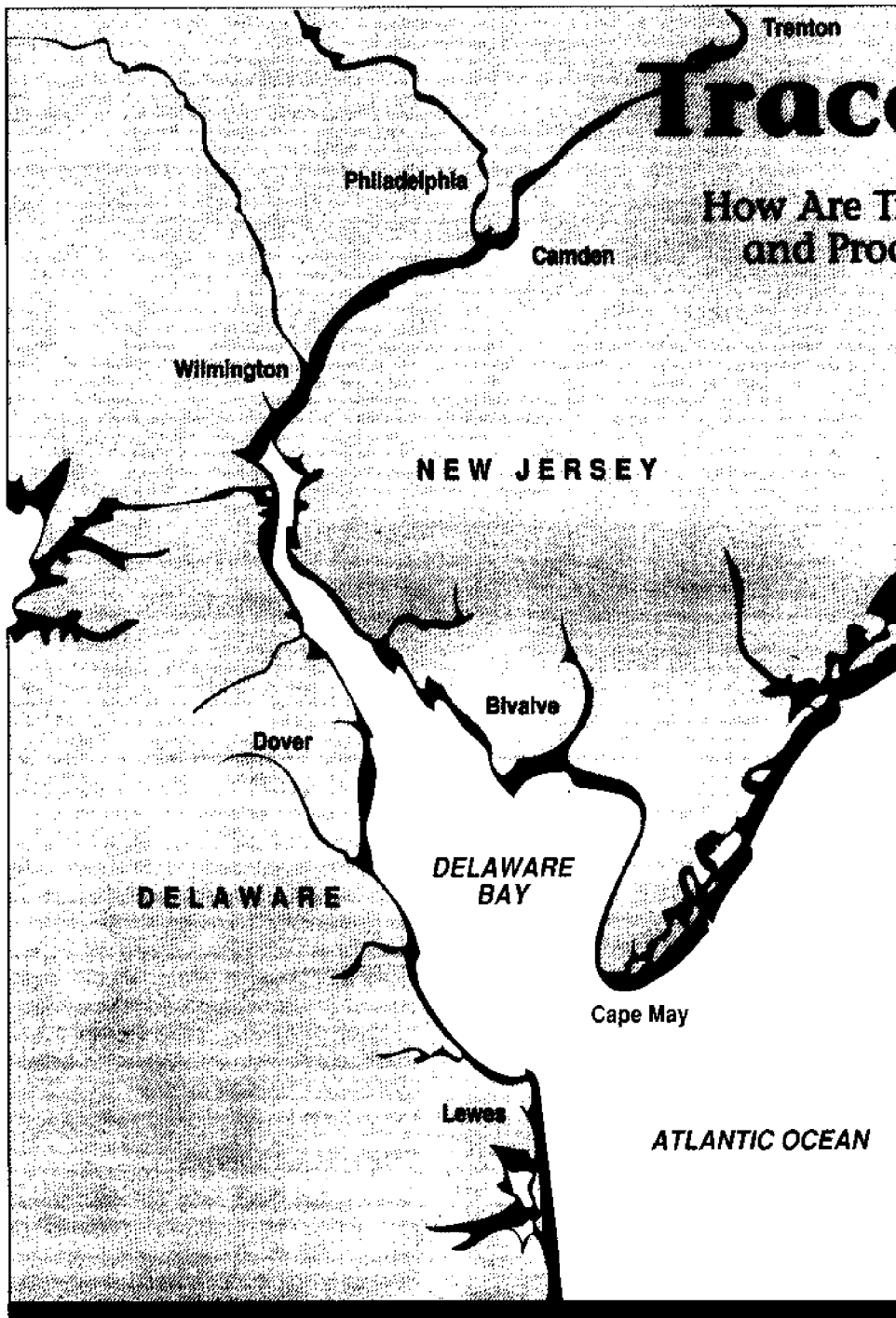


# DELAWARE ESTUARY SITUATION REPORTS

This series of reports is devoted to discussion of current issues relevant to conservation, use, and development of Delaware Estuary resources, and of concern to managers, decision makers, and the general public.

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## Trace Metals

### How Are Trace Metals Transported and Processed in Delaware Bay?

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This report is designed to answer the following questions about trace metals: What are trace metals? Where do trace metals in aquatic environments come from? What happens to trace metals that enter the estuary? These basic questions must first be answered before we can pose a more relevant question: do trace metals pose problems or risks for people or for the living resources of the Delaware Estuary?

Trace metals are important because they can be both essential for all life and harmful when introduced by humans to the natural aquatic environment in unnatural amounts. Generally speaking, if the amount of sunlight is adequate, then the quantity of some major or minor nutrient will always limit how much algal growth occurs in natural waters. However, when people are present and using such waters to dispose of trace metals concentrated, for example, during ore refinement or the manufacture of metal products, it is just as likely that a toxic metal is limiting plant growth. It doesn't take much metal disposal in coastal waters and estuaries to have an adverse effect on marine life because toxicity can occur at very low levels, e.g., one millionth of a gram ( $\mu\text{g}$ ) of metal per kilogram or liter of water. This is roughly equivalent to a grain of sand in an Olympic-sized swimming pool.

With the support of the National Oceanic and Atmospheric Administration (through the University of Delaware Sea Grant College Program), the National Science Foundation, and other agencies, our research team has been studying these questions extensively over the past decade, especially relative

*The Delaware Estuary, a multi-purpose bistate resource.*



University of Delaware  
 Sea Grant College Program

to the Delaware Estuary. We have constructed a special laboratory and developed lab procedures that may be described as "ultraclean" because they eliminate extraneous sources of trace metals that can contaminate environmental samples. This has greatly increased the reliability of our measurements. This report explains many of the concepts of trace-metal chemistry in estuarine and coastal environments and illustrates these concepts with findings from our research on the Delaware Estuary.

