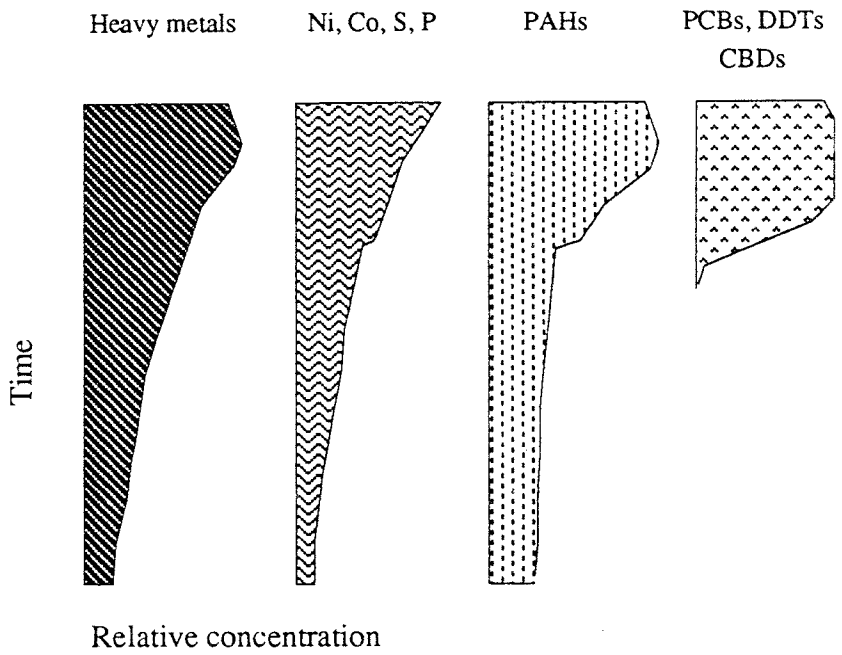
NOAA Technical Memorandum NOS/ORCA 65

National Status and Trends Program
for Marine Environmental Quality

Historical Reconstruction of Contamination Using Sediment Cores: A Review



Rockville, Maryland
March 1992

noaa National Oceanic and Atmospheric Administration

U.S.Department of Commerce
National Ocean Service

Coastal Monitoring and Bioeffects Assessment Division
Office of Ocean Resources Conservation and Assessment
National Ocean Service
National Oceanic and Atmospheric Administration
U.S. Department of Commerce
Rockville, MD

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Abstract

Historical reconstructions of contamination using cored sediments have been performed in the United States and abroad, in marine as well as freshwater environments. Most studies have dealt with trace metals, while a few reported results for organic contaminants. With some exceptions, these studies show an increase in sediment contamination during the late 1800s, followed by an acceleration in the rate of contamination in the 1940s, and a plateau or a maximum in the 1960-1970s. Little is known about the trends of coastal pollution over the last decade, as only a few studies have been carried out since 1980. From these studies, however, it appears that Pb concentrations have decreased in most areas of the world following the implementation of laws regulating the use of leaded gasoline in automobiles. On the other hand, concentrations of elements such as Cu and P have continued to rise since 1980. In a few instances, concentration of banned contaminants, such as pesticides and polychlorinated biphenyls (PCBs), have not decreased as expected, indicating that some input is still present.

Introduction

Out of the large number of chemical elements and organic compounds existing today, some are recognized as being toxic and can influence the environment in various ways. They can be directly toxic to living organisms as heavy metals or man-made organic contaminants. In these instances, the pollutant may jeopardize the development, reproduction, or even the existence of plants or animals living in the area. Pollutants can also be indirectly harmful,

as in the case of excess nutrients. In this case, large quantities of P or N in a water body favor the development of specific species of primary producers whose proliferation may be detrimental to other plant or animal species. The sources of these pollutants are numerous (fossil-fuel burning, automobile exhaust, industrial activity, sewage, etc.) and their mode of introduction into the environment is also variable (air, water). Depending on all these variables, the resulting pollution is either locally and/or globally distributed (Table 1). Because of their large adsorption capabilities, fine-grained sediments represent a good repository for these pollutants. They can serve as a record of the temporal changes in contamination, and thus can be used for historical reconstructions. For more than three decades, pollution of the aquatic environment has been intensively studied (1-19). In the late 1970s, Goldberg and several other researchers began to use cored sediments as historical records of coastal pollution (20-24). This was made possible by the development of new dating tools, and, in particular, by the application of radioactive isotopes (20, 25-44). The most commonly used isotopes are: ^{228}Th ($T_{1/2}$=1.91 years), ^{210}Pb ($T_{1/2}$=22.3 years), ^{137}Cs ($T_{1/2}$=30 years), ^{32}Si ($T_{1/2}$=276 years), ^{226}Ra ($T_{1/2}$=1620 years), ^{14}C ($T_{1/2}$=5730 years), and finally, ^{239}Pu and ^{240}Pu ($T_{1/2}$=2.4 x 10^4 and 6.6 x10^6 years, respectively).

Because of their short half-lives, the most useful tools for the study of recent sediments are ^{228}Th, ^{210}Pb, and ^{137}Cs. To ensure reliable dating, and therefore to be useful in historical reconstructions, the cored material must be undisturbed, fine-grained, and collected in an area with a relatively fast sedimentation rate. Such conditions are more likely to be found in lakes, explaining why most of the early research was done on lacustrine sediments. However, lakes are not always ideal environments for such studies. Because of their low buffering capacity, they are generally very sensitive to acidification processes, a phenomenon not reported for marine waters. Lake acidification plays a key role in the behavior of contaminants in the sedimentary column, and consequently on the preservation of the historical records of human contamination. For example, trace metals such as Pb, Zn, and Cu retained in lacustrine sediments at neutral pHs will be mobilized at low pHs and redistributed in the core, and can even pass into lake waters. In fact, solubilization does not affect all metals in an identical way, causing difficulties in interpreting the results. For example, since Zn is more soluble than Pb, more Zn can be extracted from the sediments. The release of toxic metals originally sequestered in the sediments into the lake waters will modify or obliterate the historical records and could constitute a new threat to

POLLUTANT NAME	POLLUTANT SOURCES: Car Exhaust	Smelters	Fossil Fuel uses and spills	Industrial Discharges	Agriculture	Mining	Sewage and Solid Waste	Urbanization	POLLUTANT CLASS
N	+		+	+	+++		++	+	Nutrients
P				+	+++	+	++	+	Nutrients
S	+	++	+++	+	+	+	+		Nutrients
Co			+	++			+	+	Metals
Ni			+	++			+	+	Metals
V			++	+					Metals
Cr			++	++		+	+		Metals
Cu		++	++	+++	++	++	+		Metals
Zn		++	++	+++		++	++	+	Metals
Ag		+		+++		+	+		Metals
Cd			+	+++			+		Metals
Hg			+++	+++	+	+	+		Metals
Pb	+++	+++	++	++		++	+	+	Metals
As		+	++	++	++	+	+		Metals
Sn		+	++	++		+	+	++	Metals
PAH	++	+	+++	++			+	++	Organic Compounds
PCB				+++			+	++	Organic Compounds
CBD				++	+		+		Organic Compounds
DDT				+	+++		+	++	Organic Compounds
Lindane				+	+++		+	+	Organic Compounds

AIR — WATER

TRANSPORT MEDIUM

TABLE 1: Sources and Transport Medium of the Pollutants Most Frequently Studied in the Literature. For a Given Pollutant, the Number of "+" Represents an Estimate of the Relative Importance of Each Source

aquatic life. In this case, the sedimentary layers play the role of localized, active sources of pollution. In addition, the isotopes used for dating the sedimentary strata, such as ^{210}Pb or ^{137}Cs, can also migrate under acidic conditions, rendering it impossible to establish a valid chronology.

