POLLUTANT—PARTICLE ASSOCIATIONS AND DYNAMICS IN COASTAL MARINE ENVIRONMENTS: A REVIEW*

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ABSTRACT

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A wide variety of substances, including known or potential pollutants, become associated with particles in coastal marine environments. This association may result from: (1) ion exchange, precipitation, or hydrophobic interactions with the particle surface, (2) co-precipitation with iron and manganese hydrous oxide coatings, (3) complexation with organic substances bound or aggregated with particles, (4) incorporation into mineral lattices, organisms or fecal material, or (5) flocculation of colloidal organic and inorganic matter during river and sea water mixing. The transport, accumulation and fate of such chemically-reactive pollutants in coastal marine environments are governed to a great extent by particle dynamics. Understanding of the mechanisms and processes affecting pollutant—particle associations and dynamics allows the prediction of the fate of a wide variety of pollutants in estuarine, coastal and marine environments.

INTRODUCTION

A wide variety of substances, with known or potential pollutant capacity, are transported into the coastal marine environment from the continents via river discharge, ocean dumping, or eolian processes. A few of these substances are relatively unreactive in the marine environment, and consequently their transport pathways are conceptually straightforward and mediated by water mass movements. A much greater number of these substances, however, are highly reactive and have a strong affinity for association with fine-grained particles. The movement of these reactive pollutants, their removal from the water, and their accumulation in the sediments are thus governed to a great extent by sedimentary processes.

The dynamics of fine-grained particles and particle-associated pollutants in coastal marine environments are extremely complex because: (1) intense short-term flow events are often more important to sediment transport than current flow that occurs on a regular basis during normal conditions, (2) fine particles often undergo numerous episodes of deposition and resuspen-

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sion, and (3) numerous physical, chemical, and biological processes affect the fate of particles and reactive pollutants, especially in estuarine zones where fresh water mixes with sea water. As a result, transport calculations for particle-associated pollutants are much more difficult to make than those for dissolved substances.

During recent years there have been numerous studies measuring the distribution of contaminants in the environment. Most of these studies, however, merely report pollutant concentration data on particles, with little attention devoted to the biogeochemical cycles that affect the dynamics of particles and associated pollutants in estuarine, coastal, and marine environments. Several of the input, removal, mixing, and regeneration processes involved in these geochemical cycles are schematically portrayed in Fig. 1. The extent to which the fate of a specific pollutant is affected by each of these processes depends on the chemical form and concentration of the pollutant, as well as on the chemical characteristics of the sorbing particle and the transporting medium. The particles involved in these cycles may be riverborne, airborne, resuspended from the bottom by currents and organisms, or generated within the water column by biological production, colloidal flocculation, or bioaggregation.

Most of the studies concerned with these processes have used geochemical signatures on particles to trace particle transport, differentiate particle

GEOCHEMICAL PROCESSES AFFECTING PARTICLE-POLLUTANT
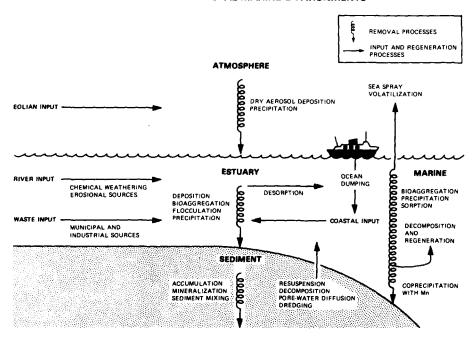DYNAMICS IN COASTAL MARINE ENVIRONMENTS

Fig. 1. Schematic illustration of the biogeochemical processes which affect pollutant—particle dynamics.

sources, and quantify particle—pollutant fluxes (Martin et al., 1981). Such signatures can be metal/aluminum ratios (Eggiman et al., 1980; Sholkovitz and Price, 1980) or any adsorbed substance having a known source and history of input, such as radionuclides and synthetic organic compounds (Bopp, 1979; Olsen, 1979). Natural and anthropogenic radionuclides are particularly useful in that they can also serve as geochemical clocks to determine the rates of processes affecting particles and pollutants in aquatic environments (Templeton and Preston, 1966; Pickering, 1969; Broecker et al., 1973; Murray and Murray, 1973; Hetherington and Jeffries, 1974; Robbins and Edgington, 1975; Aller and Cochran, 1976; Bacon et al., 1976; Duursma, 1976; Simpson et al., 1976; Turekian, 1977a, 1977b; Goldberg et al., 1978; Olsen et al., 1978; Simpson et al., 1978; Williams et al., 1978; Li et al., 1979; Livingston and Bowen, 1979; Nittrouer et al., 1979; Olsen et al., 1980; Santschi et al., 1980; Benninger and Krishnaswami, 1981; Cutshall et al., 1981; Li et al., 1981; McKinley et al., 1981; Aston and Stanners, 1982; Bacon and Anderson, 1982). Quantitative estimates for the transfer rates associated with the processes illustrated in Fig. 1 are of prime importance for determining pollutant—particle fluxes, developing accurate pollutant—particle transport models, and predicting the fate of particles and their associated pollutants in the marine environment.

Pollutant Classification

Figure 2 diagrams a broad spectrum of substances with known or potential pollutant capacity. These substances are classified first as organic and

POLLUTANT CLASSES

ORGANIC	INORGANIC
I. PETROLEUM AND COAL HYDROCARBONS	I. HEAVY METALS
A. CRUDE OIL	A. Cd, Hg, Pb*
(ALKANES, CYCLOALKANES, AROMATICS)	B. Fe, Mn, Zn, Cu**
B. REFINED PETROLEUM PRODUCTS	C. OTHERS
(PETROL, KEROSENE, DIESEL, HEATING OILS, ASPHALTS)	
C. COMBUSTION AND CONVERSION PRODUCTS	
(PAHs, CO_2, SYNFUELS AND BYPRODUCTS)	
II. SYNTHETIC ORGANICS	II. RADIONUCLIDES
A. HALOGENATED HYDROCARBONS	A. TRANSURANICS
(PCB's, DDT, KEPONE, MIREX, DIELDRIN, CHLORDANE,	(PLUTONIUM, AMERICIUM, CURIUM)
HEXACHLOROBENZENE, CHLOROFLUROCARBONS,	B. FISSION PRODUCTS
TRICHLOROETHANE)	(^{137}Cs, ^{90}Sr)
B. PHTHALIC ACID ESTER PLASTICIZERS	C. ACTIVATION PRODUCTS
(PVC, DEHP)	(^{60}Co, ^{54}Mn, ^{65}Zn, ^{51}Cr)
C. OTHERS	D. NATURAL
(SURFACE ACTIVE AGENTS, ORGANOPHOSPHATE	(URANIUM-THORIUM DECAY
PESTICIDES, SYNTHETIC PYRETHRENOIDS)	SERIES)
III. MUNICIPAL WASTES	III. INORGANIC AND INDUSTRIAL WASTES
A. SEWAGE SLUDGE	A. DREDGE SPOILS
B. NUTRIENTS	B. PROCESSING BYPRODUCTS
(PHOSPHOROUS, NITROGEN, CARBON, SILICON)	(ACIDS, ASH)
	C. SLAGS, MINE TAILINGS
IV. BIOLOGICAL	
A. PATHOGENS	
B. PLANKTON BLOOMS	
(DISSOLVED O_2 DEPLETION)	

*METALS MOST STUDIED IN TERMS OF POLLUTION AND TOXIC EFFECTS.
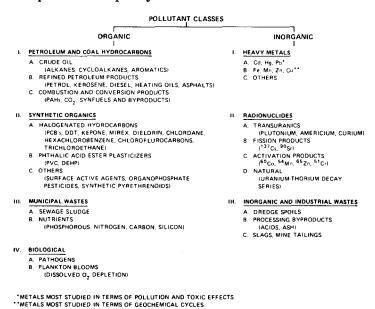**METALS MOST STUDIED IN TERMS OF GEOCHEMICAL CYCLES.