### What Are "Trace Metals?"

The vast majority of the Earth's atmosphere, hydrosphere, and geosphere is comprised of just a few elements: hydrogen, oxygen, nitrogen, carbon, silicon, and aluminum as well as the lighter alkalis (sodium and potassium) and alkaline earth metals (magnesium and calcium). However, other elements are present in relatively small proportions, or trace amounts. Metals, in general, are a group of elements that in their pure forms have some similar properties, such as the ability to conduct electricity and to be molded into industrial structures (e.g., wires, rails, and girders). However, metals are usually found in the Earth's crust in forms that bear little resemblance to their pure, elemental forms. More often, metals react with nonmetals to form salts and other compounds that exhibit a wide range of solubility and reactivity in seawater.

Certain trace metals, such as cadmium, chromium, copper, lead, mercury, and zinc, are moderately rare in the natural environment, while others, such as iron and manganese, are more common. Other elements, such as arsenic and selenium, are *metalloids* rather than true metals—that is, they have properties of both metals and nonmetals—but are often considered in this category. Most trace metals occur in a variety of *species*, a word used in chemistry to denote the different forms that an element may take.

Many trace elements (e.g., iron, manganese, copper, cobalt, selenium, and zinc) are essential for life within certain concentration limits. However, above required concentrations, many of these elements (e.g., zinc, copper, and selenium) can have adverse effects. The same thing may be said of trace elements that are not essential for life (e.g., cadmium, mercury, lead)—above minimal concentrations these elements are toxic. Since industrial activities such as metal refining, production, and plating commonly concentrate and release trace metals to the environment, levels may accumulate that are considered hazardous to aquatic organisms.

### Properties of Trace Metals

Trace metals can be grouped according to their fundamental chemical properties (Table 1). Type A metals tend to form positively charged ions that will react with suspended particles and negatively charged ions such as oxygen. Type B metals are inclined to form stronger associations with organic matter. They therefore tend to be more stable in water.

Both types of trace metals are found in natural waters either as dissolved species or attached to particles. This distinction is often defined by filtration procedures. Typically, chemical species passing through filters with a pore size less than 0.4 micron (a micron is one millionth of a meter) are called "dissolved," recognizing that this includes metals present as *colloids*, undissolved particles small enough to remain suspended in fluid indefinitely. Dissolved metals and colloids will not settle to the bottom and can only be removed from natural waters by forming precipitates, adhering to surfaces (adsorption), clumping together to form larger particles (flocculation), or becoming a part of living organisms (assimilation). Metals attached to or forming particles larger than 0.4 micron are removed from natural waters largely by physical settling to the sediments.

### Trace Metals in the Coastal Zone

Coastal waters represent a mixing of fresh and saline waters in a zone between land and sea. Sources of fresh water and its associated chemicals include direct atmospheric precipitation and indirect runoff in rivers and groundwaters. The saline sources are ocean waters, which are circulated landward by tidal forces, often across relatively shallow shelves.

Zones of mixing confined to drowned river valleys or lagoons are termed estuaries. To facilitate commercial transportation, urban populations and their industrial activities are often located at or near the *fall line*, the inland limit of tidal influence in an estuary. Dredging is often used to maintain navigational channels. Historically, these activities have made coastal waters, and estuaries in particular, vulnerable to trace-metal contamination.

Land clearing for industrial and agricultural activities and subsequent erosion have converted most coastal waters from being clear to *turbid*, or clouded with suspended particles. This is especially true of the upper, freshwater reaches of estuaries where large particle loads are trapped and resuspended by the opposing hydrological forces of river currents and tides, forming a so-called *turbidity maximum*. The turbidity of this geochemical zone affords an excellent environment for particulate reactions such as adsorption and flocculation to occur.