Acidification is absent in estuarine and coastal environments, but there is a greater chance of finding sediments bioturbated (mixed by biological activity) or physically disturbed by wave or current actions. A few exceptions exist in localized deep basins, such as those in Southern California (Santa Monica, San Pedro, etc.) where anoxic conditions prevail, consequently reducing the impact of mixing. It is important to note that in deltas, and in general where the sedimentation rate is extremely high (several cm/yr), contaminants can be diluted by coarse sedimentary particles or by uncontaminated marine particles, resulting in weak or absent signs of contamination. However, in areas where fine-grained marine sediments are rapidly accumulating (~1cm/yr), the difficulties associated with mixing processes are minimal, generally giving rise to acceptable results. In addition, some metals, such as Fe or Mn, are remobilized after sediment deposition by diagenetic processes. Under specific conditions, the same processes could also affect other metals and redistribute them in the core. In order to get reliable results, then, it is essential to have excellent knowledge of the environment and of the problems specific to each studied area.

Results from the major studies performed in the United States and abroad are presented and then discussed. In most of the studies, the superposition of two levels of pollution has been observed: (1) a large-scale pollution due to contaminants transported, occasionally great distances, by air or by rivers; and (2) a more local contamination due to spatially restricted sources, generally where pollutants are discharged into water bodies (sewage, dumps, etc).

A) HISTORICAL STUDIES OF COASTAL AND ESTUARINE SEDIMENTS

I. The Coastal United States

The earliest comprehensive studies on the subject were conducted off the coast of California (20, 31, 47-66). They were performed on sediments taken from 2,000 m deep basins (Santa Monica, San Pedro, Santa Barbara, San Nicolas, Soledad Basins, etc.) located 30 km offshore. These sediments

accumulated rapidly enough (0.3 to 0.9 cm/yr) to be easily dated using varves, which are fine layers of sediments deposited yearly, and the radiotracers ^{210}Pb, ^{137}Cs, $^{239}Pu/^{240}Pu$, and $^{228}Th/^{232}Th$. These basins are characterized by anoxic or hypoxic conditions, preventing severe bioturbation and providing almost undisturbed cores. Additional work was performed in the Tia Juana River Estuary, along the Mexican border, near San Diego (56). All of these studies showed an obvious contamination of recent sediments by trace metals when compared to the background concentrations in nonpolluted areas or in sediments older than 300 to 400 years (5, 67). In particular, they demonstrated that contamination by Pb, Zn, Cr, Cd, Cu, Ag, V, and Mo from discharges in the Los Angeles area and by atmospheric deposition started in the early 1800s and rapidly accelerated in the early 1900s. Another sharp increase occurred in the 1940s (especially for Pb), with the climax of contamination appearing in the sediments deposited around 1970. The 1970 sediments are seven times more enriched in Pb than those from 1900, due mostly to atmospheric deposition. Studies of isotopic composition indicate that lead in California's coastal sediments is derived mainly from the combustion of leaded additives in gasoline. More recently, Finney and Huh (62-63) have shown that pollution levels of most trace metals in the marine sediments of that area have decreased drastically since the 1970s (about 40% for Pb and Cr), mostly due to improvement in wastewater treatment and to the decline of leaded gasoline use. However, in recent years, Ni, Co, P, and S concentrations appear to have increased in sediments from Southern California (Fig. 1) for reasons that remain unclear.

Contamination history has been studied in other places along the Pacific Coast, and, in particular, off the coast of Washington State and in Puget Sound (68-74). In this area, earlier studies focused mostly on the dating of sediments (38, 39, 69, 75-82) and on the problems related to the intense mixing processes observed in the top layers of all cores. Nittrouer *et al.* (39), and Carpenter *et al.* (43, 83) showed that, in general, about 15 cm are mixed on the Washington shelf, but that as much as 36 cm of surficial sediments can be bioturbated in some areas of Puget Sound. Nevertheless, given the fairly fast sedimentation rate in this area (about 1 cm/yr), there is good temporal resolution in the cores. In Puget Sound, the increased concentration of chemicals parallels urbanization of the Seattle-Tacoma area. In particular, contamination by heavy metals (Pb, Hg, Ag, Cu, Cd) and polynuclear aromatic hydrocarbons (PAHs) started in the 1800s, reached a maximum in the sediments deposited between 1945 and 1965, then decreased in the 1970s (84). Chlorinated butadienes (CBD), polychlorinated biphenyls

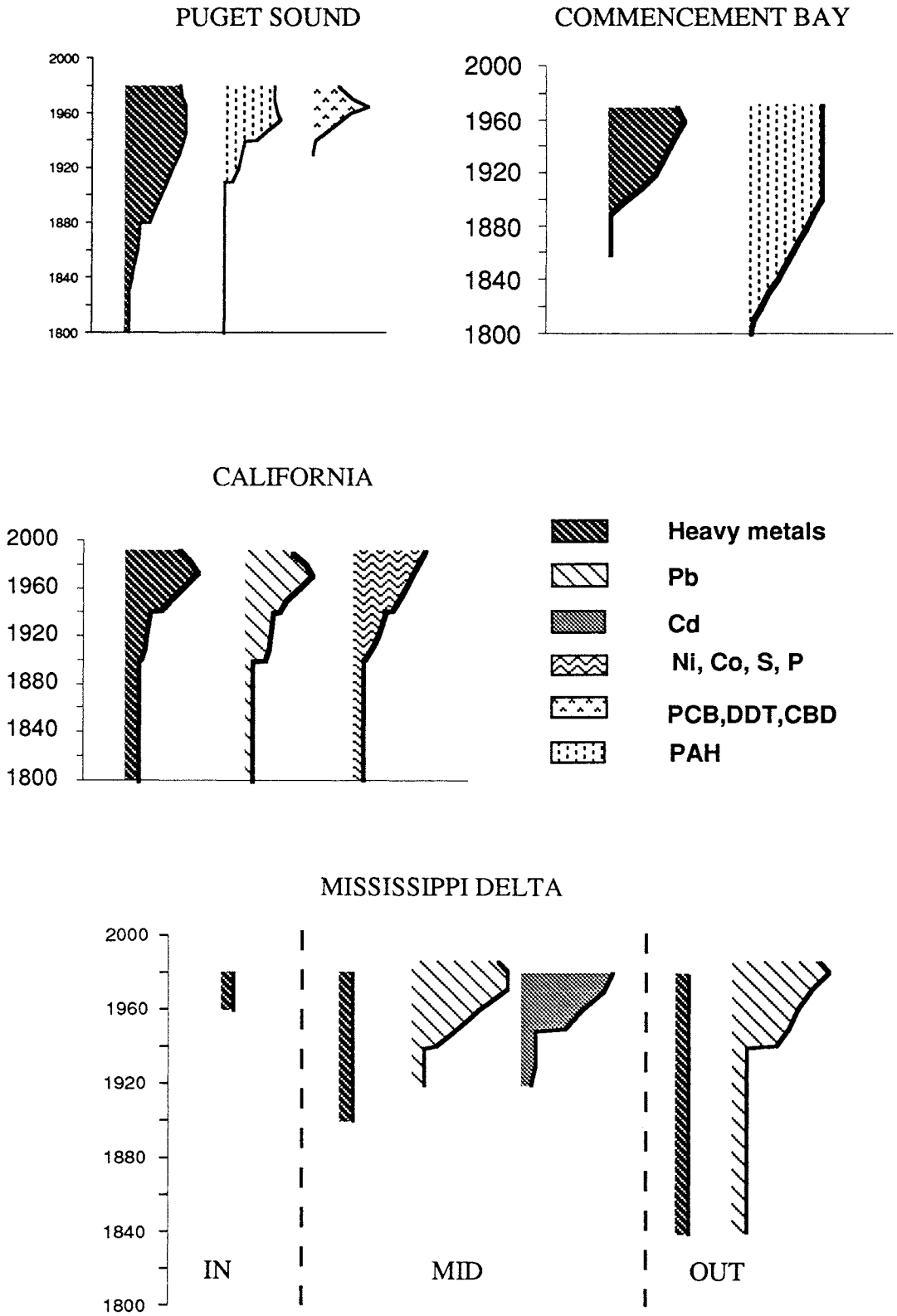

FIGURE: 1- Historical Profiles of Sediment Contamination along the West and Gulf Coasts of the United States (see page 28 for details).

