problem with age dating of reservoir sediment is the concept of sediment focusing. This concept was developed to correct for postdepositional resuspension and redistribution of sediment in parts of the lake (Hermanson, 1991). A common focus correction factor is derived from the inventory of ^{137}Cs in the sediment column compared to the estimated total ^{137}Cs fallout at the sampling site (Hermanson, 1991). The same concept was found to not work well for lakes and reservoirs where the catchment area far exceeds the lake area. Such is the case for most reservoirs (Van Metre *et al.*, 2000). In these cases where the catchment area is 10–100 times the lake area, sediment focusing in the lake basin is overwhelmed by the concentration effect of atmospheric fallout over the catchment area being funneled into the lake or reservoir. The catchment area focus corrections are calculated the same way as lake basin focus corrections except that there may be some variation in the ^{137}Cs flux to large catchment areas and that there will almost always be a correction factor greater than 1. These focus corrections must be calculated in order to compare the contaminant fluxes between the sites within a lake basin and between lake basins.

9.03.4.3 Selected Reconstructed Metal Trends

9.03.4.3.1 Lead and leaded gasoline: consequence of the clean air act

Of the six heavy metals discussed in this chapter, Pb has been studied extensively with respect to the environmental effects. Clair Patterson, the father of environmental Pb studies, in one of his many major publications concerning the global Pb cycle (Patterson and Settle, 1987), noted that during pre-industrial times Pb in the troposphere originated from soil dusts and volcanic gases. In modern times (1950–1980) the proportion of natural Pb in the atmosphere is overwhelmed by the industrial sources of smelter emissions and automobile exhausts. Lead air pollution levels measured near our Nation's roadways decreased 97% between 1976 and 1995 due to the consequence of the Clean Air Act that eliminated leaded gasoline which interfered with the performance of catalytic converters.

For remote locations on a more global scale, Boyle *et al.* (1994) showed that the stable Pb concentration in North Atlantic waters decreased at least three-fold from 1979 to 1988. Wu and Boyle (1997) confirmed and extended this time series to 1996 whereby the concentration of stable Pb apparently stabilized at 50 pmol kg^{-1} in surface waters near Bermuda. Shen and Boyle (1987) presented a 100-year record of Pb concentration in corals from Bermuda and the Florida Straits showing that Pb peaked in the 1970s and declined thereafter. Veron *et al.* (1987) found high Pb concentrations in northeast Atlantic surficial sediments and noted that the quantity of Pb stored in these sediments is of the same order of magnitude as the amount of pollutant Pb present in the water column.

On a more local level, man's activities in the urban/suburban environment have produced a strong imprint of Pb on the land surface. In the US, automobile and truck travel are the primary means of moving people and goods around the continent. With the introduction of leaded gasoline in the 1950s, the mean annual atmospheric concentration of Pb nearly tripled in value, especially near population centers (Eisenreich *et al.*, 1986). A substantial proportion of these atmospheric emissions of Pb have been deposited relatively close to the source. Figures 7(a)–(c) presents the age-dated sedimentary Pb profiles for reservoirs and lakes from urban–suburban–rural localities. One can see that the peak concentrations decrease from 700 to 300 to 100 μg g^{-1} as the distance from urban centers increase. All but two of the Pb peak concentrations date between 1970 and 1980, and

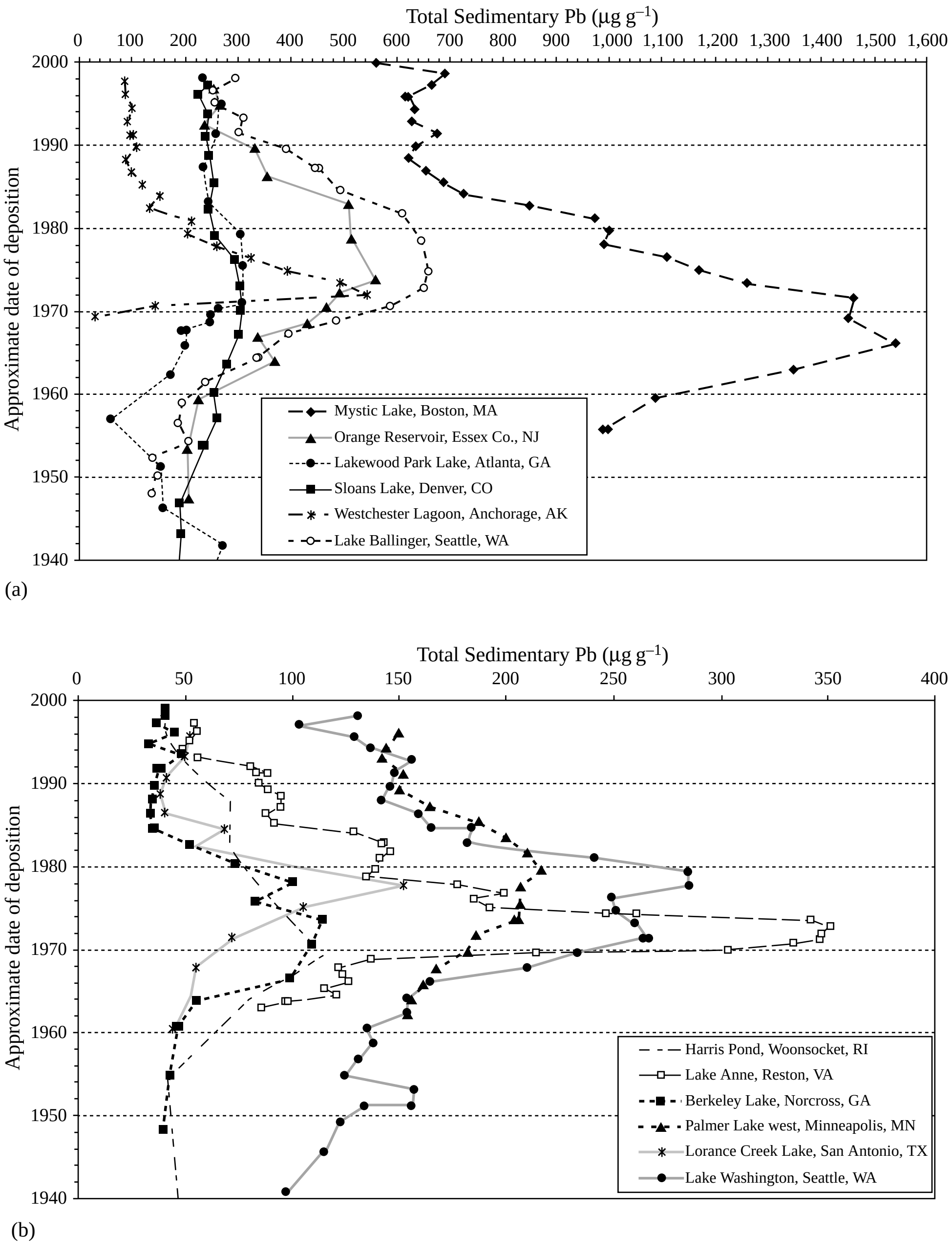


Figure 7 Temporal distribution of total sedimentary lead in sediment cores from (a) urban reservoirs, (b) suburban reservoirs and lakes, and (c) atmospheric reference site reservoirs.