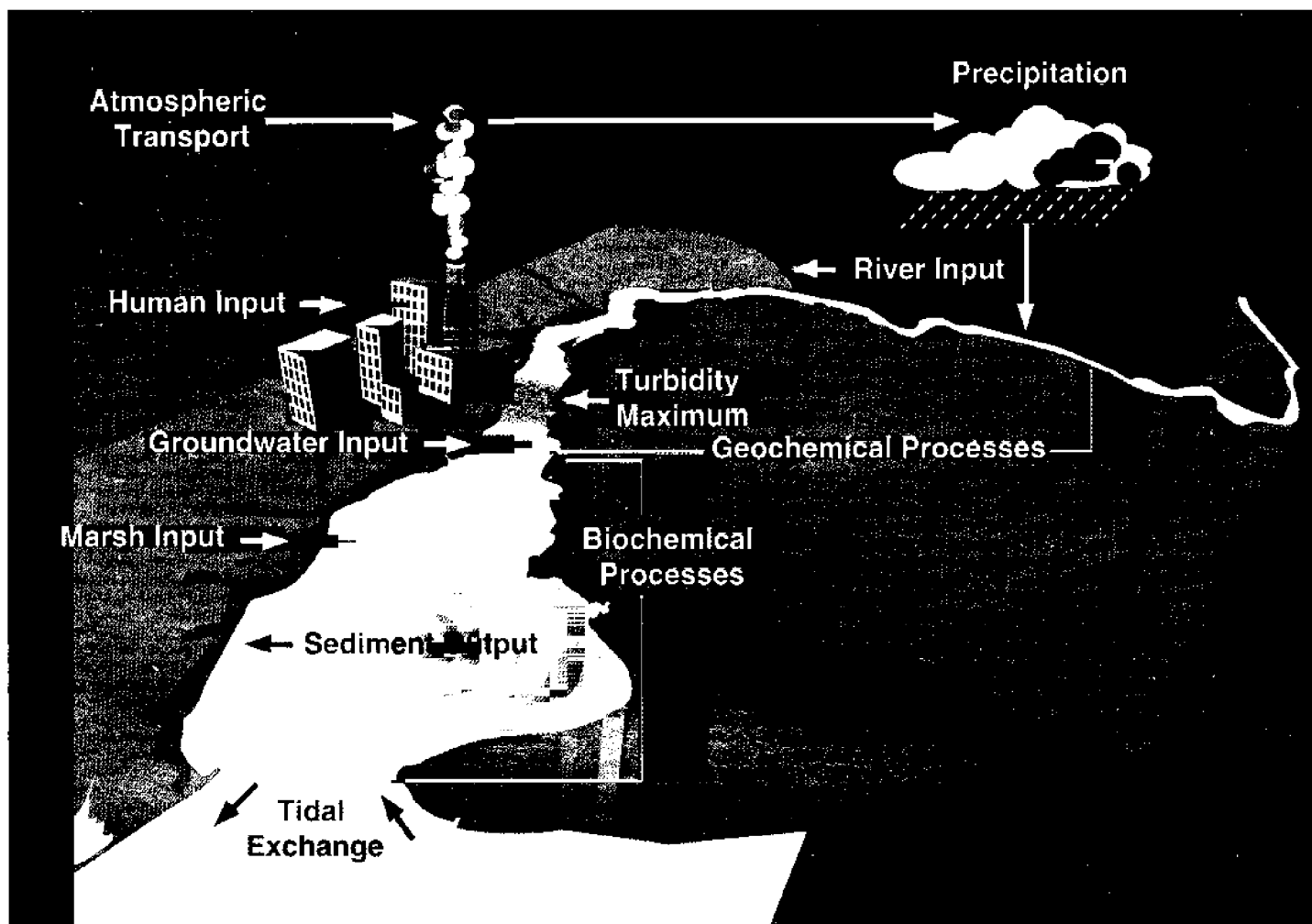
Because suspended particles limit the penetration of light, photosynthetic plant life in the turbidity zone is limited. As particles settle out, however, the estuary downstream of the turbidity maximum becomes a biochemical zone. That is, the more abundant light allows more *primary production*—the photosynthesis of organic molecules by green plants, which release natural organic compounds during their growth, death, and decay. Figure 1 is a diagrammatic representation of an estuary as a biogeochemical reactor.

### Trace-Metal Sources

Scientists have long recognized that trace metals enter rivers and groundwaters through the natural weathering of rocks into soils and through additional human sources including wastes associated with metal-ore refinement, sewage discharge, and the use of metal-based biocides (e.g., antifouling marine paints) and corrosion control measures (e.g., sacrificial anodes). However, we have been learning that the sources of trace metals and their routes to the sea are far more complex than previously imagined.

**Table 1**  
**Chemical Properties of Trace Elements**

Type A	Type B
<ul style="list-style-type: none"> <li>◆ Iron (Fe), manganese (Mn), cobalt (Co), chromium (Cr)</li> <li>◆ Forms inorganic ions in seawater</li> <li>◆ Particle reactions (precipitation, adsorption, flocculation)</li> <li>◆ Removal by sedimentation</li> </ul>	<ul style="list-style-type: none"> <li>◆ Zinc (Zn), nickel (Ni), copper (Cu), cadmium (Cd), silver (Ag), lead (Pb), mercury (Hg)</li> <li>◆ Forms organic complexes in seawater</li> <li>◆ Biological reactions (assimilation)</li> <li>◆ Removal by tidal export</li> </ul>



*Figure 1. A diagrammatic representation of the Delaware Estuary as a biogeochemical system. The processes that influence the behavior of trace metals in the estuary and the major inputs and outputs depicted would also be found in many estuaries with similar characteristics.*

To begin with, natural weathering reactions are being disturbed by the fallout of atmospheric pollutants, which not only fundamentally alter or accelerate chemical weathering by increasing the acidity of precipitation, but contribute large amounts of toxic trace metals in themselves. These metals originate concurrently with acids in the burning of fossil fuels for power or during metallurgical processing.

Second, runoff containing weathered or atmospherically deposited trace metals often finds its way into aquifers, where it can be retained or recharged according to subterranean chemical reactions and hydraulic characteristics. Third, when the fresh discharge enters the saline waters of estuaries, a series of reactions can adhere trace metals to particles for sedimentation or form trace-metal complexes with organic chemicals for discharge to the sea. Fourth, even when deposited in the sediments, estuarine trace metals can be subsequently remobilized back to the water by reactions associated with organic matter decomposition that increase the solubility of trace metals, or by the action of

salt ions displacing metals attached to particles. Last, the sea itself may introduce trace elements to the estuary by accumulating metals from atmospheric fallout over the large area of the coastal shelves and carrying them landward with the tide.

### Trace-Metal Reactions

Upon reaching the estuarine environment, trace metals display a variety of behaviors. The presence of sea salt has a profound effect on the behavior of other dissolved substances. Pure fresh water acts as an insulator for dissolved substances; their atoms may be held close together yet not feel the effects of other atoms nearby. However, salt adds charged particles to the mixture: positively charged sodium ions and negatively charged chlorine ions. These ions act like magnets, pulling small particles together to form larger particles. Upon encountering the first traces of sea salt, many trace metals carried by rivers are converted from dissolved to particulate forms through the

processes of precipitation, adsorption, or flocculation. In precipitation, metal ions react with other ions to form new oxide salts. In adsorption, metals react to more insoluble solids (e.g., rust), or are exchanged on reactive surfaces. In flocculation, also referred to as "salting out," tiny (colloidal) particles clump together to form larger ones in the presence of seawater.