Fig. 2. A classification of substances with known or potential pollutant capacity.

inorganic, then each class is subdivided into groups. The groups are determined primarily by the chemical characteristics of the samples analyzed and by the instruments with which the analyses were performed, for example atomic absorption spectrometry (heavy metals), alpha, beta, and gamma spectrometry (radionuclides), gas chromatography (hydrocarbons), and mass, volume, and BOD measurements (municipal and industrial solid wastes).

The sources, chemical characteristics, and input histories of these pollutants into the marine environment have been extensively described in several publications (NAS, 1971; Goldberg, 1975; NAS, 1975; Windom and Duce, 1976; NOAA, 1979; Farrington, 1980) and will not be reviewed here. We present a review and overview of the biogeochemical aspects of pollutant—particle associations and dynamics.

POLLUTANT—PARTICLE ASSOCIATIONS

Many chemically reactive pollutants, including synthetic organics, hydrocarbons, and some radionuclides and trace metals become appreciably associated with particles when discharged into turbid aquatic environments. This association may result from: (1) ion exchange, precipitation, or hydrophobic interactions with the particle surface, (2) co-precipitation with iron and manganese hydrous oxide coatings, (3) complexation with organic substances bound or aggregated with particles, (4) incorporation into mineral lattices, organisms or fecal material, or (5) flocculation of colloidal organic and inorganic matter during river and sea water mixing (Sayre et al., 1963; Jenne and Wahlberg, 1968; Saxby, 1969; Edzwald et al., 1974; Burton, 1976; Burton and Liss, 1976; Sholkovitz, 1976; Boyle et al., 1977b; Gibbs, 1977; Turekian, 1977b; Duinker, 1980; Gearing et al., 1980). One of the most basic geochemical tools for assigning a quantitative value to this association is the distribution coefficient.

Distribution coefficient

The distribution coefficient (K_d) is defined here as

$$K_d = C_p/C_w ,$$

where C_p is the concentration of a specific pollutant associated with a given weight of particles and C_w is the concentration of the pollutant in an equal weight of water. Ideally, this ratio is a measure of the equilibrium partitioning of a pollutant between dissolved and particulate phases. This distinction between "dissolved" and "particulate", however, is generally operational (such as passage through a 0.45-μm pore-size filter) and is one of the most important problems with using and determining distribution coefficients in natural water systems. In this respect, C_w includes not only pollutants in true solution but also pollutants associated with dissolved and colloidal organic matter or sorbed onto particles small enough to pass through the

filter, and C_p often includes pollutants that are sorbed from solution by the filter as well as those associated with particles trapped during the filtration.

Distribution coefficients for highly reactive pollutants, such as insecticides, polychlorinated biphenyls (PCBs), and plutonium are generally of the order of 10^5. Consequently, in an aqueous system having a suspended matter concentration of $\sim 10\,\text{mg}\,\text{l}^{-1}$ (which is typical of near-shore coastal areas), approximately 50% of the mass of such pollutants will be sorbed into suspended particles and the other 50% will be "dissolved" in the water. In a system with a suspended matter concentration of $\sim 100\,\text{mg}\,\text{l}^{-1}$ (such as the Mississippi River, Columbia River, and Hudson River during high flow), more than 90% of the mass of these pollutants will be transported in association with particles and the remaining 10% will be in the water. In shelf and slope waters, where suspended particle concentrations are on the order of $1\,\text{mg}\,\text{l}^{-1}$ or less, much of the pollutant mass is transported with the water phase, but particulate phases play an important role in the removal of these pollutants from the water column, and the bottom sediments are their major sink.

The distribution coefficient for a specific pollutant may vary depending on the chemical form and concentration of that pollutant. For example, plutonium may exist in at least two oxidation states, a reduced state (either III or IV) that is readily sorbed and strongly bound to particles and an oxidized state (either V or VI) that has a much greater tendency to remain in solution (Bondietti and Trabalka, 1980). Similarly, Bopp (1979) showed that the lower-chlorinated biphenyls (di- and tri-chlorobiphenyls) have a lower distribution coefficient ($\sim 10^4$) relative to the higher-chlorinated biphenyls (penta- and hexa-chlorobiphenyls), which have a K_d value of the order of 10^5.

Variations in the distribution coefficient for a specific pollutant may also reflect changes in the physicochemical characteristics of the particulate and water phases. Fine-grained particles generally have a greater affinity for pollutants relative to coarser particles because they have greater surface areas (for binding sites and organic or manganese coatings) per unit weight and are enriched in layered aluminosilicate minerals (which contain more binding sites per unit area). In addition, coarser particles are generally enriched in quartz, which is relatively unreactive compared to organic and clay phases in natural waters. Studies on the sorption behavior of radio-caesium indicated that ^{137}Cs is strongly associated with potassium-rich, fine-grained particles (illite clays) in freshwater systems but remains in solution in marine waters because ^{137}Cs must compete with seawater cations (especially potassium) for binding sites on particle surfaces (Tamura and Jacobs, 1960; Rogowski and Tamura, 1970; Aston and Duursma, 1973; Hetherington and Jefferies, 1974; Patel et al., 1978).

Inorganic flocculation and ionic sorption-desorption

Inorganic flocculation is a complex physico-chemical reaction in which

river-borne suspended colloids coagulate into larger particles in the presence of increased electrolyte concentrations. Inorganic colloids are electrically charged particles with large surface areas per unit mass (Pravdic, 1970). In fresh waters, repulsive charge effects tend to keep colloids apart, but as the ionic strength of the water increases, such as occurs during transport into an estuarine environment, interactions between the seawater ions and the charged colloids reduce the repulsive forces, allowing flocculation into larger particles (Kranck, 1975).

Because the flocculation process depends on colloid collision and cohesion, the rate of flocculation is therefore influenced by the concentration and composition of the suspended matter and by the extent of turbulent mixing as well as the salinity (Meade, 1972). With adequate particle concentrations, flocculation of most colloids is complete above a salinity of $\sim 4\%_{00}$ (Dyer, 1972). Whitehouse et al. (1960) showed that different clay minerals have different rates of flocculation (e.g., kaolinite has less surface charge and therefore flocculates more rapidly than illite). Edzwald and O'Melia (1975) proposed that the distribution of clay minerals in recent sediments of the Pamlico Estuary (where kaolinite is found upstream of illite) is a result of their relative stabilities to flocculation.

The colloid charge originates from unsatisfied or broken bonds at the crystal surface and from the substitution of structural cations in the mineral lattice by cations having a different valence state. The charge at the colloid surface may be positive (as for aluminum hydroxide at high pH) or negative (as for silica or clay minerals). The negative charge of clay minerals is usually attributed to substitution of Mg^{2+} for Al^{3+} and Al^{3+} for Si^{4+} without concomitant substitutions of OH^- for O^{2-}. To balance this negative charge, clay particles tend to sorb cations between their structural layers or at their surface. The surface-sorbed ions are subject to ion exchange. In this manner, ionic species of a wide variety of pollutant metals and radionuclides can become associated with colloidal particles in freshwater systems and may subsequently be flocculated and deposited, or desorbed by ion exchange with seawater cations, as these particles are transported into the marine environment.