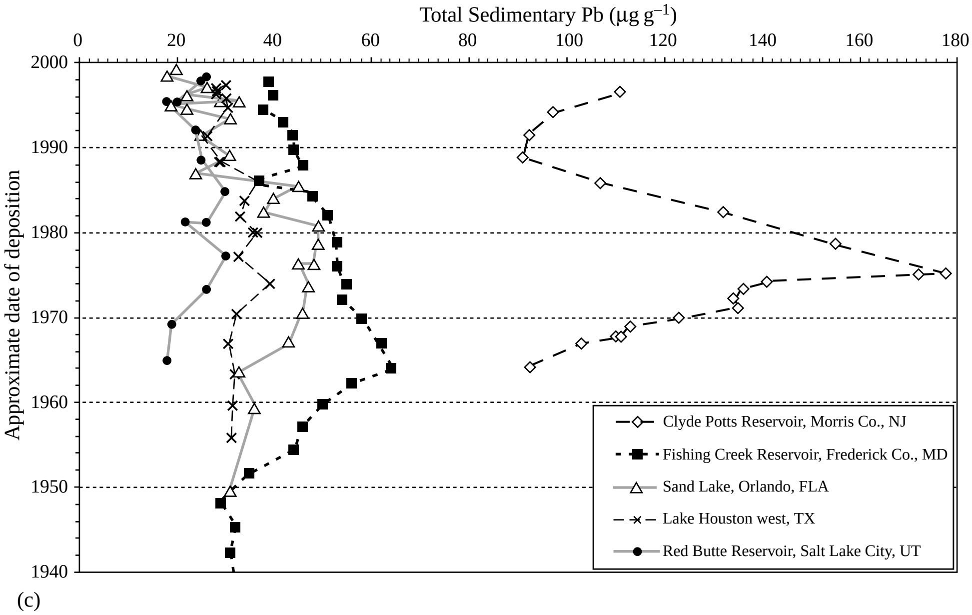


Figure 7 (continued).

are consistent with the decline in US atmospheric Pb concentrations following the ban of unleaded gasoline in 1972 (Callender and Van Metre, 1997). Sedimentary Pb data from many urban centers around the US (Boston, New York, New Jersey, Atlanta, Orlando, Minneapolis, Dallas, Austin, San Antonio, Denver, Salt Lake City, Las Vegas, Los Angeles, Seattle, and Anchorage) have been subjected to statistical trend analysis (B.J. Mahler, personal communication, 2002) and the results plotted in Figure 8. It is obvious that essentially all urban reservoirs and lake records show a very significant decline in Pb since 1975 and that this trend is most probably a result of the ban on leaded gasoline that was instituted in 1972.

9.03.4.3.2 Zinc from rubber tire wear

Contrary to the distribution of Pb in sediment cores whereby peak concentrations occurred during the 1970s, the concentration of sedimentary Zn often increases to the 1990s. It was observed in the atmospheric emissions of metals that waste incineration was one of the major contributors to the second tier of Zn emissions to the US atmosphere. Figure 9(a) presents age-dated sedimentary Zn data from a spectrum of urban/suburban sites around the US It is obvious that the general trend of sedimentary Zn is one of increasing concentrations from 1950s to 1990s. However, the general increasing trend for Zn is not as prevalent as that for Pb and at a few of the urban/suburban/reference sites noted for the Pb trend map there is no significant trend in sedimentary Zn concentration (B.J. Mahler, personal communication, 2002). Figure 5 shows that rubber tire wear is the most important and increasing contributor to the second tier of Zn emissions to the US atmosphere. Tire tread material has a Zn content of about 1% by weight. A significant quantity of tread material is lost to road surfaces by abrasion prior to tire replacement on a vehicle. In Figure 9(b) the anthropogenic Zn data for urban/suburban core sites is regressed against the mass sedimentation rate (MSR) for each core site. When MSR-normalized anthropogenic Zn is plotted against average annual daily traffic (AADT) data for the various metropolitan areas shown in Figure 9(a), a significant regression results (Figure 9(c)) suggesting that there is a causal relationship between anthropogenic Zn and vehicle traffic. Councell *et al.* (2003) produced data that estimates the magnitude of the Zn releases to the environment from rubber tire abrasion. Two approaches, wear rate (g km^{-1}) and tread geometry (abrasion to wear bars), were used to assess the magnitude of this nonpoint source of Zn in the US for the period 1936–1999. For 1999, the quantity of Zn released by tire wear in the US is estimated to be between 10,000 and 11,000 t.

Two specific case studies focused on the impact of vehicle tire wear to the Zn budget of watersheds in the Washington, DC metropolitan area. For Lake Anne, a suburban watershed located 40 km southwest of Washington, DC, the wet deposition atmospheric flux of Zn was 8 $\mu g\ cm^{-2}\ yr^{-1}$ (Davis and Galloway, 1981) and the flux of Zn