However, this pattern of forming larger particles in the presence of seawater can also be reversed. For example, with increasing salinity, some adsorbed trace metals can be desorbed, or converted back to dissolved form through the action of ion exchange, where one ion is substituted for another in a compound. The metals most affected are those that tend to form large, positive ions with low charge, including manganese and cadmium. These metals tend to desorb at lower salinities because of the greater availability of ion exchange sites along with higher numbers of particles in the turbidity maximum, the same salinity zone where other metals tend to be rapidly removed from solution by flocculation.

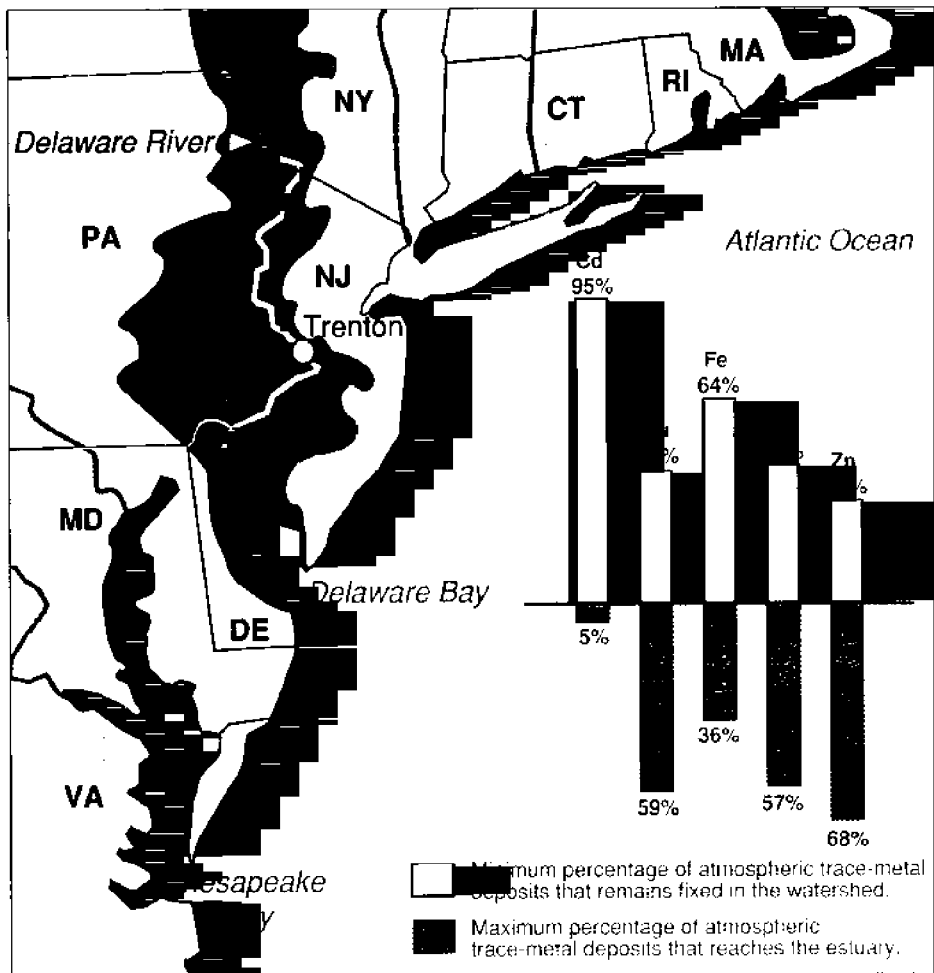


Figure 2. Of the total amount of atmospheric input for several trace-metals that fall on the Delaware Estuary watershed (black area on map), the minimum percentage that remains in the watershed is shown by the white bars. The remainder (blue bars) reaches the estuary across the fall line at Trenton, either directly through surface runoff or indirectly by groundwater seepage.

Trace metals also play several unique biogeochemical roles in estuaries. Some become involved in primary production by algae, which can result in uptake and recycling of trace metals along with organic matter. Trace metals can react with nutrients like phosphate or reduced species like sulfide, forming solid precipitates (e.g., iron phosphate) that become buried in the sediments. And some trace metals involved in sedimentary reactions can provide energy for bacterial activity in the sediments, thus contributing to the cycling of other elements, including nutrients.

### Trace-Metal Removal

As a result of their behavior, trace metals have a number of removal sites in the estuary. Type A trace metals, which readily flocculate from dissolved to particulate form, may settle out as integral components of the bottom sediments. In major East Coast estuaries, including the Delaware, bottom sediments are extensively dredged to maintain shipping channels

and are removed from the system to dry land. Very fine, flocculated precipitates may also remain suspended long enough to be transported to settling areas such as the surrounding salt marshes or exported to offshore coastal areas.

After deposition in estuarine sediments, degradation of organic matter by bacteria can dissolve particulate trace metals, resulting either in their return to the water column or in the formation of new solid phases. This re-release of metals from the sediment to the water, termed *diagenesis*, is largely promoted by the sulfate ion. Bacteria use sulfate as an oxidizing agent in a process referred to as sulfate reduction. Since a primary by-product of sulfate reduction is sulfide, many trace metals in estuarine sediments are converted to solid sulfide precipitates, such as iron sulfide or manganese sulfide, removing them from the water.

Trace metals may also be removed from estuaries through uptake by organisms and incorporation into the marine food web, which may eventually lead to

human consumption. In addition to absorbing or removing dissolved trace metals from the water, many aquatic organisms can actively excrete organic compounds called *chelators* that bind to trace metals, converting them to stable dissolved forms that can be more readily incorporated into living tissues.

However, estuarine organisms are usually viewed as merely a temporary repository for trace metals, since the organisms will eventually die and be deposited in the sediments or washed to sea like other forms of trace metals. Ultimately, trace metals have just two major pathways out of an estuary: incorporation into estuarine sediments, or export in dissolved and particulate form to offshore waters.