(PCBs), and DDT appeared in the 1930s and reached their maximum in the late 1960s, then decreased (85). In Commencement Bay, concentrations of PAHs peaked in the sediments as early as 1900. Contamination by heavy metals (As, Ag, Hg, Pb, Sb) and CBDs appeared in the 1900s, reached its climax in the late 1960s, then decreased after the 1970s (Fig. 1).

The only historical studies using cores in the Gulf of Mexico dealt with the Mississippi River Delta (86-88) and with oil-drilling sites located in the northwestern part of the Gulf (89). In the Mississippi Delta, sediment pollution is mostly associated with long-range transportation of contaminants by the Mississippi River. The cores, taken at increasing distances from the mouth of the river, showed an accumulation rate of sediments ranging from 2 cm/yr at 6 km to 0.15 cm/yr at about 70 km, based on excess ^{210}Pb activity. Due to the very fast accumulation of large sedimentary particles in the inner portion of the delta (the area located within 2 km of the river mouth), one meter long cores sample only 15 years of material. In this case, most of the analyzed metals (Fe, Al, Cu, Zn, Ni, Co, Cr, V, Cd, Pb) have been diluted by the coarse sediments (4,13,16) and exhibit a constant profile.

In the mid-delta, an area located between 2 and 20 km from the river mouth, the concentrations of all the analyzed elements appear to be uniform for the last 75 years, except for Pb and Cd. The onset of sediment contamination occurred in 1940 for Pb and 1950 for Cd. By 1981, the concentrations in Cd had increased steadily by two orders of magnitude and give no signs of decreasing. The Pb contamination (which showed an increase of concentration of about 65%) is due, here too, largely to the use of leaded gasoline in automobiles (87). In a later paper, Trefry *et al.* (88) showed that Pb concentrations decreased after 1970, and stabilized in 1980 around a value higher than the original background. In the outer delta zone, located between 20 and 70 km from the river mouth, the concentration of all metals, with the exception of lead, remained constant over time. Increased Pb concentrations first appeared around 1840 in the outer delta, with a clear acceleration after 1940, and displayed a peak in the late 1970s before falling off in the 1980s (Fig. 1). In sites associated with oil drilling platforms, only very localized (125 m from the site) contamination of the top sediments was observed for Ba, Hg, and Zn, and more slightly for Cd, Cu, and Pb (89).

Some East Coast areas have been studied: the Savannah River Estuary (24), the Chesapeake Bay (9, 23, 45, 90-95), the Hudson-Raritan Estuary and

Long Island Sound (96-102), and Buzzards and Narragansett bays (22, 103-110). In these areas, marine sediments are contaminated by atmospheric deposition superimposed on local pollution. On the contrary, in salt marshes, the sediments receive contaminants mostly from the atmosphere, reflecting the general atmospheric pollution along the East Coast (95-96).

In the Savannah River Estuary (24), the chronologies were established using ^{210}Pb and ^{239}Pu-^{240}Pu, and the sedimentation rate has been shown to range between 0.3 and 2 cm/yr. In the Wilmington River, the concentrations of three metals (Pb, Cr, V) increased in the late 1960s, while the release of plutonium from the Savannah River Nuclear Plant is evident only in a core taken in the Savannah River in 1976, 18 km upstream from the mouth. In the estuary itself, a lower concentration of the metals results from their dilution by entry of oceanic solid particles and no clear temporal trend was observed (Fig. 2).

In Chesapeake Bay (23), the chronologies of the cored sediments were also derived from ^{210}Pb and $^{239}Pu/^{240}Pu$ activities. The sedimentation rates are high, ranging from 1 to 8 cm/yr, and the mixed layer can reach a thickness of 30 cm due to active bioturbation. Cores collected in the northern part of the Bay, near the mouth of the Susquehanna River, show very high concentrations of heavy metals but no variation over time. Due to the fast accumulation rate (8 cm/yr), the northern cores were too short to reach the sediments with no anthropogenic influence. In contrast, in the cores located further south, although the absolute concentrations in heavy metals are generally lower than for the northern cores, there is an increase of contamination over time. In particular, Pb, Zn, and Cu increase with time in the sediments cored near the Choptank River, and Pb, Zn, and Ni increase with time for the core sampled near the Rappahannock River. These data illustrate the increased input of metals to the Bay sediments in the past 35 years due to human activity, but no time evolution was provided. The various elements appear to have different origins (9): Mn, Fe, Co, Ni, and Zn come generally from river discharge, shore erosion, and salt-water advection from the ocean in addition to human activity; Cr and Cu originate from direct industrial discharge; Cd from waste waters; and Pb mostly from atmospheric dust and rain (Fig.2).

Using radioactive dating of cored sediments, the average deposition rate in Long Island Sound (42, 96, 97, 114) has been estimated to be 0.45 cm/yr. The concentrations of Pb, Zn, Cu, and Cd show a pulse of high values around 1830,