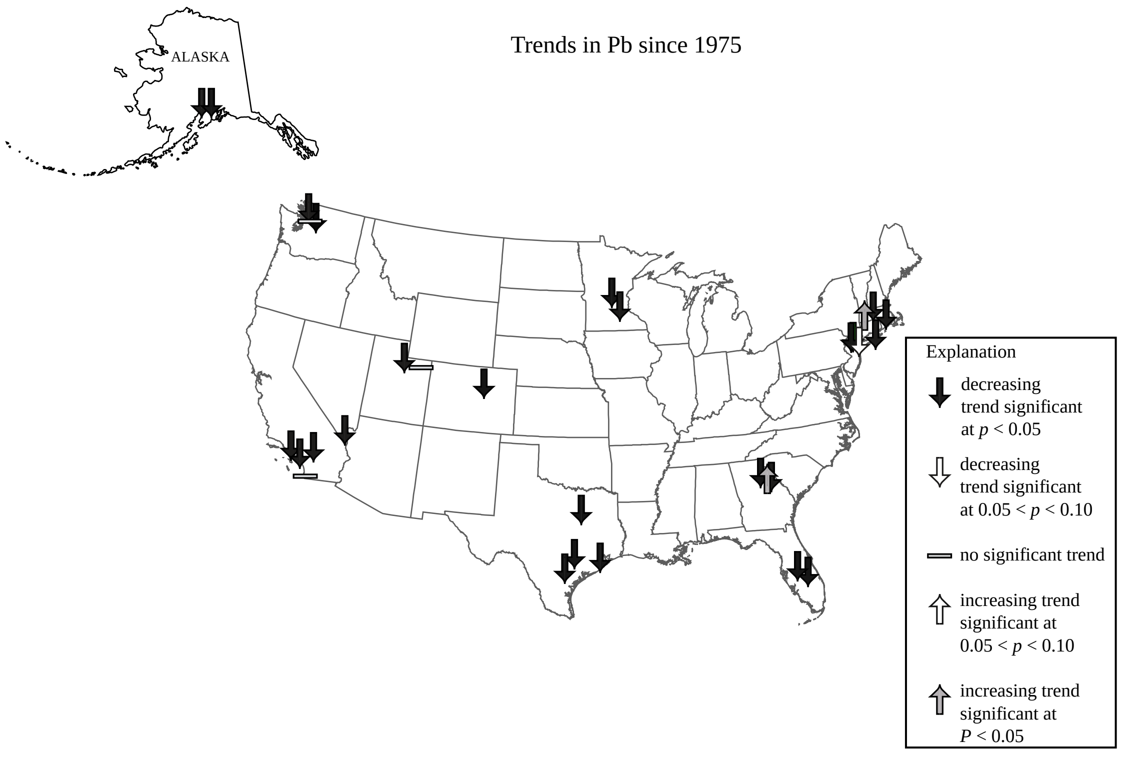


Figure 8 Map showing statistical trends in lead from sediment cores located throughout the US.

estimated from tire wear was 31 μg cm^{-2} yr^{-1} (Landa *et al.* 2002). The measured accumulation rate of Zn in age-dated sediment cores from Lake Anne is 41 μg cm^{-2} yr^{-1} (Landa *et al*, 2002) suggesting that tire-wear Zn inputs to suburban watersheds can be significantly greater than atmospheric inputs. In a rural/atmospheric reference site watershed, located ~90 km northwest of Washington, DC, the atmospheric Zn flux is 12 μg cm^{-2} yr^{-1} (Davis and Galloway, 1981) and that from tire wear is only 1 μg cm^{-2} yr^{-1} (Landa *et al.*, 2002). There are only dirt roads leading to cabins in this protected watershed and it is obvious that vehicle tire wear is only a minor component of the Zn flux in this remote watershed. One conclusion drawn from these case studies and the substantial set of age-dated sediment core Zn profiles is that those watersheds that are impacted by vehicular traffic receive significant amounts of Zn via tire abrasion and that this Zn-enriched particulate matter is fluvially transported to lakes and reservoirs.

9.03.4.3.3 Metal processing and metal trends in sediment cores

While the relationship between Pb and Zn distributions in reservoir and lake sediment cores and environmental forcing functions (leaded gasoline use and vehicular traffic) are clear, the same is not true in the case of other metals such as Cd, Cr, Cu, and Ni. These metals do have one common, major source: nonferrous and ferrous metal production. Approximately 70% of the Cd and Cr anthropogenic emissions, 50% of the Cu, and 21% of the Ni anthropogenic emissions come from mining–smelting–metal processing. In an attempt to interpret metal trend maps for these four metals, historical US metal mining and production statistics have been shown in Figure 10. Copper is the only metal whose production increased during the past 25 years. Starting in 1985, the primary production of Cu has increased from about one million metric tons to a maximum of about two million metric tons in 1998 (Figure 10). Arizona has the largest Cu mining production followed by Utah, New Mexico, and Montana. Thus, all the major point sources of Cu exist in the western states. Figure 11 shows the statistical trends (since 1975) for Cu in sediment cores from 30 reservoir and lake sites around the US (B.J. Mahler, personal communication, 2002). Increasing or decreasing trends in the upper part of sediment cores were tested statistically for eight trace metals. Significant trends in sediments deposited since 1975 were tested using a Spearman's rank correlation