### Trace-Metal Inputs to the Delaware Estuary

In the remainder of this report, specific findings are reported for the Delaware Estuary that illustrate the concepts introduced above. The references cited are primarily the published works of the author and are not meant to comprise a comprehensive review of estuarine trace-metal research. Although these findings are specific to the Delaware, the concepts should generally apply to other large estuaries with similar characteristics. The differences in trace-metal behavior between estuaries are thought to depend as much on differences in their physical characteristics as on their biogeochemistry. This should be borne out as similar studies progress in other estuaries.

The Delaware River is by far the dominant source of fresh water to the Delaware Estuary. By the time the river reaches the fall line near Trenton, New Jersey, it carries a cumulative load of trace metals from atmospheric deposition (precipitation), natural weathering reactions, and human-derived sources in the vast watershed upstream. However, not all the trace metals deposited on the watershed reach the estuary through surface runoff or groundwater transport. This is illustrated in Figure 2, which shows the maximum percentage of total atmospheric flux for several metals deposited in the watershed that reaches the river at the fall line. *Flux* is defined as the amount of metal passing a particular point or area over time. As Figure 2 indicates, the atmospheric flux that remains in the watershed generally equals that entering the estuary at the fall line. (Cadmium, a heavy metal, is an exception because it is more complexed in the watershed.) This means that the watershed represents a large reservoir of trace metals that have been building up, presumably in the soil,

over the last two centuries of industrial activity. The propensity of these metal reserves to be remobilized at a later date depends both on the nature of the trace metals and the future use of the watershed and its associated groundwaters.

The Delaware River's metal burden, the total amount of metals carried by the river at a given time, varies seasonally, with minimum burdens occurring during the drier summer months and maximum loads during the wetter winter and spring. Particle-reactive metals such as iron enter the estuary in increased loads during the spring runoff. This most likely reflects the melting of the winter snowpack and the associated release of its accumulated trace metals. Other metals such as zinc show a much more uniform seasonal distribution.

The impact of metropolitan discharge can be seen by comparing concentrations of dissolved trace metals above and below the Philadelphia-Camden region of the upper Delaware Estuary. When the input of metals crossing the fall line north of Philadelphia is compared with that entering the estuary to the south, we find that 25–50% are introduced in the urban area (Church et al. 1988). Compared to other rivers on the East Coast, the Delaware has among the highest concentrations of trace metals (Table 2). Its levels are similar to those of the Hudson River, with New York City located near its point of entrance to the Atlantic Ocean.

For the last decade, we have monitored trace metals in precipitation at Lewes, Delaware, near the mouth of Delaware Bay (Church et al. 1984, Church and Scudlark 1991). Trace-metal concentrations there appear to match or exceed those of other sites around the Chesapeake Bay region suggesting regionally

important sources (Scudlark et al. 1994). Thus, values from Lewes should be representative of the Delaware watershed and can be used to compare wet atmospheric inputs with riverine inputs. Since metal concentrations in precipitation often exceed local river waters, their flux to the watershed and estuary could be significant.

### Trace-Metal Behavior in the Delaware Estuary

Before we discuss the behavior of specific metals in the Delaware Estuary, let's imagine what would happen if we added a large quantity of a single trace metal to the upper reaches of a hypothetical estuary. At this point in the estuary, the salinity is zero. As this fresh water moves downstream, it is gradually diluted with seawater until the salinity of the estuary matches that of the ocean at about 30 parts per thousand (‰). If we plot the concentration of the trace metal versus salinity at points downstream, we would expect to see the concentration of the metal gradually decreasing by dilution (Figure 3). Theoretically, if no other processes are adding or removing the metal along the way, our graph will be linear, and the metal is said to exhibit *conservative* behavior.

Now, imagine the effects on our plot if a new source of the metal is added downstream, or if a reaction between the metal and sea salt suddenly removes the metal from solution. A plot that curves upward suggests that more of the metal is being added, while a downward curve suggests removal during downstream mixing. This type of behavior is termed *nonconservative*. In general, Type A metals (iron, manganese) tend to be nonconservative, while Type B metals (copper, zinc) are more conservative.

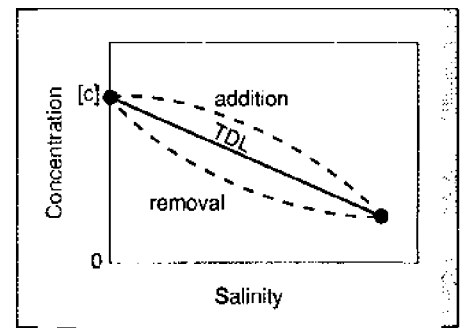


Figure 3. Theoretical dilution line (TDL) of a dissolved trace metal as salinity increases through dilution with seawater downstream from its source [c]. Dashed lines indicate the effects of trace-metal addition or removal processes on the TDL.

We have gathered this type of data for seven trace metals in the Delaware Estuary on 13 seasonal research cruises between 1978 and 1982. Figures 4 and 5 present the data collected for manganese and copper, representative Type A and B metals, respectively (Church 1986). These plots, which present both dissolved and particulate trace-metal concentrations versus salinity, reveal reactions between specific metals and sea salts.

As trace metals enter the Delaware Estuary, their geochemical behavior also responds to particulate matter present in the estuary. Trace metals are incorporated into estuarine particulates via three avenues: (1) the physicochemical processes that occur with the mixing of fresh and salt waters, such as adsorption and flocculation, whereby dissolved trace metals are converted to particulate form; (2) physical resuspension of particles bearing trace metals that had settled to the bottom; and (3) processes that incorporate trace metals into particles of biological origin.