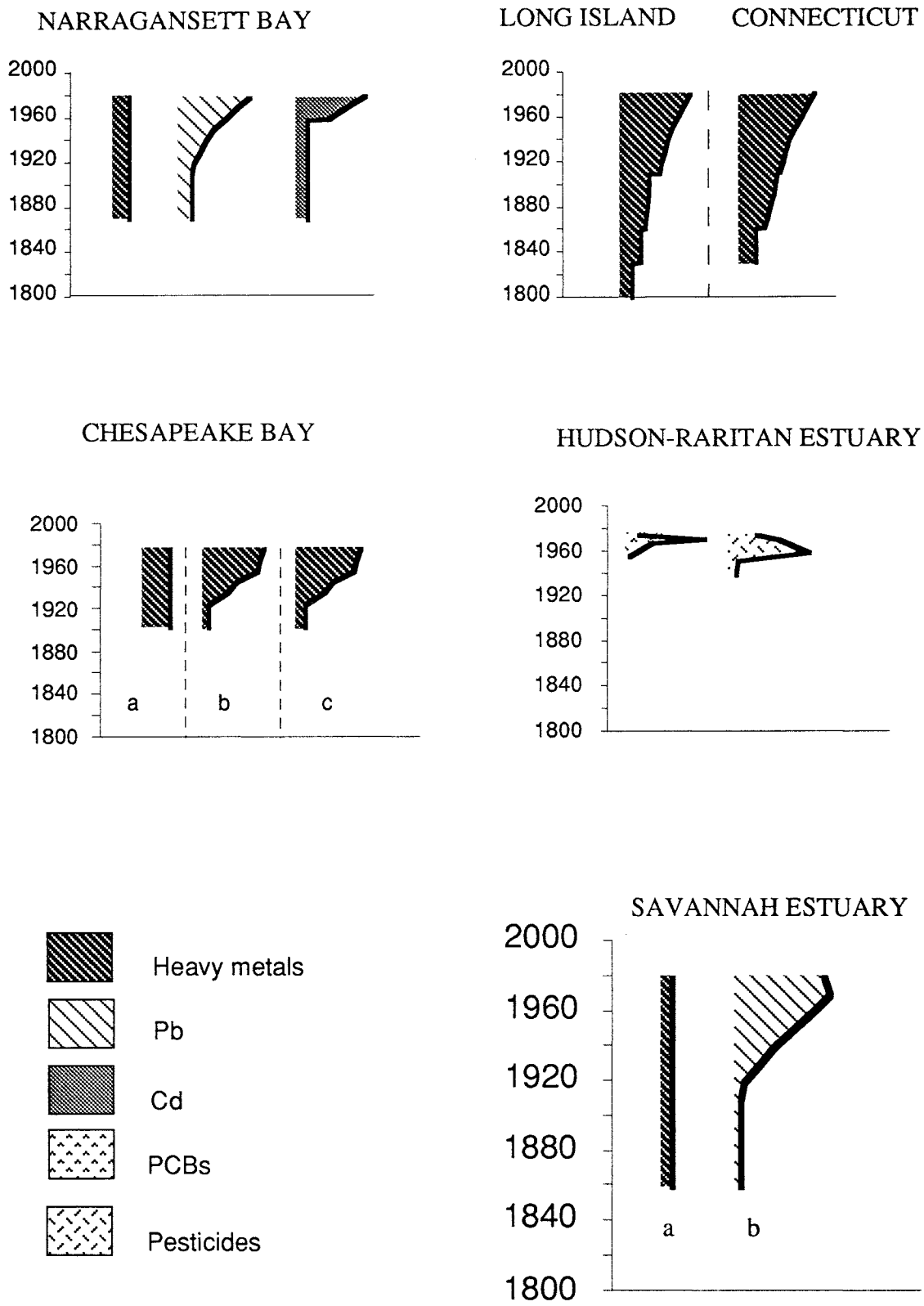

FIGURE : 2- Historical Profiles of Sediment Contamination along the East Coast of the United States (see pages 28-29 for details).

a slow increase after 1865, followed by a sharp increase after 1910. The concentration of these metals in the top sediments do not show any decrease since about 1965. Studies performed in the Hudson-Raritan Estuary (99,100) show that severe PCB pollution of the marine sediments occurred after 1956, followed by a large increase, leading to a peak in 1970. After this date and until 1980, the authors describe a strong decrease in PCB concentrations (Fig. 2). It is important to note that studies performed in marine sediments collected in selected locations of the Hudson Raritan Estuary give excellent results, while in Long Island Sound, the top mixed layer is very thick (at least 15 cm) and the sedimentation rate very low, rendering the marine cores inadequate for establishing a chronology of the contamination. These marine cores can only be used for estimating the total inventory of pollutants. In Long Island Sound, chronological information can only be retrieved from the salt marshes and only for atmospherically transported contaminants. In this special environment, the dense roots of aquatic vegetation preserve the deposits from post-depositional disturbance.

In Buzzards and Narragansett bays (22,108,109), Mn, Fe, Al, Ni, V, Co, and Ag do not show any variation in their concentration with the depth of the core, whereas Pb, Zn, Cu, Cd, and Cr concentrations are higher in recent strata compared to those deposited several decades ago. In Narragansett Bay (22), Goldberg *et al.* calculated a sedimentation rate of about 0.17 cm/yr using ^{210}Pb and Pu isotopes as well as natural markers, such as the shell layer deposited during a 1954 hurricane. They observed the onset of Pb, Zn, Cu, and Cr contamination in the 1920s, with severe Cd pollution appearing in the 1960s. No obvious surficial decrease of heavy metal concentration was reported in this 1977 paper (Fig. 2).

Cores from salt marshes of the Atlantic Ocean (111-113, 115), in particular those collected in Connecticut, show increasing concentrations of Cu, Zn, and Pb since 1860. These profiles mostly reflect atmospheric contamination related to the industrialization of New Haven, and more widely, to the eastern United States (Fig.2).

II. Other Coastal Areas

Aside from the United States, very few studies have been performed in North America. Along the Pacific Coast of Canada (116-118), the analysis of

sediments cored in British Columbia in the Saanich Inlet (116) shows that Pb, Cu, and Hg concentrations have increased steadily since the early 1900s, reaching a maximum in the 1970s. Along the Atlantic Coast, a study of the Saguenay Fjord of Quebec revealed Hg and PAH pollution of the fjord sediments (118, 119). The increase in Hg started in 1948, spread seaward, and reached a maximum between the 1960s and the 1970s. This corresponds to the construction in 1947-1948 of a chlor-alkali plant in nearby Arvida. The decrease in liquid effluent released from the plant in 1970-71 resulted in a decrease of Hg concentrations in the sediments (118). PAH contamination in the sediments of the same area is related to the development of the aluminum industry. The PAH concentrations increased gradually from preindustrial times until 1926, followed by a dramatic increase in the 1940s. Until 1964, most of the pollution came through atmospheric transport, whereas between 1964 and 1976, there was an additional discharge directly from the scrubbers of the aluminum plants.

Most of the other studies conducted abroad were done in northern and western Europe (15, 41, 120-130). In England (122-124), the increase in sediment pollution observed in the 1850s in the Severn and in the Tamar Estuaries is mostly due to local sources: mining of Cu, Pb, As, Sn, Mn, and Zn ores along the Tamar Estuary, and coal mining associated with heavy industrialization and manufacturing around the Bristol Channel. The decline of these activities after 1948 was reflected in the sediment contamination. Sediments from the Hayle Estuary (128-129), located in a historical mining area of Cornwall, show exceptionally high concentrations of Sn, As, Cu, Pb, W, and Zn. In this study, the distribution of these heavy metals in the estuary is correlated with the pollution from past mining activities (through mine waste discharge into streams) that reached a maximum in 1869, but is also associated with changes that took place during the development of the urban area of Upton Towans (188).

Samples taken in Norway from an oxic basin in Ranafjord show that sediments deposited after 1890 are enriched in Pb, Zn, and Cu due to local mining activities. Maximum contamination by Pb and Zn occurs in the sediments deposited around 1970 (120). The presence of high concentrations of As, Hg, and Fe in the surficial strata are related to the discharge of local industries (discharges from a coke plant and iron works, and coal particles or ore dust introduced locally), in addition to the distant atmospheric transport of pollutants generated throughout all of northern Europe (e.g., Hg associated with coal burning).

In the Baltic Sea (126-130), heavy metal contamination began after 1880 (Hg, Cd, and Zn in the Gulf of Finland and Hg in the Bothnian Sea) following the industrial revolution of northern Europe. Man-made organic contaminants appeared later in the marine sediments: PCBs after 1940, DDT after 1945, and lindane and plasticizers (DEHP) after 1950. Concentrations of the nutrients P and N also increased rapidly in the sediments after 1965, demonstrating the rapid eutrophication of the Baltic Sea associated with the heavy use of fertilizers and detergents in the surrounding countries.

In southern Europe, a few studies have been done in Italy (125) and in France (149-150). Near Venice (Italy), the increase in Pb, Zn, and Cu in surficial sediments is due to anthropogenic activities and to sewage discharges. Along the French coast of the Mediterranean Sea, Hg and other heavy metal contamination observed in marine sediments since the beginning of the industrial revolution was transported by the Rhone River from central Europe. A peak in Hg pollution was reached around 1973 (149). In addition, more local sources of pollution are present. For example, in the Baie des Anges, near Nice, contamination of the sediments by heavy metals (Pb, Zn, Cu, Hg and Cd) due to urban sewage and industrial discharge appeared after 1900, and increased significantly during the 1950s (150).