The sorption—desorption characteristics of various metals and radionuclides on clay minerals in estuarine and coastal marine environments have been studied by many investigators (Aston and Duursma, 1973; Bothner and Carpenter, 1973; Murray and Murray, 1973; O'Connor and Kester, 1975; Murray and Fukai, 1975; Bourg and Filby, 1976; Duursma, 1976; James and MacNaughton, 1977; Bewers and Yeats, 1978; Frenet-Robin and Ottmann, 1978; and Patel et al., 1978). Most of these studies involved laboratory experiments to document the extent of sorption—desorption in relation to variations in particle composition and water characteristics. Patel et al. (1975) indicated that pollutants sorbed by ion exchange exhibit a better relationship with sediment clay content than those sorbed by other processes. Tamura and Jacobs (1960) indicated that illite has a particularly

high affinity for ^{137}Cs as a result of caesium substitution for potassium in the clay mineral lattice. Caesium[137] introduced into estuarine environments in fallout from atmospheric testing of nuclear weapons or in controlled releases from nuclear power facilities apparently does not have enough time to become incorporated into the clay mineral lattice before ion exchange causes desorption in more saline environments (Reil, 1970; Jinks and Wrenn, 1976; Patel et al., 1978; Olsen et al., 1981a).

The desorption of several other metals, including Co, Ag, Mn, Zn, Cd, Hg, and [226]Ra have been noted in the estuarine environment (Evans and Cutshall, 1973; Lindberg et al., 1975; Graham et al., 1976; Evans et al., 1977; Li et al., 1977; and Bothner et al., 1980). In most of these cases, however, the "release" was attributed to resuspension of sediments, decomposition of organics, or the cycling of reduced metal—hydroxides rather than to desorption from clay minerals. Hunter and Liss (1979; 1982) suggested that organic and metal—hydroxide coatings on colloidal particles may affect surface electrical properties, resulting in a suppression of coagulation rates and ion exchange. This would agree with the findings of Gibbs (1977) and Trefry (1977) that metal—hydroxide coatings and organics are the major transport phases for sorbed metals and that only a small fraction of these metals are available for ion exchange. Consequently, processes involving organic flocculation—decomposition and Fe—Mn oxidation—reduction may overwhelm ion sorption and exchange on clay materials.

Organic complexation and flocculation

Dissolved and colloidal organics, which occur naturally in all aquatic systems, have a strong capacity for binding metals and other pollutants and thus exert considerable control over the mobilization, transport, removal, and accumulation of contaminants in the environment (Saxby, 1969; Schnitzer and Kahn, 1972; Rashid, 1974; Singer, 1974; Nissenbaum and Swaine, 1976; Reuter and Perdue, 1977; Means and Wijayaratne, 1982). Humic substances generally comprise about 60 to 80% of these dissolved organics. The remaining fraction is composed of polypeptides, polysaccharides, carbohydrates, proteinaceous matter, and free amino acids. Because these latter organic compounds are easily degradable and rapidly metabolized by microbial activity, their concentrations remain low in natural waters.

Chemically, river humic substances are complex and relatively stable polymers of amino acids, hexosamines, quinones, polycyclic aromatics, and oxygen-containing functional groups (Lindberg et al., 1975). The dominant functional groups are carboxyl (-COOH) and phenolic hydroxyl (-OH) groups, but several amino ($-NH_2$) and sulfur-containing (thioether and thioketo) groups may also be available for complexation or chelation. Marine humic substances are somewhat less oxygenated than river humics and contain only about half the amount of carboxyls and phenolic groups but contain more sulfur and nitrogen (Nissenbaum and Swaine, 1976). Schnitzer

and Kahn (1972) have indicated that about 60% of the total weight of a fulvic acid molecule is in the functional groups.

The acidic character of these humic polymers (that is the ability to give off H^+) allows them to exist in river water as negatively charged hydrophilic colloids and to interact with cations of heavy metals forming organic—metal complexes by ion exchange, surface adsorption, or chelation (Reuter and Perdue, 1977). Ferric iron (Fe^{3+}) has the strongest affinity (stability constant) for complexing with humic polymers, whereas Hg^{2+} and Cu^{2+} are the most strongly associated of the divalent trace metal cations (Mantoura et al., 1978; Sholkovitz, 1978). Mantoura et al. (1978) found that the stabilities of the divalent metal—humic complexes follow the Irving-Williams order,

Hg, Cu > Zn ~ Ni > Pb > Co > Fe > Mn ~ Cd > Ca > Mg,

which is dependent on the orbital configurations of the electrons according to crystal field theory (Stumm and Morgan, 1970). Lees (1950) indicated that as many as sixty carbon atoms may be associated with one copper ion in a saturated copper—humic complex. Consequently, these organic—metal complexes are relatively stable in natural waters and can withstand large variations in pH even in the presence of large amounts of excess cations. Although the ability of humic substances to bind pollutant metals in the marine environment is undoubtedly affected by the presence of high concentrations of Ca and Mg (Stumm and Morgan, 1970; Mantoura et al., 1978), the magnitude of this effect on specific metals is not well known (Reuter and Perdue, 1977). Slowey et al. (1967) found that the major portion of Cu in seawater is associated with organic matter, and several studies have shown strong correlations between metal and organic matter concentrations in coastal marine sediments (Calvert and Price, 1970; Bruland et al., 1974; Jones and Jordan, 1979). Recently, Balistrieri et al. (1981) suggested that the adsorption properties of marine particles are controlled primarily by organic coatings.

The hydrophilic nature of organic—metal complexes may cause an increase in the solubility and mobilization of a wide range of contaminants, including Cu, As, Pb, Hg, Cd, Co, Ag, Ni, Sn, Al, U, Th, and perhaps transuranic radionuclides that otherwise would not be readily transported in a solution phase (Saxby, 1969; Rashid, 1974; Picard and Felbeck, 1976; Sholkovitz, 1976; Nash et al., 1981; Bondietti, 1982). Although the ability of humic substances to reduce Fe(III) to Fe(II), leach minerals, and mobilize metals has been well documented in soils and peats, similar processes have been only recently identified in sediments. Presley et al. (1972) indicated that humic substances can comprise between 40 and 70% of the organic matter in sediments and that organic complexes with metals, initially leached from silicates and metal oxides, may be responsible for the mobilization of Zn, Cu, and Ni from sediments in Saanich Inlet.

In the major rivers of the United States, concentrations of humic substances may range as high as $100\,\mathrm{mg\,l^{-1}}$ but average about $10\,\mathrm{mg\,l^{-1}}$ (Reuter

and Perdue, 1977). Thus concentrations of dissolved organic matter greatly exceed those of other dissolved trace elements or pollutants in river waters. As a result of their colloidal nature, humic substances and their complexed pollutants are rapidly flocculated from solution when river water mixes with seawater in an estuary (Sholkovitz, 1976). This flocculation process usually accounts for the removal of no more than about 10% of the dissolved organic matter but may result in almost total removal of dissolved iron (Boyle et al., 1977b; Moore et al., 1979). This suggests that iron in some way may enhance the flocculation of humic substances. In addition, experimental studies have indicated that other metals and trace elements may be associated with these iron-rich flocs and may also be removed from solution. Experiments by Sholkovitz (1978) suggest almost total removal of dissolved Fe and P, 20 to 40% removal of Mn, Cu, Ni, and Al, and less than 10% removal for Co and Cd by the dissolved Fe—humic flocculation process.

Hydrophobic associations with surfaces

The solubility of a pollutant substance in a polar medium, such as water, is determined largely by its ability to interact electrochemically through hydrogen bonding or ion—dipole interactions. If the substance is non-polar, that is, uncharged and unable to engage in electrochemical interactions, it will probably have a very low solubility and a strong affinity for phase boundaries such as air—sea interface or the surface of particles. This tendency of non-polar substances to adhere to one another or to phase boundaries in aqueous environments has been called hydrophobic bonding (Parks, 1975).