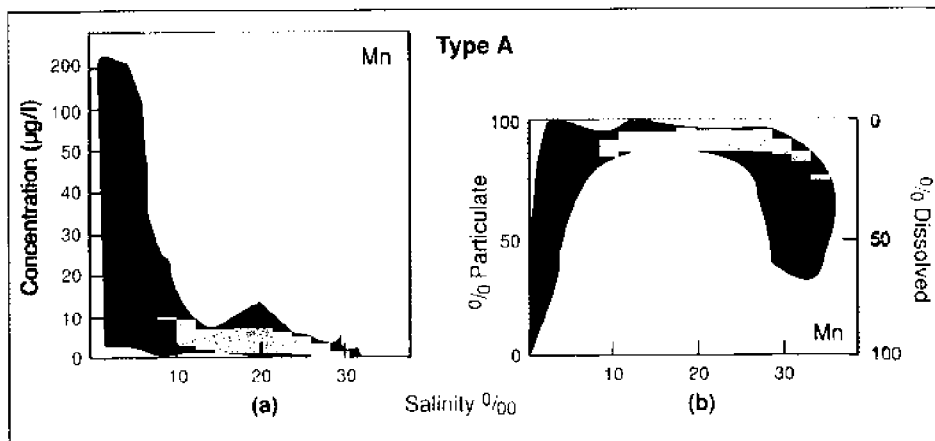
The first type of particle formation was discussed in a previous section. Dissolved Type A metals like manganese appear to be almost completely removed at the lower salinities near the turbidity maximum as they are converted from a dissolved to a particulate state (Figure 4a). At the same time, there is a corresponding increase in the percentage of particulate Type A metals, followed by a gradual decline as the particles settle out (Figure 4b).

The second type, physical resuspension, depends strongly on a hydrologic feature such as the turbidity maximum and settling patterns between this point and the estuary mouth in what is termed the *estuarine delta*. The position and intensity of the Delaware turbidity maximum is seasonally controlled—it migrates according to the balance of tidal and freshwater flows (Biggs et al. 1983). Heavier

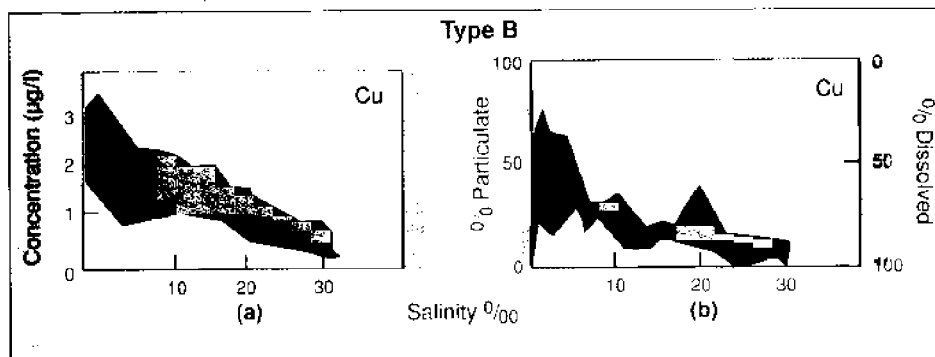
Table 2  
Concentration of Dissolved Trace Metals in  
Some East Coast Rivers in µg/l

	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Delaware <sup>1</sup>	0.17	0.42	2.36	32.9	155	3.86	0.27	12.1
Susquehanna <sup>2</sup>	0.089	1.0	1.21	57.3	655	5.75	0.21	2.62 <sup>b</sup>
Southeastern U.S. (avg.) <sup>3</sup>	0.078		0.56	30.7	18	0.26		0.64
Hudson <sup>4</sup>	0.25		3.24	31.9	10.7	2.41		8.83
Connecticut <sup>5</sup>	0.10		4.17	113	45.9			0.98 <sup>c</sup>
Potomac <sup>b</sup>								0.55

<sup>1</sup>Church et al. 1988. <sup>2</sup>R/V Cape Hatteras cruise, 3–10 March 1982. <sup>3</sup>Windom and Smith 1985. <sup>4</sup>Klinkhammer and Berdel 1981. <sup>5</sup>Wasilenchuck, D., University of Connecticut, personal communication, 1983. <sup>b</sup>Miller and Boyle 1985.



**Figure 4.** (a) Dissolved concentration and (b) percent dissolved and particulate loadings versus salinity for a representative Type A metal, manganese (Mn). Note that salinity increases downstream in the estuary. The shaded areas envelop most data points measured on 13 seasonal research cruises between 1978 and 1982. The concave shape of the graphs reveals the non-conservative, particle-reactive behavior typical of Type A metals, resulting from the conversion of dissolved to particulate forms as salinity increases.



**Figure 5.** (a) Dissolved concentration and (b) percent dissolved and particulate loadings versus salinity for a representative Type B metal, copper (Cu). The shaded areas envelop most data points measured on 13 seasonal research cruises between 1978 and 1982. The linear shape of the graphs reveals the conservative behavior typical of Type B metals, resulting from gradual dilution and biological processing downstream.

freshwater flows in the late winter and early spring both intensify the turbidity maximum and push it farther downstream. However, as Biggs and his colleagues have demonstrated, the amount of sediment crossing the turbidity maximum from upstream fluvial sources is not nearly enough to account for the amount of sediment settling in the estuarine delta and salt marshes. This is because the vast majority of upstream sediment tends to settle into the navigation channels and is removed by dredging. It therefore appears that either net erosion and widening of Delaware Bay is taking place or, more likely, that the bulk of the sediment in the salt marshes and estuarine delta must be derived from offshore sources.

The third type of particulate formation is biological. The high concentration of particles in the turbidity maximum tends to limit photosynthesis and the uptake of essential nutrient compounds. This leads to nutrient transmission to lower reaches

of the estuary where they can be utilized by phytoplankton (Pennock 1985). Thus, secondary biological particles can be produced at higher-salinity reaches. These include the shells of microscopic organisms that have assimilated trace metals into their structures or the particulate aggregates formed by deposit-feeding organisms. The latter serve as reaction sites for trace-metal uptake.