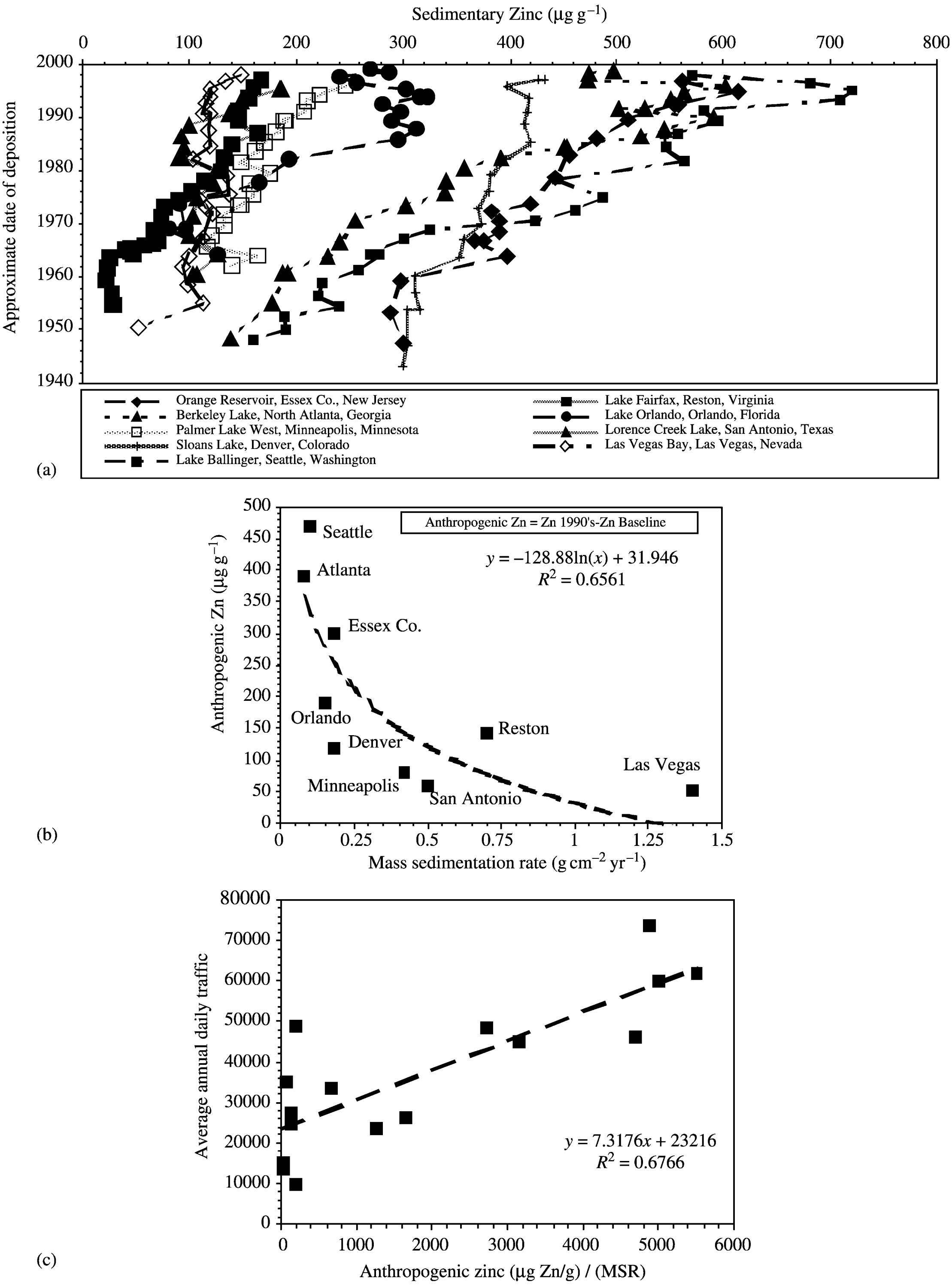


Figure 9 (a) Temporal distribution of total sedimentary zinc in US reservoir sediment cores, (b) regression of anthropogenic zinc versus MSR for US reservoir sediment cores, (c) MSR-normalized anthropogenic zinc versus average annual daily traffic for urban and suburban watersheds throughout the US

(Helsel and Hirsch, 1992). Trends were determined to be significantly increasing or decreasing based on a p value of less than 0.05 (B.J. Mahler, personal communication, 2002). The Cu trend indicators in Figure 11 show that there are increasing trends significant at $p < 0.05$ at the core sites in Washington–California–Nevada and that there are no

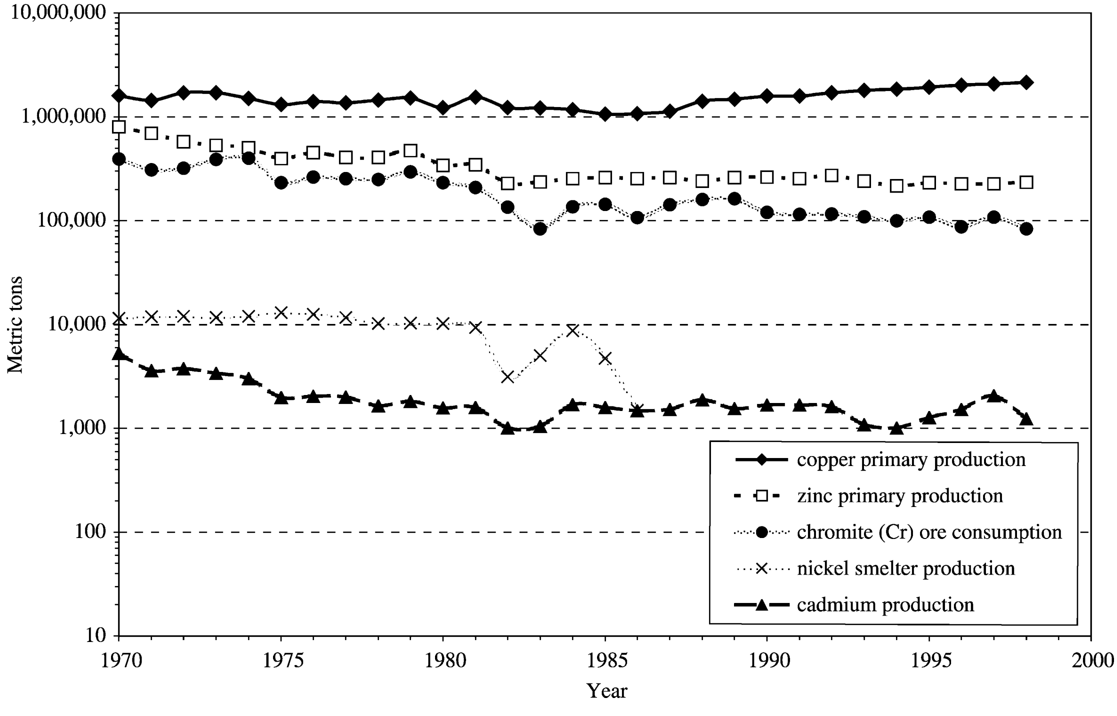


Figure 10 Historical production of nonferrous metals in the US Data from US Geological Survey, Mineral Resources Program.