Many of the organic molecules in petroleum hydrocarbons (Farrington, 1980) and halogenated hydrocarbons (PCBs, DDT, DDE, chlordane, dieldren, kepone, and other commercially-produced toxic organic chemicals) are non-polar or have non-polar functional groups. In natural waters, these surface active organic compounds are readily sorbed with their hydrophobic (non-polar) functional groups oriented away from the aqueous phase and any polarized chemical structure directed toward water. Typical water—particle distribution coefficients for halogenated hydrocarbons fall between 10^3 and 4×10^5 (Bopp, 1979) and consequently sediments are an important sink.

Another important chemical property of non-polar organic pollutants is their affinity for other less-soluble organic phases. For example, the solubility of DDT in water is less than $10^{-4}\, g\, l^{-1}$, whereas its solubility in vegetable oils, kerosene, and gasoline is $\sim 10^2\, g\, l^{-1}$, and its solubility in benzene (another aromatic organic chemical) is $\sim 10^3\, g\, l^{-1}$ (NAS, 1971). The distribution coefficient of DDT between river oils and water is 1.5×10^6 (Hartung and Klingler, 1970). Consequently, there is a strong tendency for organic pollutants to become associated and accumulate with other organic phases, whether that be lipid or adipose tissue in organisms (Clayton et al., 1977),

oils in sea surface films (Duce et al., 1972), dissolved or particulate humic substances in seawater (Boehm and Quinn, 1973; and Pierce et al., 1974), or organic detritus in sediments (Bopp, 1979).

Sorption studies with non-polar hydrocarbons have shown that the extent of sorption is directly related to particle surface area (increasing with decreasing particle size) and to the percentage of organic matter in particles (Hiraizumi et al., 1979; Pavlou and Dexter, 1979; and Gearing et al., 1980). The extent of sorption can be modeled using a Freundlich isotherm that relates the amount of a substance sorbed (X) to the concentration of the substance in solution (c) and the mass of sorbing particles (m)

$$X/m = Kc^{1/n},$$

where K and n are constants that can be determined from the slope and intercept of the line connecting measured values of log (X/m) as a function of log (c).

At the air—sea interface organic compounds may adhere to form a coherent thin film. These films that may result from oil spills and discharges from industrial and municipal outfalls, as well as from natural causes, are often visible by their damping effect on capillary waves. Duce et al. (1972) and Pattenden et al. (1981) found that concentrations of Pb, Fe, Ni, Cu, fatty acids, hydrocarbons, and halogenated hydrocarbons are enriched as much as 50 times in the top 100 to 150 μm of Narragansett Bay relative to water 20 cm below the surface and suggested that the high metal concentrations reflect complexing with the surface-active organic substances. The extent that non-polar hydrocarbons in this microlayer are aggregated into sinking particles, volatilized into the atmosphere, photochemically degraded, emulsified into the water, incorporated into organisms, or deposited as coatings on eolian particles penetrating the sea surface is relatively unknown.

Biological incorporation, aggregation, and cycling

Pollutant incorporation into biogenic particles, with subsequent organism migration, food chain transfer, or fecal pellet deposition, provides a rapid and ecologically important transport system in the marine environment. It has been well established that biological processes can concentrate nutrients, trace elements, and pollutants (Goldberg, 1957) and that biological cycles play an important role in controlling the distribution of these substances in the ocean (Turekian, 1968; Broecker, 1974; Brewer, 1975). Pollutant associations with organisms are a result of direct uptake from ingestion of sediment particles, organic—pollutant complexes or other contaminated food and passive sorption as water passes over gills, mucous layers, tests, or other exposed surfaces (Livingston, 1976). Bio-assimilation varies depending on the chemistry of the incorporated pollutant. For example, hydrophobic chlorinated hydrocarbons (DDT and PCBs) are fat soluble and become associated with lipid tissues, whereas metals may complex with protein functional

groups. Pollutants may be removed from the organism after assimilation by secretion or before assimilation by test molting or in the form of particulate fecal material.

Several investigators suggested that sinking biogenic particles (primarily fecal pellets) are important in removing nutrients, trace elements, and pollutants from surface sea waters and transporting them to greater depths in the ocean (Krishnaswami et al, 1976; Bishop, 1977; Lal, 1977). Bishop (1977) indicated that more than 98% of the mass flux through the upper 400 m in the equatorial Atlantic could be attributed to particles greater than 53 microns and Wiebe et al. (1976) found that even at depths between 2000 and 4000 m, fecal pellet fluxes were on the order of hundreds per square meter per day.

Harding and Phillips (1978) showed that phytoplankton can accumulate substantial amounts of PCBs from seawater. Elder and Fowler (1977) reported high concentrations of PCBs in fecal pellets from grazing zooplankton in the Liguran Sea, suggesting that sinking biogenic particles are important in transporting PCBs into the deep sea. Higgo et al. (1977) measured extremely high concentrations of plutonium in zooplankton fecal material and also suggested that pellets are an important factor in the vertical transport of plutonium in the ocean. Several other studies have indicated that biogenic particles may contain significant amounts of other trace elements and pollutants, including Cd, Ce, Nb, Zr, Po, Pb, Zn, Al, Fe, Mn, P, and petroleum hydrocarbons (Osterberg et al., 1963; Conover, 1971; Martin and Broenkow, 1975; Bacon et al., 1976; Eaton, 1976; Krishnaswami and Sarin, 1976; Lal, 1977; and Bennett and Carpenter, 1979).

As these biogenic particles sink (following nutrient, trace element, and pollutant uptake in ocean surface waters), recycling of the organic matter occurs, leading to the regeneration of nutrients and to a release of some of the associated trace elements. This recycling (or oxidation of the organic matter) is most pronounced in the thermocline below the mixed layer (i.e., at oceanic depths between 400 and 800 m) and is identified by both a depletion in dissolved oxygen and by an increase in phosphate, silicate, and nitrate (Fig. 3). Bacon et al. (1976) found that about 50% of the incorporated ^{210}Po regenerated in the water column as particulate organic material sank through the thermocline, whereas only about 5% of the ^{210}Po associated with inorganic particles was recycled. Sclater et al. (1976), Boyle et al. (1977a), and Bruland (1980) demonstrated that the distribution of Cd, Ni, Zn, and to some extent Cu are strongly correlated with nutrient profiles in the ocean, indicating that the distributions of these metals are greatly influenced by biological cycling (Fig. 3).

In shelf and coastal areas, where concentrations of suspended particles are considerably greater, the mass of pollutants incorporated into marine organisms and removed from the water by fecal pellets appears to be minor in comparison to the mass of pollutants removed by sorption onto particles resuspended from the bottom (Li et al., 1979). For example, Santschi et al.
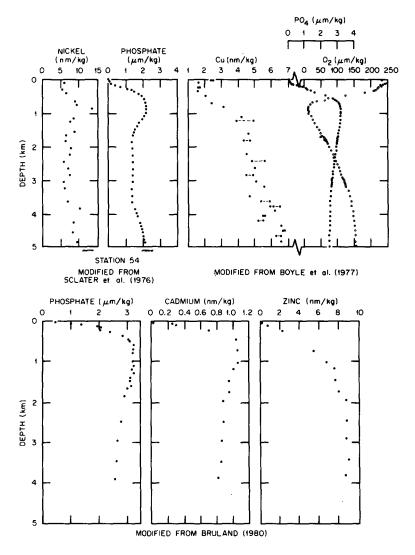
Fig. 3. The distribution of dissolved Ni, Cu, Cd, and Zn and its correlation with nutrient (PO₄) and oxygen profiles in the ocean. These data indicate that the distribution of several metals is greatly influenced by biological cycling.