In Asia, Hoshika and Shiozawa (131) have studied the Beppu Bay in Japan (Kyushu Island). They observed in the center of the bay a steady increase of Zn and Cu in the sediments from 1910-1920 to the present, due to local industrial discharge. In a station closer to shore, Zn and Cu concentrations increased after 1920, reached their maximum in the 1970s, and then experienced a slight decrease in the 1980s related to the control of contaminant discharge. In China, sediments from the Jin Zhou Bay, on the Yellow Sea (132), show very serious contamination in Pb, Zn, Cu and Cd. The low concentration of these metals before 1850 corresponds to the natural background of the area. Between 1850 and 1942, a moderate increase is evident due to human activity (domestic sewage and agricultural runoff) which becomes considerably higher after the opening, in 1941, of a Zn plant. The industrial contamination reached its peak around 1975, and generally persisted into the 1980s.

B) HISTORICAL STUDIES OF FRESH-WATER SEDIMENTS

I. United States Fresh-Waters

There is a wealth of literature available on core sediments collected in lakes and ponds (57,133-161) as compared to marine systems (57), as there is a greater likelihood of retrieving undisturbed cores of fine grained sediments deposited under anoxic conditions. However, as noted, they are more susceptible to acidification than marine environments (133-143), and the data obtained in these cases, if they are useful, must be used with caution.

In the northeastern part of the United States, lake acidification is related to acid rain, a consequence of severe atmospheric contamination by fossil-fuel burning. In order to reconstruct the evolution of pH levels in lakes, a technique based on the change in diatom species as a function of decreasing pH (134) is used. It was first successfully applied in Sweden (135) and Norway (136). Applied to northeastern U.S. lakes, this technique showed that in weakly buffered lakes, a rapid decrease in pH has occurred since the 1920s. For example, such a decline has been documented between 1930 and 1970 in New York State, and between 1920 and 1950 in New England. In Wisconsin and Rocky Mountains lakes where the pH was originally low owing to the nature of the regional bedrock, no drastic change in pH was observed.

In lakes and ponds from the eastern part of the United States and Canada (Maine, New Hampshire, New York, and Quebec), atmospheric deposition of Pb, Zn, and sometimes Cu and Hg, is observed in sediments as early as 1850-1860 (Fig.3). For Pb, the noticeable increase in concentration observed in the 1940s is due to the use of leaded gasoline. After 1960, Zn and Hg started to decrease in the lacustrine sediments, not as a result of reduced input, but because acid rain lowered the pH of the lakes, releasing the metals from the sediments into the water (110,112-114). For the organic contaminants, a study of PCB and HCB content in peat cores collected in bogs from the U.S. Northeast (120) showed that the 1930 onset of PCBs in the peat profiles coincides with the date of the beginning of PCB production. The maximum levels of concentrations in the sediments (25 ng/g), followed by their decrease, coincides with the 1967-1970 peak in PCB production and with the 1971 voluntary ban of their use. Since 1979, all new uses of PCBs have been banned, but very high concentrations of PCBs are still present in the surficial sediments of many lakes (Minnesota, Ontario,

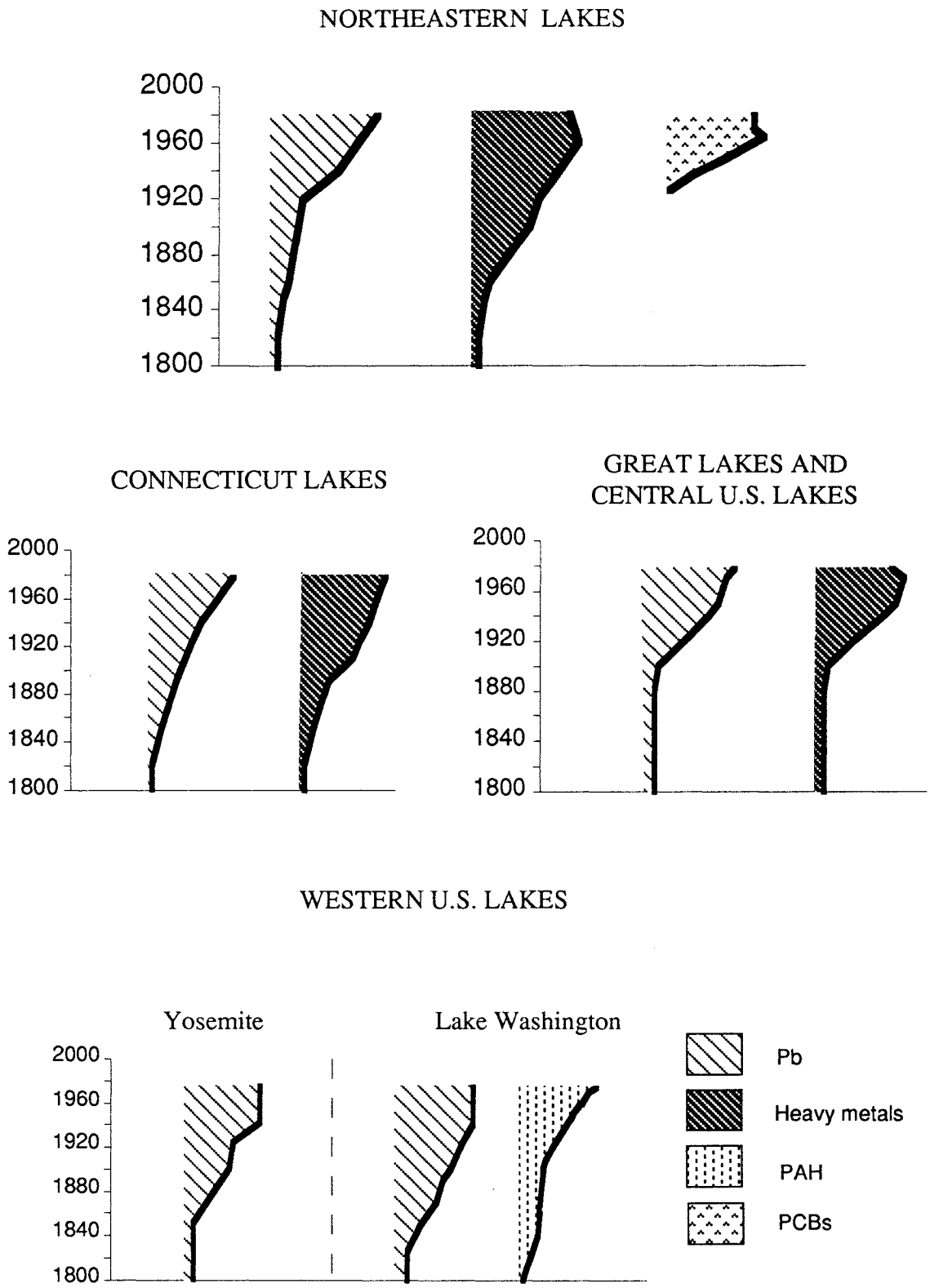

FIGURE : 3 - Historical Profiles of Sediment Contamination in North American Lakes (see page 28-29 for details).