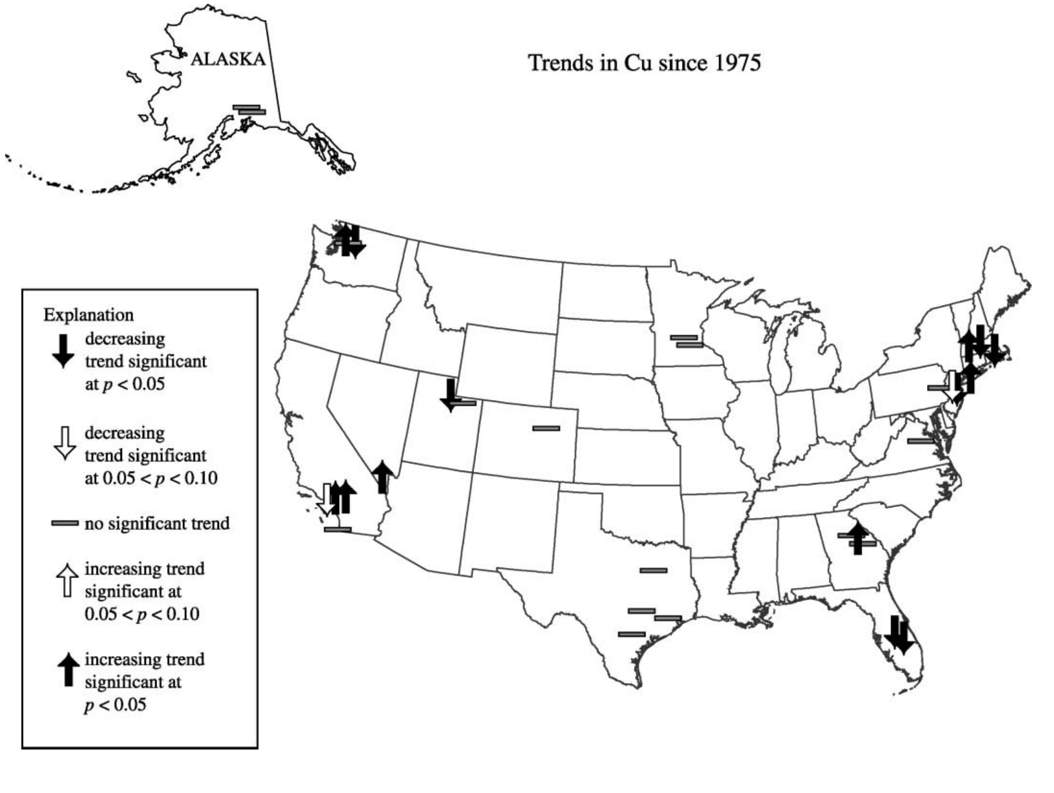


Figure 11 Map showing statistical trends in copper from sediment cores located throughout the US.

significant trends in Cu at core sites in the Midwest and Southwest. Such a pattern suggests that an increase in Cu mining in the Rocky Mountain States may cause airborne emissions that impact the western US but that these emissions are not transported east to the mid-continent. Along the Atlantic coast, from Georgia to Massachusetts, there are some sites that show an increasing trend in sedimentary Cu. It should be noted that many of the east coast sites are small ponds used for water supply and recreation and that some have been treated with $CuSO_4$ to control the algae. In addition, many of these sites are located in the east coast urban/suburban corridor and obviously receive a multitude of anthropogenic contaminants.

Limited space does not allow for the presentation of all metal trend maps such as those presented for Pb and Cu. Of the three remaining metals (Cd, Cr, Ni), the trends in Ni since 1975 is representative of the other metals as well. For the western half of the US, there are nine sites where there is a significant decreasing trend in Ni (Figure 12). This corresponds to the decrease in Ni smelter production for the 1970s and 1980s (Figure 10). There are a few increasing Ni trends along the east coast of the US, a pattern that may reflect the location of many nickel consumption facilities in Pennsylvania, West Virginia, and New Jersey. The trends in Cr since 1975 are very similar to those for Ni; for the western half of the US there are eight sites where there is a significant decreasing trend. Along the east coast of the US there is only one site in the Boston area that shows an increasing trend. Thus, the overall decreasing Cr trend for the US reflects the four-fold decrease in chromite (Cr ore) consumption by metallurgical and chemical firms in the US since 1970 (Figure 10). The trends in Cd since 1975 are not as strongly skewed toward decreasing trends as those for Ni and Cr. This is probably due to the fact that much of the Cd in the US is recovered by the processing of Zn ore and as one can see from Figure 10, Zn production has leveled out in the 1980s and 1990s. In fact, the preponderance of coring sites in the US (20 out of 30) show no significant trend in Cd.

9.03.4.3.4 *Reduction in power plant emissions of heavy metals: clean air act amendments and the use of low sulfur coal*

Only recently have electric utility power plant emissions been included on the US Environmental Protection Agency's (USEPA) Toxic Release Inventory which reported that electric utilities ranked highest for industrial toxic air emissions in 1998. These emissions were likely to be an important component of toxic air releases in the past, particularly prior to the passage of the Clean Air Act of 1970.

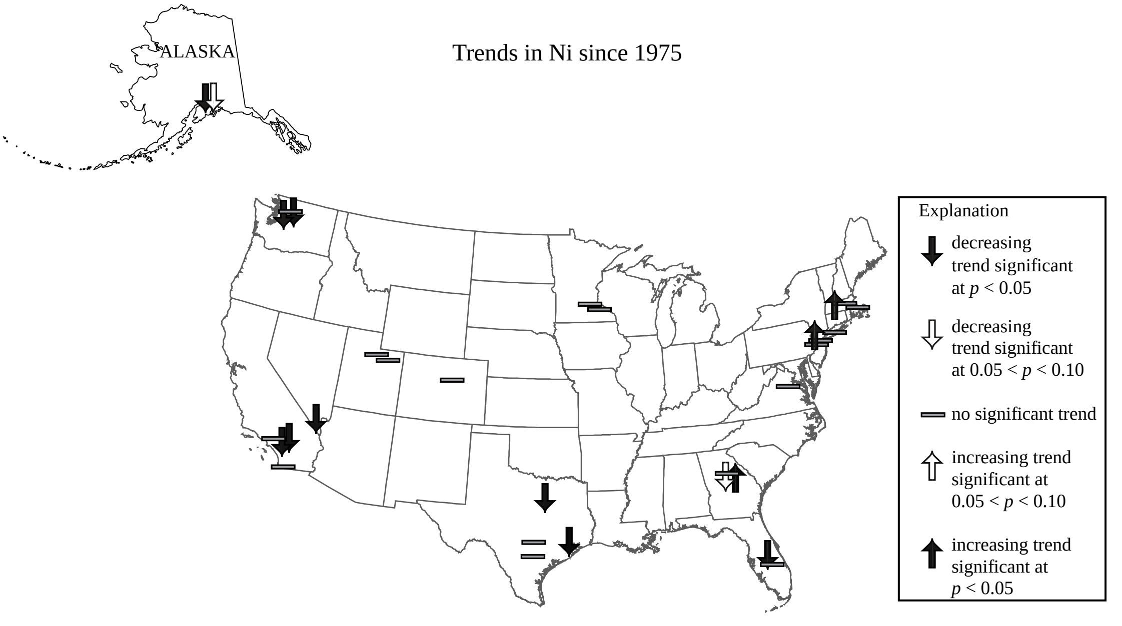


Figure 12 Map showing the statistical trends in nickel from sediment cores located throughout the US.