(1980) calculated that the removal rate of plutonium by zooplankton grazing in the waters of the New York Bight is $\sim 1.6 \times 10^{-3}$ dpm cm^{-2} yr^{-1} (~ 100 Bq cm^{-2} yr^{-1}), which is almost an order of magnitude less than the Pu removal rate ($7-14 \times 10^{-3}$ dpm cm^{-2} yr^{-1} or $420-840$ Bq cm^{-2} yr^{-1}) calculated from [228]Th removal. This would agree with the laboratory results of Fisher et al. (1980) that live or dead marine plankton cells and glass beads accumulate Pu at similar rates, indicating that initial uptake was a passive phenomenon depending primarily on the concentration of particle surfaces.

Metal-hydroxide scavenging

Manganese, and to some extent iron, are important elements in geochemical cycles affecting pollutant—particle dynamics because: (1) oxidation—reduction reactions are continually moving Mn and Fe in and out of solution, and (2) the precipitation—dissolution of Mn—Fe hydroxides is an effective mechanism for scavenging or remobilizing many elements and pollutants. Manganese and iron are readily liberated from host rocks during weathering, are quite soluble in their divalent (manganous or ferrous) form, and are, therefore, easily transported in water. In the presence of oxygen and a catalytic site (such as the surface of particles, colloids or pre-existing Mn—Fe oxides), soluble divalent forms will oxidize and precipitate out of solution as hydrous Mn—Fe oxide coatings on particles or nodules.

Oxidation is an electrochemical process involving the loss of electrons from a chemical element. Similarly, the gain of electrons by an element constitutes reduction. Because both processes involve the exchange of electrons, the potential (Eh) of a specific medium for oxidation or reduction can be measured and expressed in terms of millivolts. The effects of Eh and pH on the equilibrium stability fields of iron and manganese are illustrated in Fig. 4. The shaded area represents the modest range of Eh—pH conditions in soils and surface sediments (Jenne, 1968). In reducing environments (low
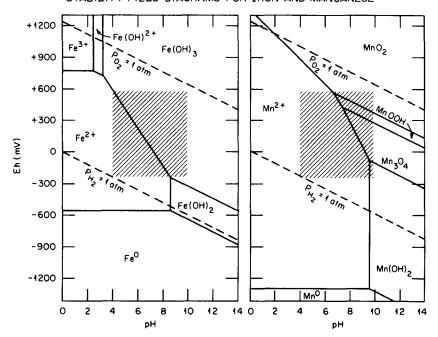
STABILITY FIELD DIAGRAMS FOR IRON AND MANGANESE

Fig. 4. Eh versus pH stability field diagrams for iron and manganese ($a_{Fe,Mn} = 10^{-4}$ M; $pCO_2 = 0$; $P_{total} = 1$ atm; $T = 25°C$) as modified from Jenne (1968).

pH or Eh), manganese and iron can occur as soluble manganous (Mn^{2+}) and ferrous (Fe^{2+}) ions. In oxidizing environments (high pH or Eh), manganese and iron form relatively insoluble oxides and hydroxides (Fig. 4). With changes in the environmental Eh—pH conditions, Mn and Fe can thus cycle between soluble and particulate phases. Such changes occur during transport from freshwater (pH $\sim$ 6.5) to seawater (pH $\sim$ 8) and after deposition from oxic water to anoxic sediments. For example, Evans et al. (1977) and Morris et al. (1982) indicated that Mn may be reduced and released from estuarine sediments causing the concentration of dissolved Mn to increase in the water column. As this water is transported to the ocean, Mn is once again oxidized onto particles giving rise to the elevated Mn concentration on coastal suspended matter. As the particles settle, particulate manganese may be transported back toward the river by estuarine circulation or deposited in shelf sediments where it may be reduced and recycled again.

Because freshly precipitated Mn—Fe hydroxides act as efficient scavengers (by sorption or co-precipitation) for other metals (Murray, 1975), the cycling of these hydroxides may affect the dynamics of a wide variety of other elements and pollutants. Jenne (1968) and Jenne and Wahlberg (1968) indicated that the ubiquitous occurrence of Mn—Fe as coatings, rather than discrete crystalline particles, allows Mn—Fe hydroxides to exert chemical controls on sorption that are far out of proportion to their concentrations and proposed that such coatings are the principal control for fixation of Zn, Cu, Ni, Co, radiocobalt, and plutonium in soils and freshwater sediments. Lewis (1977) showed that the precipitation of Mn—Fe hydroxides in the Susquehanna River system rapidly scavenges ^{210}Pb from solution, and Turekian (1977b) stresses the importance of Mn—Fe cycling in the removal of reactive metals from estuarine and coastal waters. In a classic study, Krauskopf (1956) indicated that adsorption by hydrated Mn—Fe oxides may be one of the most important mechanisms controlling the concentration of thirteen rare metals (Au, Cu, Ni, Pb, Bi, Cd, Co, Hg, Ag, Cr, Mo, W, and V) in seawater. More recently, Spencer et al. (1981) suggested that the redox cycling of Mn and Fe hydroxides from reducing (organic-rich) sediments along the continental margins may cause these boundary areas to act as a sink for ^{210}Pb and other elements and thus exert considerable control on the minor element chemistry of the oceans.

POLLUTANT—PARTICLE DYNAMICS

Pollutant—particle transport

During recent years much attention has been devoted to the geochemical cycles that affect the dynamics of particles and associated pollutants in estuarine, coastal, and marine environments. The pioneering studies, in this respect, used radionuclides to trace water mixing (Bowen and Sugihara, 1960; Broecker, 1963; Osterberg et al., 1965), sediment transport (Sayre et al., 1963; Perkins et al., 1966; Pickering, 1969), and exchange processes between sediments and water (Aston and Duursma, 1973; Evans and

Cutshall, 1973; Murray and Murray, 1973). In the Columbia River, Perkins et al. (1966) found that: (1) [46]Sc, [54]Mn, [58]Co, ^{59}Fe, ^{60}Co, [65]Zn, and [95]Zr-[95]Nb were primarily associated with particulate phases, (2) ^{51}Cr, [106]Ru, [124]Sb, and [140]Ba were mainly in the dissolved phase, (3) the total radionuclide activity of the river increased when high flows resuspended bottom sediment, and (4) during this resuspension significant amounts of [46]Sc, [54]Mn, [58]Co, ^{60}Co, and [65]Zn were released. In contrast, Johnson et al. (1967) and Cutshall et al. (1972) found that although seawater leaching removed up to 40% of [54]Mn from Columbia River bottom sediments, [65]Zn, ^{60}Co, ^{51}Cr and [46]Sc remained bound to particles.

In rivers, such as the Mississippi, Yukon, and Amazon, where suspended-particle concentrations are high, Gibbs (1977) and Trefry (1977) showed that more than 90% of the total Fe, Mn, Co, Cu, Zn, Cr, and Ni loads are transported with particles. Sequential leaching studies showed that the bulk of these metals are in the crystal lattice of the particle (Fig. 5) and that their input into the marine environment is a result of natural weathering processes. These lattice-bound metals do not appear to undergo any significant desorption from river particulates as they are transported across the freshwater—seawater interface (Trefry, 1977).

In more polluted rivers, however, appreciable quantities of Fe, Mn, Cu, Co, Ni, Zn, Pb, Cd, and Hg may be associated with metal—hydroxide coatings or organic phases (Presley et al., 1980). Metals associated with these phases can be released or remobilized from particles during organic decomposition or reduction of Mn—Fe hydroxide coatings. Such processes generally occur after the particles have been deposited rather than during their transport.