Quebec, and Nova Scotia). This is due to underwater reworking of previously contaminated sediments and/or to contamination by present-day PCB use. Numerous studies were also performed in the Great Lakes area. Pb, Zn, and Cu concentrations began to increase around 1850 in Great Lakes sediments (Lakes Superior, Erie, Huron, and Michigan) due to the increase in atmospheric pollution (109,118). A sharp Pb increase associated with the use of leaded gas in cars, occurred during the period 1920-1940. In the case of Lake Erie, a small decrease in Zn and Cu concentrations in the sediments of the late 1970s (Fig. 3) may be related to the decrease of industrial emissions, but also to the acidification of rain, which tends to keep Zn and Cu in solution but has less influence on the less soluble Pb (100,101,105,108,109,119).

All these studies emphasize the role of a global source of contamination. In other areas, local pollution is superimposed on this global input. Near New Haven, CT, Pb, Zn, and Cu found in ponds are directly related to fossil fuel burning, but the strong increase in concentrations of Pb, Ag, Cd, Cu, Ni, Zn, and V while the town of New Haven grew after 1910 shows that a more complex source of pollution exists, including sewage, industrial discharge, and domestic and industrial fossil fuel-burning (102). In lakes from the western part of the United States (57,103,106,107,117), Pb and PAH contamination are related to the influence of smelting and car emissions. They can be traced as early as 1923 in Lake Washington, near Seattle, WA, and 1940 in Thompson Canyon, near Yosemite Park, CA. In addition, PAH concentrations due to washout of street dust and asphalt particles (106-107) appear in the sediments of Lake Washington around 1840, and reach their maximum around 1975 (Fig.3).

In lakes located in the central United States, local sources are prevalent. For example, in Clearwater Lake, MO, contamination of the sediments by mining activities begun in 1967 is predominant, whereas in Standley Lake, CO, the pollution comes mostly from river discharge. The contamination level in the lake decreased in the late 1970s — the same time that pollution levels decreased in the local stream system.

II. Other Freshwater Environments

Besides the United States and Canada in North America, numerous studies have been performed on freshwater systems in Europe, but only one in

Asia. In these studies, again, various modes of contamination have been recognized.

In England, a country that has a long coal-burning history, the acidification of the lakes began in the mid-1800s. In Sweden and Finland, which are primarily influenced by emissions from Central and Eastern Europe, the acidification of lakes began between 1890 and 1930. On the other hand, acidification of lakes in Norway, which is primarily influenced by emissions from Western Europe and the United Kingdom, began after 1945. In the rest of Northern Europe (Germany, Austria, The Netherlands, Belgium, and Denmark), lake acidification began 30 to 50 years ago. The analysis of European soils (140-142), in particular semirural soils collected in southeastern England, displays a fourfold concentration increase in PAHs since 1880-1890, with even greater increases for some specific compounds. This is caused by fallout and direct accumulation of atmospheric PAHs derived from the combustion of fossil fuels in urban and industrialized areas (142). This also represents an estimate of the global atmospheric pollution present in many industrialized countries.

In Japan, Goldberg *et al.* (21) studied the moat sediments at the Imperial Palace in Tokyo, and detected the presence of strong enrichment in Zn, Cu, Cr, and Ag in the sediments deposited around 1945, in association with a wartime economy. A decrease in the concentrations of these metals is observed until 1955 (peacetime industry), followed by another increase and peak in 1975. Pb and Cd increase monotonically from 1945 to 1970, due to the widespread use of lead in gasoline and to the industrial release of Cd. This trend was reversed between 1970 and 1975 due to tighter controls on the use and release of pollutants. Co and Ni display a smaller but constant increase from 1945 to 1975.

Finally, snow strata from the North and South Poles are also affected by atmospheric deposition of pollutants and display an increase in Pb over time. In North Pole ice sheets, Pb concentrations increase from less than 0.001 μg Pb/kg ice around 800 B.C. to more than 0.200 μg Pb/kg ice in 1969, with a very sharp rise occurring after 1940. The levels of Pb in South Pole ice sheets are generally below the detection limits before 1940 and rise to about 0.020 μg Pb/kg ice after 1940. The increase of Pb with time in the arctic snows is ascribed mainly to lead smelteries before 1940 and to burned lead alkyls after 1940. There is a partial atmospheric barrier between the tropospheres of the Northern and Southern

Hemispheres, which hinders the migration of aerosol pollutants from the Northern Hemisphere to Antarctica (151).

In most of the other European freshwater studies, global and local sources are mixed. For example, studies of sediment contamination in ponds and lakes in Belgium, Switzerland, and Norway all show noticeable pollution of the sediments starting around 1850 for Pb, Zn, Cd (due to industrialization and subsequent atmospheric pollution), for PAHs (due to urban runoff of street dust), and later for As (related to agricultural uses of As-rich pesticides and fungicides). Pb, Cu, and As concentrations reached their maximum in 1950 (124,125), PAHs in the 1940s, and Cd and Zn in the 1970s. In the 1980s, a decrease in Cd and As was observed (106,107,111,115,126).

Historical changes in the enrichment of fluvial deposits with heavy metals have been studied in northern Europe (143,144). In particular, the study of the Meuse River shows that enrichment of the sediments with Pb, Zn, and Cd started more than 300 years ago, and reached its climax in the middle of the 19th century. This period represents the heyday of mining and related industrial activities in the catchment of the Meuse River (145). In the Rhine River, a study by Salomons and De Groot (146) shows that Pb, Zn, Cu, Cr, Cd, As, Ni, Hg, and P concentrations in the river sediments stay close to a baseline level until 1920. Between 1920 and 1958, all trace-element concentrations increased. From 1958 to 1975, Ni, Cd, P, and Cr concentrations continued to increase, while As, Pb, Zn, and Hg concentrations decreased, and Cu concentrations leveled off. The decline in As after 1958 is striking and is probably caused by the ban on arsenic-containing pesticides. The anthropogenic contribution to the total metal concentrations in sediments from the Rhine River exceeds the background by an order of magnitude. For example, it can be estimated that less than 1% of the Cd found in the Rhine sediments originated from natural sources. Numerous heavy metals display historical increases in the sediments collected in the Rhine, whereas only a few increases are observable in the coastal sediments sampled along the Belgian, Dutch, and German coasts (147). Except for Pb, Cu, Cd, Cr, and Ni, the concentrations of all the metals remain very close to the natural background level. Cr and Ni show only a slight increase in their concentrations around 1970, whereas the increases for Pb, Cu, and Cd were more obvious. Mercury pollution in the Rhone River reached a maximum in 1972, showed a decrease and a stabilization between 1975-1977, and displayed a second maximum in 1980, the year in which the papers were written (132,148).