A sediment core from one reservoir (Mile Tree Run Reservoir) located in southwestern West Virginia was selected for the purpose of identifying particulate signatures of coal-fired power plant emissions from the nearby Ohio River Valley region. Arsenic (As) and some Pb and Zn releases to the environment may reflect coal-related geochemical processes. Stream sediments from the Appalachian Basin Region are particularly enriched in As compared to the sediments outside the Basin. While some As enrichment may come from the weathering of As-rich coal, this area of West Virginia is underlain primarily by sandstone which is low in trace-element composition. Thus, the elevated As contents are not likely to have an origin in the regional country rock but might have originated from numerous large coal-fired power plants situated along the Ohio River.

Figure 13(a) shows the temporal distribution of Ti-normalized As, Pb, and Zn in the sediment core from Mile Tree Run Reservoir. These Ti-normalized metal peaks date back to 1987, 1966, and 1946, respectively (Figure 13(a)). Figure 13(b) shows the temporal distribution of Ti-normalized sulfur (S), isothermal remnant magnetization (IRM) (a magnetite proxy), and Fe in the same core. Peaks in these constituents correspond to the aforementioned dates. These dates match the maximum values in combined coal production for the states of West Virginia, Pennsylvania, and Ohio (M.B. Goldhaber, personal communication, 2002). The temporal profile for the magnetic property IRM that is indicative of the mineral magnetite is shown in Figure 13(b) (M.B. Goldhaber, personal communication, 2002).

Figures 14 (a) and (b) are scatter plots between Zn and coal production, and Zn and IRM (magnetite). Note the excellent correlations suggesting that Zn relates to atmospheric input (fly ash) from power plants. A glance at Table 2 shows that Zn in fly ash is substantially enriched compared to average soils. One can also see this relationship for Mile Tree Run watershed soils in Figure 13(a). Arsenic also has a very strong positive correlation with IRM in the Mile Tree Run Reservoir core. This element is known to be strongly associated with magnetite, an important fly ash mineral that is formed in the high temperature combustion of coal (Locke and Bertine, 1986). Such a geochemical association is not surprising in that it is thought that magnetite is formed from the pyrite in coal that is subjected to high temperature combustion. It is also well known that As is a minor element associated with pyrite.

The simultaneous decline after 1985 of the correlated Fe–As–Pb–Zn and magnetite peaks (Figures 13(a) and (b) suggests that the amount of power plant particulate emissions decreased since the 1977 amendment of the Clean Air Act that mandated reduced amounts of sulfur in the feed coal (Hower *et al.*, 1999). It appears that this action resulted in lower metal and magnetite quantities in the fly ash combusted residue. Despite this decrease, soil samples from the Mile Tree Run Reservoir watershed are strongly enriched in As, Pb, and Zn when compared to average soils (Table 2) and local bedrock (Callender *et al.*, 2001), indicating a regional power plant emissions impact on the geochemical landscape.

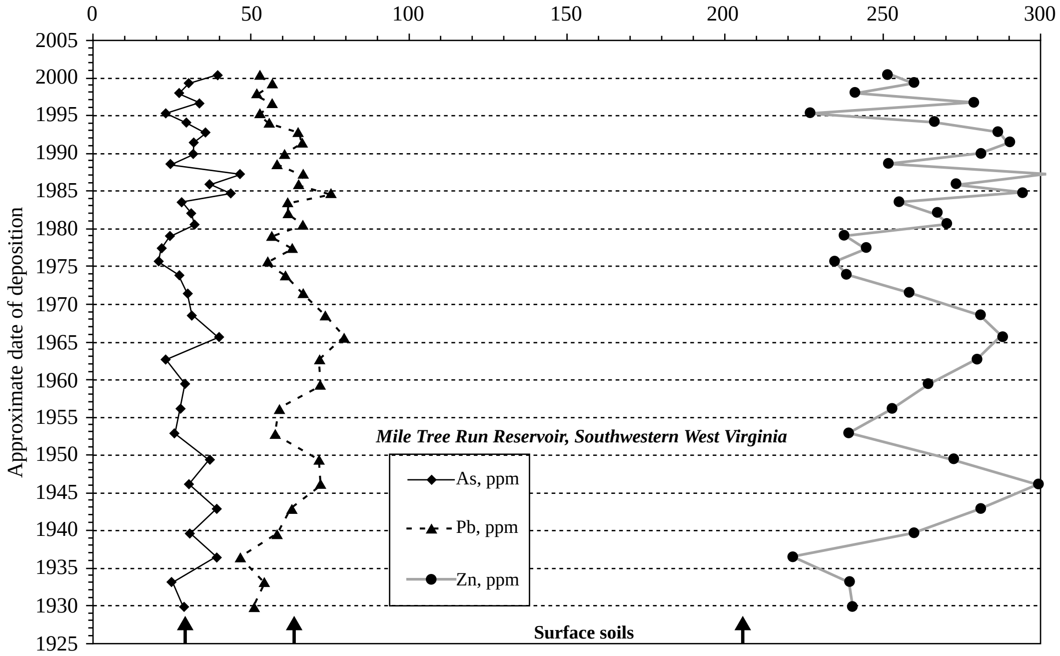
9.03.4.3.5 European lacustrine records of heavy metal pollution

Much of the recent literature pertaining to European studies of heavy metal pollution using sediment cores to track time trends focused on Pb. Petit *et al.* (1984) used the stable isotope geochemistry to identify Pb pollution sources and to evaluate the relative importance of anthropogenic sources to total Pb fluxes in a semi-rural region of western Europe. Thomas *et al.* (1984) showed that metal enrichment factors for Pb–Zn–Cd were significantly above unity, indicating a diffuse contribution through atmospheric transport from industrialized areas. A comparison with atmospheric fluxes showed good agreement for diffuse atmospheric supply of Pb, Zn, and Cd in the lake sediments (Thomas *et al.*, 1984).