Hydrocarbons in water associate with suspended particulate matter in inverse proportion to their degree of aqueous solubility, with saturated hydrocarbons (n-alkanes) adsorbed preferentially over aromatics such as naphthalenes (Gearing et al., 1980). Studies in the Providence River, Narragansett Bay, and microcosm tanks of the Marine Ecosystems Research Laboratory have indicated that: (1) approximately 90% of the saturated hydrocarbons are associated with suspended matter; (2) only about 10% of the aromatics were associated with suspended particles; (3) the particle-
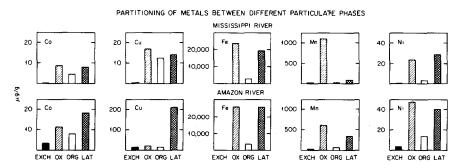

Fig. 5. Distribution of trace metals between surface exchangable, metal—hydroxide, organic and mineral lattice phases in the Mississippi and Amazon Rivers (modified from Presley et al., 1980).

associated aromatics were skewed toward the higher molecular weight end with a depletion of benzenes and naphthalenes relative to larger compounds; (4) as particle-associated hydrocarbons are transported down river, there is a loss of aromatic character due to solution in the water column; (5) the deposition of particle-associated hydrocarbons was the major transport pathway of oil to the sediments; and (6) microbial decay in the sediments causes a loss of saturated hydrocarbons leaving aromatics to predominate in deep sediments (Van Vleet and Quinn, 1977; Gearing et al., 1980).

Farrington (1980) indicated that the dumping of sewage sludge and dredge spoils is the primary source of hydrocarbons to shelf sediments in the New York Bight area. The extent to which dredge spoils and associated hydrocarbons are dispersed throughout this shelf area is still relatively unknown. Farrington and Tripp (1977) found, however, that the sediment concentration of petroleum and coal hydrocarbons decreases along the Hudson channel towards the edge of the shelf and suggested that the channel acts as a conduit or trap for hydrocarbon-contaminated particles. Hites et al. (1980) also found anomalously high concentrations of combustion-generated polycyclic aromatic hydrocarbons (PAHs) in sediments of the Hudson Canyon. They suggest that the high concentrations reflect airborne movement of urban particulate matter to the ocean surface with subsequent particle transport to the canyon where accumulation occurs.

Although aerial transfer is also an important mechanism for the input of chlorinated hydrocarbons (PCBs and pesticides) into marine systems (Harvey and Steinhauer, 1976), once in aquatic environments the dispersal and accumulation of these compounds are primarily controlled by particle dynamics. Bopp et al. (1981) showed that the bulk transport of PCBs in the Hudson River estuary occurs during spring run-off or storm events that are characterized by high flow rates and suspended-matter concentrations. The highest concentrations of PCBs, DDT, and kepone on suspended matter, however, frequently occur during summer low-flow conditions and during slack tides. This is a result of the enhanced partitioning of chlorinated hydrocarbons to organic substances (Giam et al., 1976; Sayler, 1976; Huggett and Bender, 1980) that form a greater percentage of the total suspended-matter weight in the summer and during slack tides when inorganic particles settle out, leaving the water enriched in organics. Tidal variations in the concentration of kepone in suspended matter at one location in the James River estuary were documented by Huggett and Bender (1980) and are illustrated in Fig. 6.

Studies in the Mississippi River also showed that variations in flow, current conditions, and biological activity can alter the composition (organic/inorganic ratio) of the suspended matter that, in turn, affects pollutant—particle associations and dynamics. An increase in the organic content of particulates (from <3% during high flow to 25% during low flow) brought about a corresponding decrease in Al concentrations and increase in particulate Mn, Zn, Cu, and Cd concentrations, indicating an association of these

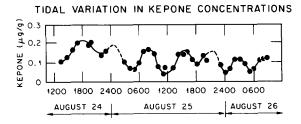TIDAL VARIATION IN KEPONE CONCENTRATIONS

Fig. 6. Tidal variations in the concentration of kepone in suspended matter collected at one location in the James River estuary at one meter above the bottom. The maxima correspond to slack tides during which time mineral grains settle, leaving the water enriched with organic phases (taken from Huggett and Bender, 1980).

metals with organic substances (Trefry, 1977; Presley et al., 1980). In addition, Sholkovitz and Price (1980) showed that tidal and geographical increases in the P/Al, Si/Al, Ca/Al, Mn/Al, Mg/Al, and Ti/Al ratios of suspended matter in the Amazon may reflect increases in biogenic activity.

It is apparent from the above that significant temporal, vertical, and horizontal inhomogeneities can occur in the concentration and composition of suspended matter in estuaries and coastal marine environments, and consequently care must be taken to acquire representative samples for pollutant analyses. In general, bed loads tend to be overlooked in most sampling programs because the transport of most pollutants with the coarser bed load is probably less significant than transport with the finer suspended load (Carpenter, 1976). In some cases, however, bed-load transport may be a major component of the total sediment transport, and if the bed sands are coated with Mn—Fe hydroxides or contain large quantities of organic—clay aggregates, pollutant transport with this load may be significant.

Pollutant—particle removal rates

The disequilibrium between a highly reactive, short-lived radionuclide and its more soluble, longer-lived parent can be used to determine the rate at which biological, chemical, and physical processes remove reactive pollutants from marine waters. In particular, two isotopes of thorium, ^{234}Th (half-life 24 d) and ^{228}Th (half-life 1.9 yr), have been used in this manner because they become rapidly associated with particles after their generation by radioactive decay of their more soluble parent nuclides (^{238}U and ^{228}Ra, respectively) in marine waters. If thorium were not rapidly removed from marine waters, it would exist in radioactive equilibrium with its parent; that is, the activity ratio of ^{228}Th/^{228}Ra, for example, would be approximately one. Actual ^{228}Th/^{228}Ra activity ratios average about 0.21 in open ocean surface water, 0.016 in shelf surface water, and 0.010 in Narragansett Bay, indicating rapid ^{228}Th removal by settling particles in these waters (Broecker et al., 1973; Li et al, 1979; Santschi et al., 1980).

This removal rate can be calculated from the model developed by Broecker et al. (1973):

$$\lambda_c = (1 - R)/(R)\lambda_t,$$

where R is the measured $^{228}Th/^{228}Ra$ activity ratio, λ_t is the radioactive decay constant for ^{228}Th, and λ_c is the fraction removed per unit time. Frequently, the removal rate constant (λ_c) is expressed as the span of time required for the initial ^{228}Th activity in the water column to be reduced to one-half by settling particles. This half removal time (T_c) is related to the removal rate constant (λ_c) by the expression

$$T_c = (\ln 2)/(\lambda_c).$$

Li et al. (1979) showed that the half removal time of ^{228}Th (and by analogy other reactive pollutants such as plutonium) from surface waters by settling particles was about 185 ± 35 d in the open ocean, 70 ± 10 d on the slope, 28 ± 2 d in outer shelf waters, and 17 ± 1 d in inner shelf waters during the fall of 1974. In Narragansett Bay, Santschi et al. (1980) reported $^{228}Th/$ ^{228}Ra activity ratios ranging from 0.002 to 0.021 with corresponding half removal times ranging from 1.5 to 15 d. In addition, they determined that the settling velocities of Th containing particles ranged between 1 and 11 m d^{-1} and that sediment resuspension was the main control on the removal behavior of thorium with fast removal occurring when sediment resuspension is high.

Pollutant—particle accumulation

The large variations in pollutant accumulation patterns that occur in estuarine, coastal, and marine environments are primarily a result of variations in particle size, organic content, net deposition rates, and sediment mixing. The ability of fine particles and organic material to effectively scavenge pollutants from the water column has been discussed previously. This ability is enhanced by the fact that fine particles are more easily resuspended than coarser particles, remain in solution longer, and are swept across wide areas before coming to rest in an environment that is topographically or dynamically suited for fine-particle and associated pollutant accumulation. Such dynamically-suited places include the turbidity zone areas of estuaries (Huggett and Bender, 1980; Cutshall et al., 1981), behind dams or other objects that hinder flow (Olsen et al., 1981b), dredged or protected areas in harbors (Summerhayes et al., 1977; Olsen et al., 1978; Bopp, 1979), marsh or cove areas (Windom et al., 1976), or topographic lows on the shelf (Carmody et al., 1973; Farrington and Tripp, 1977; Freeland et al., 1979; Nittrouer et al., 1979; Olsen et al., 1980; and Bothner et al., 1981). Rates of net accumulation and sediment mixing may also be high in these localized areas, resulting in excessive pollutant inventories or burdens as well as higher

pollutant concentrations relative to coarser-grained areas within the same environment.