WORLD SYNTHESIS

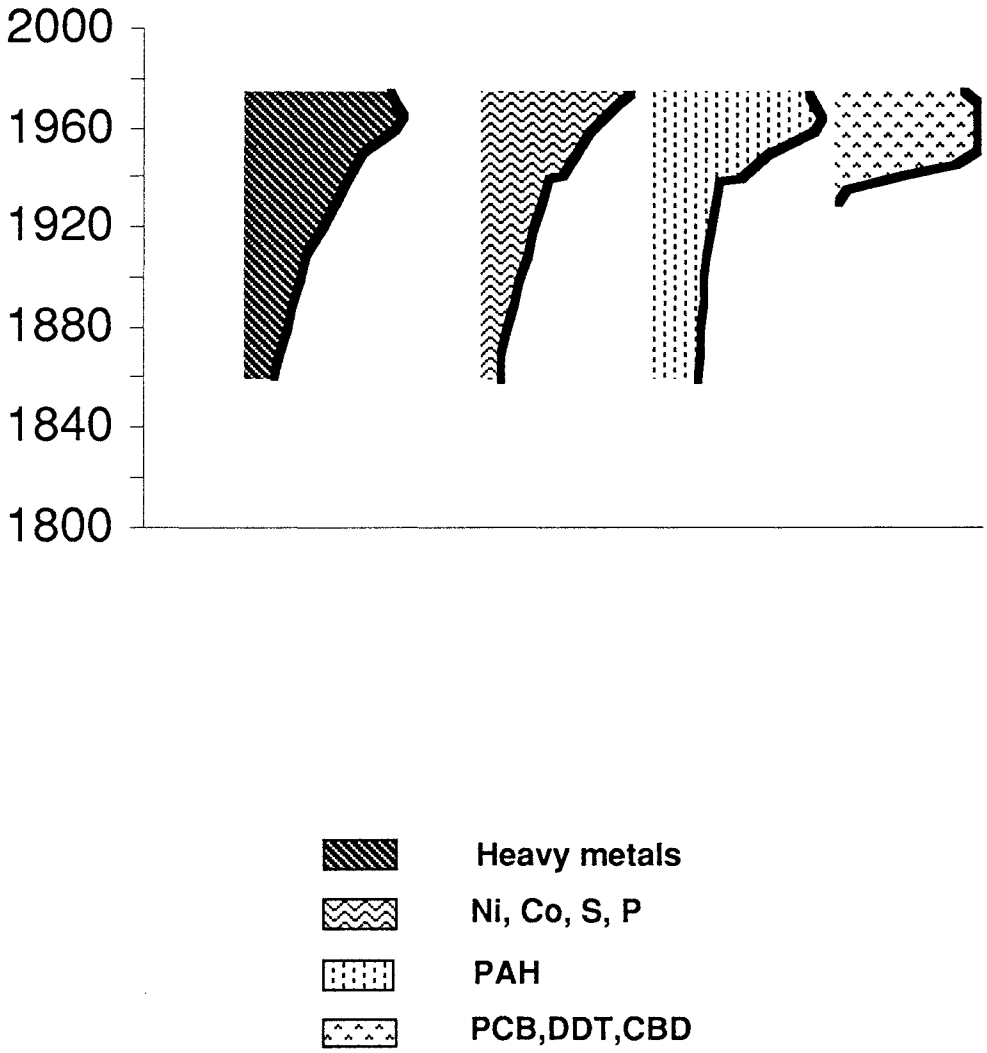

FIGURE: 4 - Historical Profiles of Sediment Contamination, World Synthesis (see page 28 for details).

DISCUSSION AND CONCLUSION

From the large amount of data gathered over the years and published through 1990, general trends in sediment contamination are emerging. For the United States, they are illustrated in Figures 1 and 2 (pgs. 10 and 13) for marine samples and in Figure 3 (pg. 18) for cores collected in ponds and lakes. A world synthesis is given in Figure 4 (pg. 22). The results obtained for trace metals will be discussed first, the organic compounds second, and the nutrients last.

Trace-metal contamination in sediments has received more attention than has sedimentary contamination by either organic compounds or nutrients. In general, heavy-metal pollution of sediments was apparant in the United States as early as the 1800s, became more prominent in the early 1900s, and showed a very sharp increase between 1940 and 1970. In Europe, settlement and human activities began much earlier than 1850, and many pollutants are associated with general population growth and the attendant industrial activity. Nevertheless, as in the United States, the influence of the late 1800's industrial revolution is well marked. Basically, there are two sources of heavy-metal inputs to biological systems: natural geological weathering and human contamination (industrial processing of ores and metals, use of metals and metal compounds, metals in human and animal excretion, leaching of metals from garbage and solid-waste dumps, etc.). Some heavy metals are always present in contaminated sediments: Pb, related to smelting activities and the use of lead additives in gasoline; Cd, which very often appears to be related to industrial effluents, sewage and waste waters; and Zn and Cu, which are mostly associated with industrial discharges. The dominant input of these trace metals to the environment (Table 1) can occur via the atmosphere (e.g., Pb) or via river waters (e.g., Cd).

From all of the studies, Pb appears to be the most ubiquitous metal contaminant being emitted into the atmosphere of the Northern Hemisphere. Pb contamination first appeared in the atmosphere as early as 4,500 years ago, when Romans began their smelting operations. All over the world, the beginning of the industrial revolution is marked first by an increase in Pb concentrations in all of the sediments deposited around 1850-1890 (57,103,106,107,117). This was followed, much later, by a sharp increase that reached a maximum or plateaued around 1978. In Europe, the first strong increase in Pb concentration occurred generally later (1945) than in North America (1920), due to the later

adoption of tetraethyl lead gasoline there. The fact that Pb contamination has been found in very remote areas and even in antarctic ice cores, where no direct pollution occurred, shows that Pb is mainly transported and deposited from the atmosphere and has become a global problem. However, following restrictions on its use in gasoline, an important decrease in its concentration is observed in North American sediments deposited after the late 1970s. Implementation of the same restrictions are starting in Europe (e.g., France in 1991), giving a basis for hope that global Pb pollution can be controlled in the near future. From the few recent studies conducted in the late 1980s, it is obvious that the present level of contamination remains, in general, higher than it was in pre-cultural times, showing that recuperation is far from complete.

Other metals, such as Hg, Zn, and Cu can be emitted into the atmosphere by the activity of smelters, coal-fired power plants, and city traffic, and, like Pb, can be transported over long distances. In these cases, more than 50% of the metal found in the local sediments can be of atmospheric origin and percentages as high as 99% for Pb, 93% for Hg, 68% for Zn, and 56% for Cu are frequent. Locally, other metals, such as As, Ni, and Co, can also occasionally come from smelter activities, but Zn, Cu, As, Hg, Cr, and Cd are associated in most cases with industrial effluents, including those from electroplating or tanning industries, chemical and chlorine-alkali plants, and others. In addition, As, Hg, and Cu are frequently found in freshwater environments where they are used as pesticides and algicides. Since about 1975, As has been banned from pesticides in Europe as well as in North America, resulting in a decline in sediment concentrations. In the case of Cd, local high concentrations can occur in sediments (up to 50,000 ppm Cd in Foundry Cove, NY, near a battery factory), but large releases of this metal are also associated with mining activities (mostly Pb-Zn ores), sewage, and fossil-fuel burning (wood, lignite, coal, and oil). This last process is mainly responsible for the emission and the wide dissemination of large quantities of pollutants in the atmosphere, including heavy and trace metals, but also organic compounds such as PAHs some of which are known carcinogens. A serious contamination problem in the world's lakes, rivers, and coastal waters is associated with Hg released by industrial plants (chlor-alkali industries, cellulose industry, paint production, battery manufacturing, and amalgamation of gold and silver), and especially by the smelting of Pb-Zn-Cu ores and the burning of fossil fuel, which release the metal into the atmosphere.

Among the organic contaminants, attention has been focused on PAHs and on man-made compounds. While nonnegligible quantities of PAHs can be found in sediments from prehuman times due to forest fires, higher concentrations appeared only a few decades ago. Most of the pollution by organic compounds started around 1940, owing to the development of new technologies, and the use of these compounds has displayed a recent, but extremely fast, growth. It is interesting to point out that as soon as a compound is manufactured, its concentration in the local sediments increases rapidly. On the other hand, after termination of its use or discharge, several years can elapse before a decrease is observed in the sediment concentrations. Due to resuspension, and physical and biological mixing, contaminated sediments previously deposited can represent a large reservoir of polluted material. Compared to the natural background, concentrations of PAHs in present-day sediments show an enrichment factor often greater than 40. PAHs are found not only in urban areas, but also in rural and remote areas due to their atmospheric transport. Along the U.S. coast, increased concentrations of PAHs are found in marine sediments from as early as the 1800s, with their concentrations increasing rapidely and steadily from the early 1900s to the 1970s. In the Great Lakes and in the northeastern part of the North American continent, fossil-fuel combustion is giving rise to acid deposition responsible for the acidification of numerous freshwater systems. In addition to fossil-fuel combustion, PAHs are also associated with urban runoff from asphalted roads and grounds which explains why a recent decrease can be observed in some areas with stricter emission controls, but not in areas where paving and asphalting is still active.