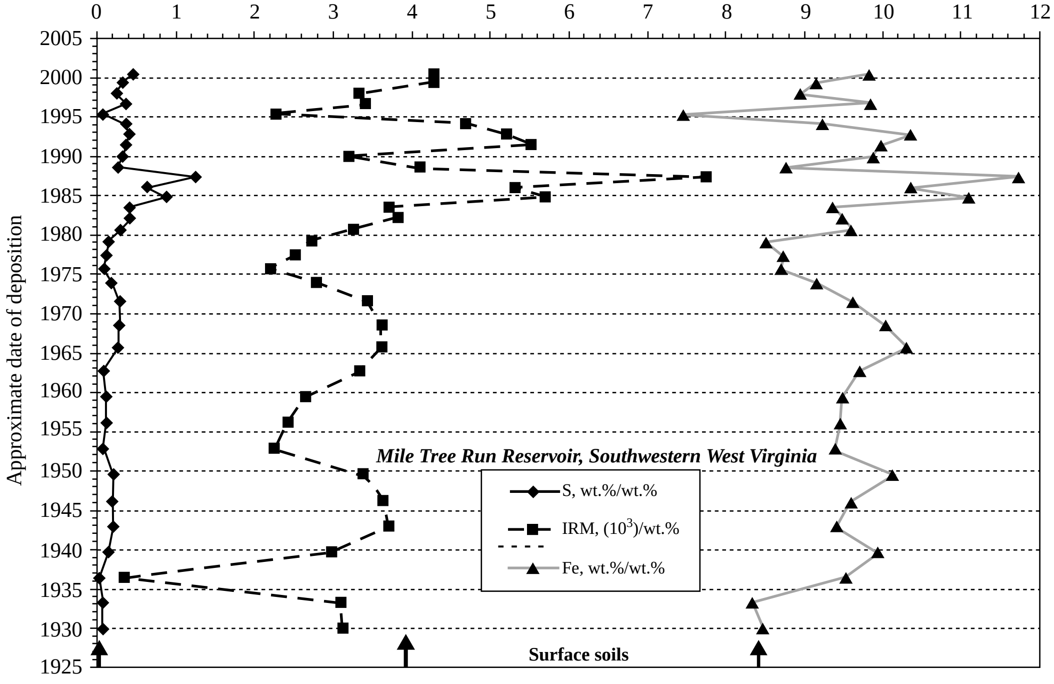
Much work has been done on Lake Constance situated on the borders of Germany, Austria, and Switzerland. The lake has undergone extensive cultural eutrophication due to the surrounding population, industrial activity, and the input of River Rhine. Muller *et al.* (1977) found that sedimentary Pb and Zn concentrations peaked around 1965. They also noted that there was a strong positive correlation between heavy-metal content and PAHs in the sediment core. Muller *et al.* (1977) suggested that coal burning was the source of this relationship. In a more recent study of Lake Constance sediments, Wessels *et al.* (1995) also noted high concentrations of Pb and Zn that began around 1960. However, they postulated that the origin of the Pb increase was emissions by regional industry and the origin of the Zn increase was a combination of urban runoff and coal burning.

Two groups, one in Switzerland and the other in Sweden, have used age-dated sediment cores from peat bogs and natural lake sediments to record the history of atmospheric Pb pollution dating back to several thousand years.

In Switzerland, Shotyk and co-workers (Shotyk *et al.*, 1998) rebuilt the history of atmospheric Pb deposition over the last 12,000 years. They cored ombrotrophic peat bogs that are hydrologically isolated from the influence of local groundwaters and surfacewaters, and receive their inorganic



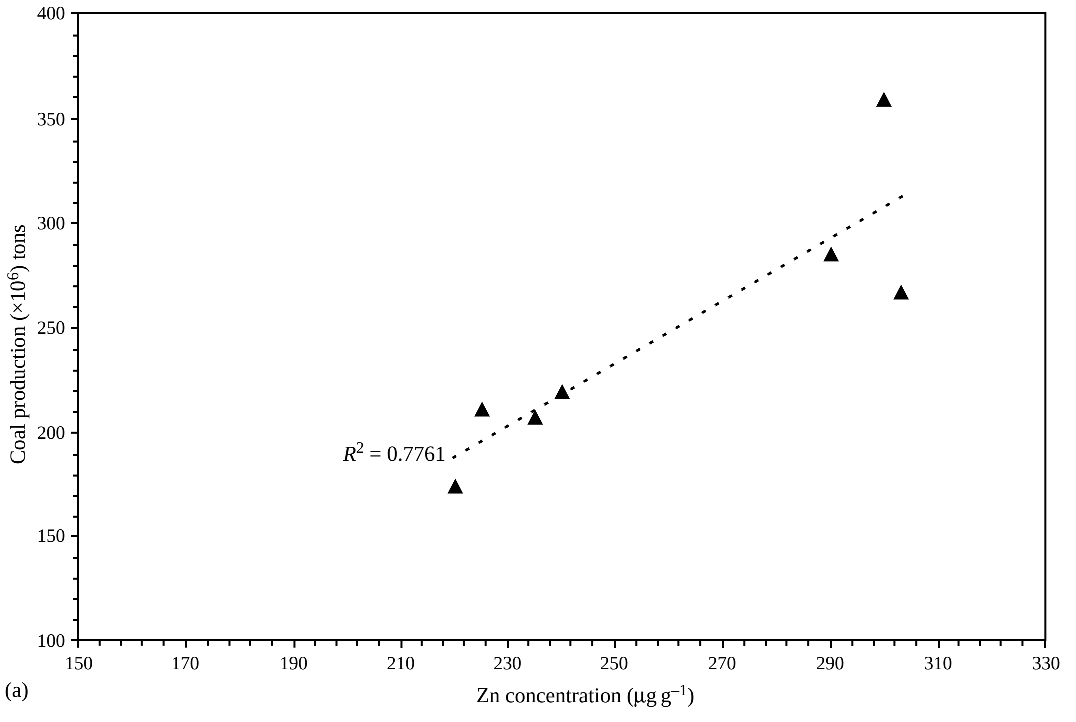
(a)



(b)

Figure 13 (a) Temporal distribution of Ti-normalized As–Pb–Zn (ppm/wt.%) in a sediment core from Mile Tree Run Reservoir, Southwestern West Virginia, USA; (b) Temporal distribution of Ti-normalized S–IRM–Fe (wt.%/wt.%) in the Mile Tree Run Reservoir sediment core.

solids exclusively by atmospheric deposition. Whereas slowly-accumulating natural lake sediments appear to be affected by chemical diagenesis, studies have shown that peat bogs provide a reliable record of changes in atmospheric metal deposition (Roos-Barraclough and Shotyk, 2003). Their radiocarbon dated core profiles of stable Pb and $^{206}Pb/^{207}Pb$ isotopic