However, these same biological processes can in turn provide the dissolved organic matter that forms stable complexes with such trace metals as copper, nickel, zinc, and cadmium, which leads to the observed conservative behavior of most Type B elements (Figure 5a). This conservative behavior pattern resembles many of the primary inorganic nutrients (nitrogen, phosphorus), suggesting that these Type B metals are involved in the biological productivity cycles of the estuary. This group of metals can indeed form robust complexes with organic material of

biological origin (Johnston 1989). Such complexes contribute to essential enzymes used by all living systems. With such processing, Type B metals are actively assimilated by producers and can be incorporated into soft tissues or hard shells. Thus, the fate of these metals in estuaries depends on the fate of such parts: soft tissues degrade into dissolved complexes for export, while hard shells are deposited into the sediments (although these shells may be subsequently redissolved under the right conditions). Alternatively, Type B metals may be incorporated into organic sulfur complexes that are produced in abundance in salt-marsh sediments (Ferdelman et al. 1991)

In general, the concentrations of the particulate portion of both types of trace metals decrease at high salinities (Figures 4 and 5). As inorganic (Type A) or organic (Type B) particles, they settle out during the months of residence time in the Delaware Estuary in either the estuarine delta or the pervasive surrounding salt marshes. Here, in the sedimentary deposits, trace metals are actively recycled as organic matter decomposes and the metals are converted to more soluble forms (Lord and Church 1983, Luther et al. 1986).

### Trace-Metal Mass Balance for the Delaware Estuary

Attempting to balance the input and output of trace metals in the Delaware Estuary can be instructive because it gives us some indication of their relative magnitude. Differences between the various pools of trace metals reveal the retention of metals by sediments versus export to coastal waters. The inputs, or sources, include riverine input ( $F_r$ , dominated by the Delaware River), atmospheric deposition ( $F_a$ , both directly to open estuarine waters or indirectly to the watershed), and groundwater (about which little is known). Other indirect sources include salt marshes ( $F_m$ ) and sediment exchange. They are considered indirect because they represent the reintroduction of metals previously processed in the sediments. The outputs, or sinks, are either sedimentation ( $F_s$ ) or tidal flushing to coastal waters ( $F_e$ ).

We have constructed a budget for total fluxes of trace metals from data collected on the 13 seasonal cruises between 1978 and 1982 (Church 1986), which can be expressed by the equation

$$F_r + F_m + F_a = F_e + F_s.$$

The left side of the equation gives inputs to the Delaware Estuary, while the right side yields outputs (Table 3).

**Trace-Metal Inputs.** The percentage of trace-metal inputs to the estuary stemming from each of the three major sources is shown in Figure 6. The Delaware River is by far the largest freshwater contribution to the estuary. Thus, the freshwater flux of the river times the concentration of the metal in the river gives the fluvial metal flux to the estuary ( $F_r$ ). Other tributaries to the estuary have been sampled on occasion, including the Chesapeake and Delaware Canal, but their metal concentrations do not vary by more than a factor of two from the estuary. Thus, their contributions to its metal load are not significant (Church et al. 1988).

Although ungauged groundwaters are estimated to equal the gauged freshwater inputs, their trace-metal contribution to the estuary is hard to evaluate. It could be significant for metals that can be naturally reduced and solubilized under low-oxygen, subterranean conditions (e.g., manganese). However, much of the groundwater flow to the estuary is thought to originate on the New Jersey side, since less than 10% of the precipitation flux into the Pine Barrens region is gauged as freshwater stream outflow. Human and industrial activity there is sparse, so the groundwater trace-metal component may not be very significant and is not included in our equation.

The amount of precipitation times the average concentration measured at our station on the Delaware coast equals the wet deposition. Dry deposition (dust) is much more difficult to measure or estimate, but our estimates are that no more than half the total atmospheric deposition is dry, depending on the metal.

Atmospheric deposition of metals to the waters of the Delaware Estuary does not appear to be a significant quantitative term ( $F_a$ ). However, this may be an under-estimation for two reasons. Since the area of the Delaware Estuary's watershed is many times that of the bay itself, the actual atmospheric deposition component that crosses the fall line, and is thus counted as fluvial ( $F_r$ ), may be significant (Figure 2). Second, the atmospheric deposition to the estuary is direct to surface waters and, thus, could be qualitatively important to phytoplankton living in well-lit surface waters.

Salt marshes are prominent features of the Delaware Estuary. They continually undergo active sulfur and metal cycling, so their metal inputs may be important (Lord and Church 1983, Eastman and Church 1984, Luther et al. 1986, Ferdeman et al. 1991). Salt marshes are almost perfect collectors of atmospheric metal input and even appear to concentrate metal fallout from a much larger area because

	Fe	Mn	Co	Cu	Ni	Cd	Zn
<b>Input fluxes</b>							
River	400.0	135.8	0.62	2.41	3.90	0.20	12.87
Marsh	885.0	102.0	0.67	0.96	0.14	0.06	3.80
Atmosphere	1.4	0.2	0.02	0.14	0.10	0.02	0.56
Total input flux	1286.2	238.0	1.31	3.51	4.14	0.28	17.23
<b>Export fluxes</b>							
Tidal exchange	176.4	19.0	0.172	2.21	2.67	0.191	7.48
Sediments (calculated)	1110.0	219.0	1.14	1.30	1.47	0.09	9.75

the tide regularly brings trace metals into the marsh where they are incorporated into the vegetation or surface sediments (Pellenburg and Church 1979, Lord and Church 1983). In addition, salt marshes are the most active sediment-accumulation zones in the estuary and are thus the ultimate repository of much of the estuary's particulate metal load (Biggs et al. 1983).