Sayre et al. (1963) and Pickering (1969) showed that the distribution of radioactivity in the bottom sediments of the Columbia and Clinch Rivers, respectively, was primarily controlled by fine-particle accumulation. The distribution of trace metals and chlorinated hydrocarbons in the sediments on the Mississippi Delta and in the Gulf of Mexico was also governed primarily by sedimentary processes (Giam et al., 1976; Trefry, 1977). Huggett and Bender (1980) showed that the highest concentrations of kepone in the sediments of the James River estuary were 15 to 60 km downstream from their source as a result of estuarine flow and the location of the turbidity maximum. Cutshall et al. (1981) showed that this area is also a zone of rapid sediment deposition (Fig. 7), and as a result kepone-contaminated sediments are rapidly being buried and diluted by uncontaminated particles. Similarly, Olsen (1979) showed that the major zone of reactor-released radionuclide accumulation in the Hudson estuary is not near the reactor site but is located more than 60 km downstream in New York's inner harbor where harbor dredging and estuarine processes are causing fine particles to accumulate at rates as high as 10 to 20 cm yr^{-1}. Particles and associated pollutants that escape an estuary appear to accumulate, with fine-grained material from other sources, in depressions along the shelf bottom (Olsen et al., 1980). These near-shore mud deposits, however, are suspended and dispersed by major storms (Harris, 1976; Freeland et al., 1979).

Physical or biological mixing of the sediments, in areas where net accumulation rates for particles are low, may also increase pollutant inventories or burdens and thus contribute to pollutant accumulation patterns. Aller et
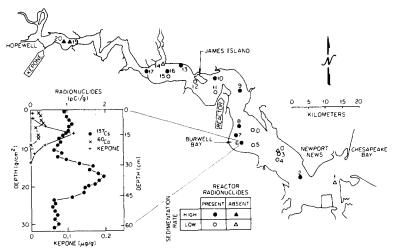

Fig. 7. The distribution ^{137}Cs, ^{60}Co, and kepone in a core collected in the James River estuary approximately 60 km downstream from the kepone source. These data indicate that estuarine sedimentary processes are causing rapid particle and kepone accumulation in specific areas (taken from Cutshall et al., 1981).

al. (1980) showed that in Long Island Sound, where sedimentation rates are $<0.1\,cm\,yr^{-1}$, [234]Th inventories can be increased in the sediments as mixing exchanges [234]Th-poor for [234]Th-rich particles with the overlying suspended material. Such a process may also be occurring in the large mud hole on the shelf off Massachusetts where Bothner et al. (1981) observed that the sediment accumulation rate is only $0.025\,cm\,yr^{-1}$ but that the inventory of excess ^{210}Pb is twice as great as the atmospheric flux.

Understanding sedimentation rates in the marine environment is important for determining the ultimate fate of particles and associated pollutants as well as for ascertaining particle-pollutant fluxes and histories. Sedimentary cores represent a historical record of metal, radionuclide, and organic (both synthetic and natural) accumulation (Goldberg et al. 1977; 1978; 1979). Changes in the amounts and types of these pollutants are clearly evident with depth in the cores (Fig. 8), due to both increased anthropogenic inputs and diagenetic reactions (reduction and mobilization, reduction and sulfide precipitation, and microbial degradation). Knowing the sedimentation rate, one can recognize pre-industrial baseline distributions and date increases in
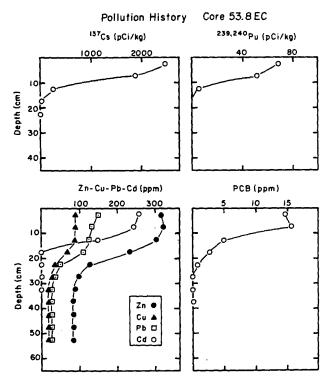

Fig. 8. The vertical distribution of Cd, Cu, Zn, Pb, PCB's, ^{137}Cs, and [239,240]Pu in the sediments of the Hudson River estuary. Despite their different chemical properties and modes of input, their depth distributions are quite similar, attesting to the ability of fine particles to transport and accumulate a wide variety of reactive pollutants (taken from Olsen, 1979).

contaminants that may suggest contaminant sources and transport paths (Carpenter, 1977). In addition, combining pollutant concentration analyses with radionuclide chronological data allows one to determine the rates of diagenetic processes that change pollutant distributions and calculate fluxes of pollutants to the sediments.

Pollutant—particle remobilization

As particles settle and accumulate, bacterial decomposition of organic matter (whether natural or anthropogenic) utilizes oxygen and recycles nutrients and other chemicals in biogenic detritus. In ocean waters, these metabolic processes primarily occur in, or just below, the thermocline, giving rise to a water layer depleted in oxygen but enriched in recycled nutrients and trace metals (Fig. 3). In sediments, these biologically mediated reactions can change Eh—pH conditions which, in turn, can make some compounds, such as Mn, more soluble and other compounds, such as Cd, less soluble (Bender, 1976). Bacterial degradation of petroleum hydro-carbons, synthetic organics, or biogenic detritus may also form more soluble organic or organic—metal degradation products (such as methylmercury complexes) that are themselves harmful and that may escape from sediments to re-enter aquatic food chains (de Groot, 1973).

The utilization of oxygen during organic matter decomposition can create anoxic conditions. Such conditions commonly occur in sediments but may also occur in the overlying waters where the bottom water is stagnant (fjords, for example) or where nutrient pollution has enhanced excessive phytoplankton growth. In anoxic sediments biologically mediated reactions may reduce carbon dioxide (CO_2) to methane (CH_4), nitrate (NO_3^-) to ammonia (NH_3), sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S), and some metals, such as iron and manganese, to more soluble divalent forms. As concentrations of dissolved metals, recycled nutrients, and other chemicals increase in sediment—pore waters, a vertical concentration gradient develops that allows for the diffussive remobilization of these substances out of the sediments and into the overlying water.

Work by Lynn and Bonatti (1965), Bender (1971), Bischoff and Sayles (1972), Calvert and Price (1972) and Morris et al. (1982) showed that solu-bilized Fe and Mn diffuses upward in sediment pore waters and either reprecipitates in the more oxidizing sediments near the sediment—water interface or are released if reducing conditions persist too close to the inter-face. Although released iron is oxidized and removed from the water very quickly, the residence time of dissolved Mn^{2+} may be of the order of 2 to 10 d before oxidation and reprecipitation (Emerson et al., 1979). Graham et al. (1976) reported that the flux of dissolved manganese from the sediments to the overlying water in Narragansett Bay is about 1 to 2 $\mu g\,cm^{-2}\,d^{-1}$ and that manganese may undergo several cycles in and out of solution. Evans et al. (1977), Turekian (1977a) and Spencer et al. (1981) indicated that

this redox cycling of manganese may play an important role in the sorption and/or release of other metals and pollutants. Olsen et al. (1981a) showed that ^{60}Co may be released from New York harbor sediments in association with the release of reduced manganese, and Grieve and Fletcher (1977) showed that cycles of zinc in the Fraser River estuary correlate well with cycles of Fe and Mn.