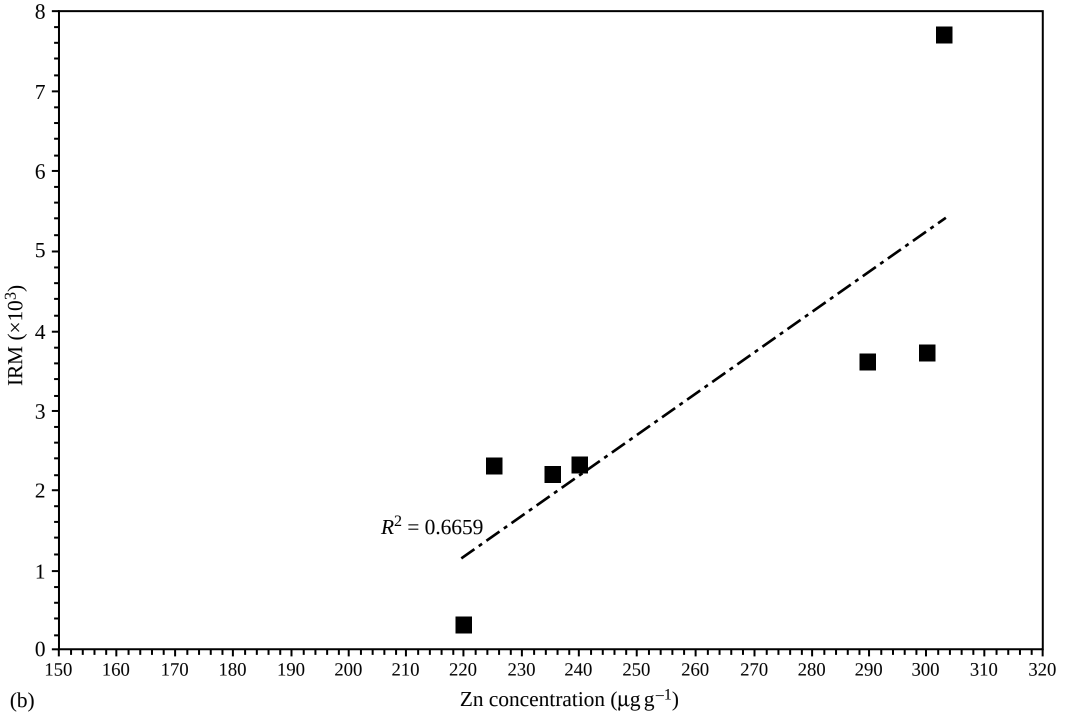


Figure 14 (a) Scatter plot of Appalachian Basin temporal coal production versus temporal concentration of Zn in a Mile Tree Run Reservoir sediment core, (b) Scatter plot of the temporal concentration of IRM (magnetite) versus the temporal concentration of Zn in the Mile Tree Run Reservoir sediment core.

ratios indicate that enhanced fluxes of Pb were caused by climatic changes between 10,500 and 8,250 years before present (BP). Soil erosion, caused by forest clearing and agricultural tillage, increased Pb deposition subsequent to this time. Beginning 3,000 yr BP, Pb pollution from mining and smelting was recorded by a significant increase in normalized Pb concentrations (Pb/Sc) and a decreasing $^{206}Pb/^{207}Pb$ ratio. Around BP 2100, Roman Pb mining became the most important source of atmospheric Pb pollution; and in AD 1830 the effects of the Industrial Revolution were recorded by a very large peak in Pb enrichment. The $^{206}Pb/^{207}Pb$ ratio declined significantly around AD 1940 indicating the use of leaded gasoline which was subsequently discontinued in AD 1979 (Shotyk *et al.*, 1998). In an earlier paper, Shotyk *et al.* (1996) noted that there were significant enrichments in As and Sb as well as for Pb dating back to Roman times (BP 2100). These enrichments in As and Sb were thought to be related to Pb mining and smelting.

In Sweden, Brannvall and his colleagues published several papers culminating in a summary paper (Brannvall *et al.*, 2001) describing four thousand years of atmospheric Pb pollution in northern Europe. They cored 31 lakes throughout Sweden; some were age-dated with radiocarbon while others had varved sediments. Their stable Pb and $^{206}Pb/^{207}Pb$ isotope data indicate that the first influx of noncatchment atmospheric Pb occurred between 3,500 and 3,000 years ago. The large world production of Pb (80,000 t yr^{-1}) during Greek and Roman times 2,000 years ago caused widespread atmospheric Pb pollution. There was a decline in the atmospheric Pb flux between AD 400 and 900. Brannvall *et al.* (2001) note that the Medieval period, rather than the Industrial Revolution, was the real beginning of the contemporary Pb pollution era. This era extended from AD 1000 to 1800. Lead peaked in the mid-twentieth century in Sweden (1950s–1970s) due to the use of leaded gasoline and fossil-fuel combustion. The recent decline in atmospheric Pb deposition since 1980 is very steep and significant. Johansson (1989) analyzed the heavy-metal content of some 54 lakes in central and northern Sweden, and noted that the Pb content of surface sediment was 50 times greater than the background concentration and that this Pb enrichment decreased substantially from south to north. Ek *et al.* (2001) studied the environmental effects of one thousand years of Cu production in Central Sweden. Metal analyses of the lake sediments showed that Cu pollution was restricted to a smaller area near the emission sources and that Pb, Zn, and Cd pollution was widespread. Sedimentary metal enrichments began about AD 1000 and peaked in the seventeenth century when Central Sweden produced two-thirds of the world's Cu supply.

Sedimentary lacustrine records of heavy metal pollution in Lough Neagh (northern Ireland) and Lake Windermere (England) suggest that there have been two periods of metal disturbance since the AD 1600. Both lakes are situated within rural catchments. In Lough Neagh (Rippey *et al.*, 1982), a change in the catchment erosion regime during the seventeenth century produced an increase in the sedimentary Cd–Cu–Pb concentrations. This change in erosion was a result of widespread and comprehensive forest clearance. A second and larger change occurred about AD 1880 when the concentrations of Cr, Cu, Zn, and Pb increased toward the sediment surface. Sediments from Lake Windermere also show a pronounced increase in Cu–Pb–Zn concentrations within the upper part of the sediment column (Hamilton-Taylor, 1979). Since the catchments are not proximal to the local anthropogenic sources such as mining, smelting, or wastewater inputs, it is possible that a substantial part of these metal enrichments are due to a more regional or even global atmospheric input that was generated by many anthropogenic processes related to the Industrial Revolution.

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