The metal contributions of salt marshes ( $F_m$ ) are secondary since they involve the reintroduction of metals first introduced by the river or atmosphere. To estimate this flux, we multiply the net tidal flushing of the salt-marsh creeks by the highest concentrations observed in the creeks. While this may be an upper estimate, salt-marsh contributions to the Delaware Estuary can be equivalent to that of the river itself. In addition, production of strong organic sulfur complexes of salt marsh origin may make this flux even more significant (Luther et al. 1986).

**Trace-Metal Outputs.** The relative proportions of various trace metals that end up in each of the two major sinks are shown in Figure 7. Trace-metal sedimentation ( $F_s$ ) is difficult to estimate because of the recycling nature of salt marshes, the only areas of significant net sedimentation for the Delaware. Thus, this term is calculated by difference, once the term for estuarine export is quantified.

However, quantifying the trace-metal export to coastal waters is also difficult, because the net flux of water is a small difference between a large tidal influx and a slightly larger tidal outflow. Nevertheless, we have estimated the net water export to within a factor of two (Church 1986). When this is multiplied by the trace-metal concentration for the lower estuary, it yields the metal export ( $F_e$ ).

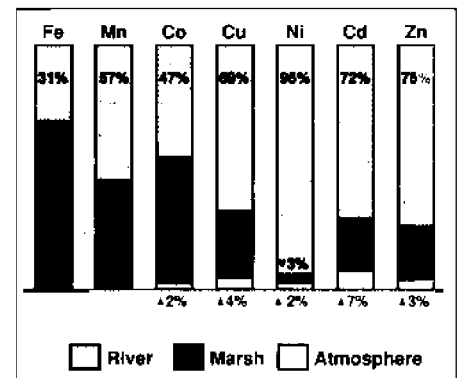


Figure 6. Percentage of trace-metal input to the Delaware Estuary from each of the three major sources for various metals.

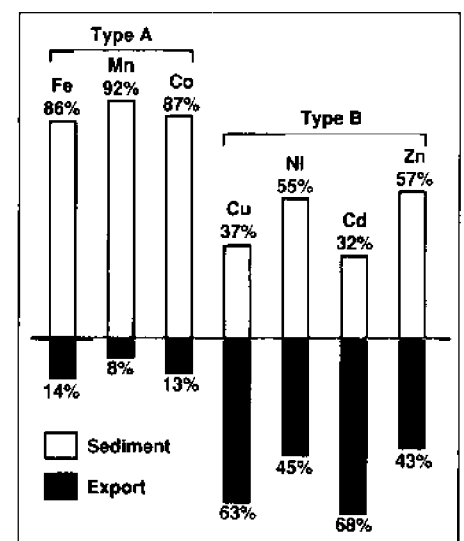


Figure 7. Percentage of trace-metal output from the Delaware Estuary via each of the two major sinks for various metals.

We see the ability of trace metals to be removed or transit the estuary as a result of the mass balance. As Figure 7 indicates, the Type A metals are to a very large degree retained in the sediments of the

estuary. However, Type B metals, which are more toxic, tend to be exported from the bay to coastal waters, probably because of the extensive opportunities for those metals to form stable organic complexes in the Delaware, which is perhaps due in part to the pervasive surrounding salt marshes. This means that estuaries in general may be important sources of these metals for coastal shelf waters.

## Conclusions and Recommendations

Trace metals comprise all those except the few major elements that dominate the Earth's geosphere and hydrosphere. While some are essential for life, many are not, and in high enough concentrations, they can be toxic. In marine waters, including estuaries, these metals are processed by geochemical and biochemical means. The distinction in these processes depends on the chemical properties of individual trace metals as well as the estuarine processes that either remove the metals or transmit them to the sea.

Trace metals are present in the Delaware Estuary in supernatural abundance because of human industrial actions that discharge directly into the water or contaminate the precipitation that falls into the watershed. Atmospheric deposition is likely to be quite important in terms of the direct input of trace metals to the whole watershed and their output as groundwater and runoff. An additional, indirect source is recycled from estuarine sediments, such as those in the pervasive salt marshes that surround the bay. The fate of geochemically reactive (Type A) metals is rapid removal as particles to the sediments. The fate of biochemically reactive (Type B) metals is primarily complexation with organic matter that is exported to coastal waters.

These consequences lead us to the conclusion that the Delaware appears to be "well buffered" for many toxic Type B metals. As this buffering is believed to be a result of organic complexing agents of salt-marsh origin, alteration of wetlands should be considered with caution. In addition to disturbing these complexing agents, the dredging or filling of salt marshes may remobilize their vast stores of trace metals from atmospheric deposition. The major export of Type B metals to coastal waters and the fate of estuarine metals in continental shelf waters should be considered a natural extension of research on estuarine metal processing, and the eventual exchange of metals with the open sea needs to be confirmed.

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## Acknowledgments

This research was supported by grants from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce, as part of the University of Delaware Sea Grant College Program under Grant Nos. NA80AA-D-00106, NA83AA-D-00017, NA86AA-D-SG-040, and NA16RG-0162. Much of the research was part of the Delaware Estuary Program with additional support from the Delaware River and Bay Authority. Additional funding was obtained from the Ocean Sciences Division of the National Science Foundation.

The author wishes to acknowledge the many talented faculty colleagues (C. Guilbertson, G. Luther, and J. Sharp), marine scientists (J. Scudlark, J. Tramontano, S. Murray) and graduate students (R. Pellenberg, C. Lord, K. Eastman, K. Johnston, and T. Ferdelman) who have been part of this research over the years. Their fine efforts have contributed significantly to the results presented in this summary report.

The author also wishes to thank the staff of the Marine Communications Office for their assistance in producing this document: Elizabeth Chajes, editor; David Barzak, art director; and Pamela Donnelly, production manager.