PCBs appeared in the late 1930s, reached their maximum in the late 1960s through the early 1970s, but generally show a slight decrease in recent years. PCBs were used abundantly in the early 1970s in industrial transformers and capacitors, hydraulic fluids, lubricants, small capacitors, plasticizers, dyes, adhesives, copy papers, etc. In the U.S., their use was restricted in 1971 to closed electrical systems. Finally, in 1977, there was a ban on their production and adoption of very strict regulations governing their disposal. Since then, a slow decrease has been observed in sediments.

The use of most pesticides (DDT, Chlordane, CBD, Mirex, etc) is also fairly recent, and their maximum concentration in sediments was reached between the late 1950s and the mid-1970s. Later, even after their use was restricted or banned in the U.S. (e.g. DDT), a general decrease has not always been observed

in the sediments. In order to better eradicate pests, agricultural pesticides are generally dispersed over very large areas (e.g., spraying of chemicals), and even after the direct source has ceased, the compound and its metabolites linger. This is due, in part, to the fact that the treated area retains the contaminant on soil particle and plays the role of reservoir of contamination (agricultural runoff or atmospheric transport by dust particles and aerosols). In addition, sediments previously deposited can themselves become a source of contamination due to resuspension and mixing processes. Finally, all countries did not ban the use of these pesticides. For example, DDT is banned in the United States but not in Mexico, resulting in the presence of the insecticide in some Southern California and Florida sediments.

Finally, nutrients appear to be fairly important in the modification of our environment. Eutrophication of lakes due to land deforestation and subsequent agricultural development as well as sewage inputs that bring N, P, and organic C to aquatic bodies is well studied and shows a rapid increase in recent years. Signs of eutrophication are also present in estuaries as well as in coastal marine waters. For example, in Chesapeake Bay, eutrophication appears to be a major and persistent problem. The increase in P is mostly related to the wide use of fertilizers in agriculture and to the addition of phosphates to laundry detergents. This enrichment in P of coastal sediments and waters may be an important factor in the evolution of our coastal marine system towards a eutrophic state, with subsequent prevalence of anoxia and substantial fish kills.

On a global scale, similar trends in contamination are noticeable all around the world (Fig. 4). Heavy metal and PAH pollution of the environment increased drastically during the last decades of the past century (155) and reached a maximum around 1965-1970. Most of these contaminants come primarily from the combustion of fossil fuels, essentially coal and lignite in the early years, followed by contaminants related to petroleum burning after World War II. Chlorinated hydrocarbons (pesticides, DDT, PCBs) first occurred in sediments deposited between 1935-1940, reaching their maximum in the period 1950-1970. Although their use has been restricted or banned in most countries, a decrease in the surficial sediments is not always observed (Fig. 4).

From this review, it appears that in most cases sediments can provide good records of human activity and can be used in historical reconstructions of trends in pollution. Most of the studies of sediment contamination were

conducted in the 1970s. Very few publications provide information on the status of the environment after implementation of the restrictions or bans imposed on certain pollutants in the late 1970s. It is therefore indispensable to obtain new data that will reveal the present status of sediment contamination around the world. In addition, organic contaminants were rarely studied in the past, and future research should emphasize them. Several problems can, however, pose a serious threat to the interpretation of the data obtained from cored sediments, the most important dealing with obtaining a reliable age for the analyzed strata.

Knowledge of the concentrations of pollutants in sediments is an important source of information used to reconstruct man's impingement on his environment. However, the real question is how the contamination presently observed in marine and freshwater sediments affects plant, animal, and human life. From the very scarce data on this subject, it appears that it is not the total concentration of pollutant present in the sediment that is important, but instead, the fraction that is readily available to the biota that is known as the bioavailable fraction. This aspect of the problem is certainly difficult to assess, but without serious efforts in this direction, no real progress can be made toward understanding the effects of various contaminants, and, finally, controlling pollution on our planet.

ACKNOWLEDGMENTS

I want to thank my NOAA colleagues for reviewing this report. Their comments were extremely useful. I am very grateful to Glen Gordon for his help in improving this paper. Special thanks are due to Bernard Gottholm and Charles Parker for their help with computer programs, and to Kevin McMahon, who patiently edited several iterations of the manuscript. In addition, I want to thank everyone who edited, reviewed, and contributed in any way to this report.

Figure Explanation

The figures are intended to portray historical profiles of sediment contamination. The vertical axis in all plots is the date in years and the horizontal axis is the relative concentration of contaminant. Chemicals with identical profiles are not repeated. For example, in Fig. 1, the "Heavy metals" profile of Puget Sound is a profile equally applicable to Pb, Cu, Cd, Ag, or Hg. The trace metals are included under the symbol of "Heavy metals"; however, they are not always the same from one geographical area to the other. They need to be defined in each case:

Figure 1-Puget Sound: Pb, Cu, Cd, Ag, Hg.

-Commencement Bay: Pb, Ag, Hg, As, Sb.

-California: Zn, Cu, Cd, Cr, Ag, V, Mo.

-Mississippi Delta:1)In (Inner part of the delta, < 2 km from the River): Pb, Zn, Cu, Cd, Cr, Ni, V, Al, Fe.

2)Mid (Middle part of the delta, 2 to 20 km from the River): Zn, Cu, Cr, Ni, V, Al, Fe.

3)Out (Outer part of the delta, >20 km from the River): Zn, Cu, Cd, Cr, Ni, V, Al, Fe

Figure 2-Narragansett Bay: Ag, Ni, Co, V, Al, Fe, Mn.

-Connecticut (salt marshes along the coast of Connecticut): Pb, Zn, Cu.

-Long Island Sound: Pb, Zn, Cu, Cd.

-Chesapeake Bay a)=Susquehanna (river mouth): Pb, Zn, Cu, Cd, Cr, Ni, Co, Fe, Mn.

b)=Choptank (river mouth): Pb, Zn, Cu.

c)=Rappahannock (river mouth): Pb, Zn, Ni.

-Savannah a)= estuary: no specification.

b)= Wilmington River: Pb, Cr, V.

Figure 3-Northeastern U.S. Lakes: Zn, Cu, Hg.

-Connecticut lakes: Ag, Cd, Ni, V.

-Great Lakes and central U.S. lakes: Zn, Cu.

Figure 4-This represents a synthesis for the world. "Heavy Metals" is a general term covering the various heavy metals studied around the world.

In Figure 2, the profile for "Lead" also applies to Cu and Zn. In Figure 2, "Pesticides" corresponds to chlorinated hydrocarbon pesticides. In Figure 3, the term "Northeastern Lakes" includes lakes and ponds from Minnesota, Maine, New Hampshire, New York, Quebec, Ontario, and Nova Scotia; "Connecticut Lakes" includes data from lakes and ponds located near New Haven, Connecticut; "Great Lakes and central U.S. lakes" profiles illustrate results from Lakes Erie, Huron and Michigan as well as Mendota, Standley, and Clearwater Lakes. Finally,"Western U.S. lakes" include Lake Washington near Seattle and Thompson Canyon Reservoir near Yosemite Park.

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