In addition to diffusion, remobilization of pollutants across the sediment—water interface may also occur with sediment resuspension by currents (Bothner et al., 1980), bioturbation (Aller, 1978), or dredging operations (Lindberg and Harriss, 1977). For example, Lindberg and Harriss (1977) studied the mechanisms for mercury release from sediments in Mobile Bay and in the Florida Everglades. Under anaerobic and reducing conditions dissolved Hg (like Cd) may be immobilized by precipitation as an insoluble sulfide. Methylation of mercury into soluble complexes may occur, but concentrations of methylated mercury were so low in the sediment pore waters that the diffusive flux of this species was a relatively unimportant mechanism for Hg remobilization in these environments. Sediment resuspension by dredging, currents, and organisms, on the other hand, had a significant effect on Hg remobilization. Several other studies, including Perkins et al. (1966), Bothner et al. (1980, 1981), and Benninger and Krishnaswami (1981) also showed that sediment resuspension is a major mechanism for the remobilization of accumulated pollutants.

Finally, the dredging of estuary sediments and subsequent dumping of this dredged material in shelf waters was shown to be the primary mechanism responsible for the net transport of a wide range of particle-associated pollutants to the marine environment. Farrington (1980) estimated that 4×10^3 Mg of hydrocarbons (or $\sim 2\%$ of the 1973 global discharge rate for production and drilling) are dumped each year into the New York Bight area. Bopp et al. (1981) estimated that 1.86 Mg of PCBs were also dumped into the New York Bight in association with dredge spoil disposal. Olsen et al. (1981a) showed that the Hudson estuary is an effective trap for plutonium and that harbor dredging is the primary mechanism by which riverborne plutonium is transferred to the shelf.

When dumped, pollutants can partition into a semi-fluid phase or a solid phase. The semi-fluid phase is typically retained in the water column for some period of time and may undergo advection from the dump site while the solid phase settles rapidly to the seabed (Joyce, 1979). In the New York Bight the dredge-spoil dump site covers an area of 36 km^2 and has a maximum height of about 14 m above the normal topography (Dayal et al., 1981). Fuhrmann and Dayal (in press) calculated that the rate of accumulation at the dump site ranges from 50 cm yr^{-1} near the apex of the deposit to 6 cm yr^{-1} at the periphery. Although no significant amounts of dissolved Zn, Cd, Cu, or Fe appear to be remobilized from the pore waters of this site, there is evidence for local resuspension and redistribution of fine particles and associated pollutants to the fringes of the dump site as a result of

storms, tidal action, and the dump events (Dayal et al., 1981). Using acoustic profiling to trace individual dump events, Proni et al. (1976) demonstrated that there is an outward pulse along the bottom away from the dump event. This pulse was observed to reach velocities of 50 to 60 cm s^{-1} providing a mechanism to erode and move particles and their associated pollutants away from the dump site.

SYNTHESIS

The general concensus of most of the reviewed studies is that many pollutants rapidly become associated with particles and that these particles are effectively trapped in the estuarine environment. This association may result from ionic sorption and flocculation (Edzwald et al., 1974), organic complexation and flocculation (Sholkovitz, 1976; Boyle et al., 1977b), hydrophobic interactions with particle surfaces (Parks, 1975), bio-aggregation (Meade, 1972), or sorption and co-precipitation with Mn—Fe hydroxides (Krauskopf, 1956; Jenne, 1968; Murray, 1975). The net transport of particles and associated pollutants is downstream in the lower salinity surface layer of an estuary, but as these particles settle to the more saline bottom layer they may be transported back upstream and effectively trapped by estuarine circulation (Postma, 1967; Meade, 1972). Rates of particle—pollutant deposition in estuaries are generally high (Olsen, 1979), and particle—pollutant accumulation patterns are governed to a great extent by estuarine sedimentary processes. Although rapid burial in estuarine sediments provides a good mechanism for the removal of various pollutants from the system (Cutshall et al., 1981), several processes, including sediment resuspension (Lindberg et al., 1975; Bothner et al., 1980), diffusion from anoxic sediments (Graham et al., 1976), and dredging—dumping operations (Dayal et al., 1981) can re-introduce pollutants to marine waters.

Dissolved nutrients that may escape an estuary stimulate productivity in near-shore coastal waters and are rapidly removed by biological processes, frequently forming plankton plumes at the estuary mouth (Malone, 1976). Other reactive pollutants supplied to shelf waters via escape from the estuary, ocean dumping, or eolian transfer will probably be removed within a month (Li et al., 1979). Major removal mechanisms for pollutants in shelf waters include sorption onto resuspended sediments (Santschi et al., 1980), incorporation into living organisms and sinking organic debris (fecal material and dead organisms), or boundary-layer scavenging in association with the redox cycling of Mn—Fe hydroxides (Bacon et al., 1976; Spencer et al., 1981). On the shelf, fine particles and associated pollutants accumulate in topographic lows, such as between sand waves (Freeland et al., 1979; Olsen et al., 1980), or in major morphological depressions, such as basins (Trefry, 1977; Nittrouer et al., 1979; Dayal et al., 1981), channels (Carmody et al., 1973), or canyons (Farrington and Tripp, 1977). Net deposition, sediment mixing, and exchange with the overlying suspended matter cause these mud deposits to act as pollutant sinks (Li et al., 1979; Aller et al., 1980; Bothner

et al., 1981). Resuspension from these deposits, however, may redistribute particles and pollutants over the shelf (Biscaye and Olsen, 1976; Bothner et al., 1981; Benninger and Krishnaswami, 1981). The ultimate fate of this mobile pool, that is, what fraction is captured and buried in shelf sediments, what fraction is carried beyond the shelf to the open ocean, what fraction is returned to the estuary, and what fraction still resides in the mobile pool of particles and pollutants moving back and forth between the sediment and water column, is unknown. Consequently, our knowledge is still insufficient to predict how a specific pollutant will be transported through an estuary, across the shelf, and into the deep sea.

In light of the important role that particles play in the transfer and fate of pollutants, it is surprising that so little is known about the spatial and temporal variations in size, surface area, concentration, composition, rate of settling, accumulation, and resuspension of particulate matter in the marine environment. In addition, more fundamental research on the biogeochemical processes and mechanisms whereby pollutants are attached to or released from particles is needed to improve our predictive capabilities. Much of the previous work on particle—pollutant associations utilized bulk samples and bulk analytical techniques. Such characterizations of the sample treated as a whole (or in bulk) have advantages in that the data is of good analytical precision, is easily quantified, and can be used to observe statistical variations or correlations in pollutant or elemental abundances within and between different areas. More research, however, should be directed toward examining the surface morphology and surface chemical characteristics of discrete particles using scanning electron microscopy with an electron microprobe, ESCA, or EDXRF. Although it is more difficult to quantify results from these techniques, they have an advantage in that one can observe directly the nature of the particulate matter, associations of different particle types, chemical inhomogeneities along the surface that may result in large differences in chemical reactivity, and specific particle—pollutant associations (Nelsen, 1978).

Finally, of prime importance in any predictive model is a quantitative understanding of the rates associated with the biogeochemical processes that affect pollutant—particle dynamics. These process-oriented transfer rates include: input rates into the marine environment (river discharge, riverborne particle fluxes, eolian fluxes, pollutant input histories, and ocean dumping), exchange rates across the air—sea interface (aerosol deposition, sea spray, hydrocarbon volatilization, and gas exchange), transport rates in the water column (advection, diffusion, turbulent mixing, biological transfer, settling, degradation, and recycling), and transfer in and out of the sediments (accumulation, diagenesis, pore-water diffusion, sediment mixing, and resuspension). Quantitative values for the above transfer rates are necessary to determine particle—pollutant fluxes and to thus define how long a specific pollutant will persist in different parts of the marine environment. Only with such an understanding will it be possible to develop accurate pollutant

transport models and to predict the fate of particles and their associated pollutants in the environment.

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