

# Section 10: The Cycling of Silver, Copper, and Lead in the Coastal Sediments of Boston Harbor and Massachusetts Bay

By William R. Martin and Linda H. Kalnejais

The fate of heavy metals in coastal sediments was investigated during a 5-year study carried out by the USGS and WHOI. The primary goal has been to determine what controls the cycling of heavy metals in the sediment column. With this information, two important questions that concern environmental policymakers in coastal, urban areas can be addressed. First, what is the ultimate fate of toxic metals that were released into the coastal ocean in the past and remain in coastal sediments today? Second, what is the fate of metals that are currently being added to the coastal ocean in the treated sewage effluent that is released now? The study has focused on the reactions of three toxic metals, silver (Ag), copper (Cu), and lead (Pb), in sediments and in sedimentary pore waters and on the potential for release of these metals from sediments to overlying water. This work complements the long-term time series studies of contaminant and sediment transport in coastal Massachusetts by the USGS (Section 7) and related studies on oxygen penetration in sediments (Section 8).

The study focuses on two contrasting sites in the Boston area (Kalnejais, 2005). Hingham Bay (Station 8, fig. 7.1), in Boston Harbor, is a shallow-water site (6 m water depth) that was heavily contaminated due to its proximity to the Nut Island sewage outfall, which operated from the early 1900s until 1998. The concentrations of Ag, Cu, and Pb remain at potentially damaging levels, although they are decreasing. At this site, organic matter is oxidized at the very high annual rate of 900 micromoles of carbon/cm<sup>2</sup>/yr. As a consequence of this rapid organic matter oxidation rate, the entire sequence of electron acceptors used for benthic metabolism (O<sub>2</sub>, nitrate (NO<sub>3</sub><sup>-</sup>), manganese oxides, iron oxides, sulfate (SO<sub>4</sub><sup>2-</sup>)) is evident very close to the sediment-water interface. The oxic layer is less than 3 mm thick (3 mm is the sampling resolution) in late summer and only reaches about 6 mm in winter. Iron (Fe) is reduced at a depth of less than 3 mm in late summer, and hydrogen sulfide (H<sub>2</sub>S) is abundant in pore waters at a depth below 6–8 cm throughout the year.

The second study site (30 m water depth) is approximately 2 km west of the Massachusetts Bay outfall for Boston's sewage effluent (Station 3, fig. 7.1). The annually averaged organic matter oxidation rate at this site is about two-thirds that at the Hingham site, 600 μmol carbon/cm<sup>2</sup>/yr. Oxygen penetration depths range from about 3.5 to 5 mm (Section 8). The maximum penetration depth is similar to that at the Boston Harbor site, but the minimum depth is significantly greater, with the result that pore water data always show that there is no dissolved Fe in the upper 3 mm of the sediment. In addition, there is no H<sub>2</sub>S in pore waters in the upper

30 cm of the sediment column. These differences between this site and the Hingham site, coupled with the fact that heavy metal concentrations in the sediments are much lower here, result in contrasting metal cycling in the two locations.

## A Conceptual Model of the Cycling of Ag, Cu, and Pb in Coastal Sediments

Two phenomena dominate the cycling of Ag, Cu, and Pb in coastal sediments. First, their cycles are closely related to that of Fe. They are removed from solution by sorption onto freshly precipitated Fe oxides in the oxic sediment layer, and they are released to solution when microbes reduce Fe oxides. Second, they form highly insoluble sulfides, so that their cycles are also closely related to the sulfur (S) cycle.

The key to metal cycling in coastal sediments is an active sediment cycling layer in the upper 10–20 cm of the sediment column (fig. 10.1). The chemical characteristics of this layer are set to a large extent by the rate of input of organic matter from both marine production and anthropogenic activities. The processing of the organic matter results in a sequence of layers in the sediments: an oxic layer is underlain by a layer in which Fe reduction and sulfate reduction occur. Fe reduction releases Fe<sup>2+</sup> to the pore waters, and sulfate reduction releases H<sub>2</sub>S. The two products combine to form highly insoluble iron sulfide (FeS). If sulfate reduction is rapid enough, FeS formation will remove all the released Fe<sup>2+</sup>, and H<sub>2</sub>S will accumulate. Both solute diffusion and rapid mixing of solids by animals living in the sediments can return chemically reduced species to the oxic layer, where they may be reoxidized, passing through the oxidation/reduction cycle many times before being buried. The intensity of the oxidation/reduction cycle is determined by the thickness of the sediment cycling layer, the presence or absence of dissolved H<sub>2</sub>S, and the mixing rate. Solute exchange across the sediment-water interface is central to this sedimentary cycling, as it both adds reactants (O<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>) from the water column and releases products, which may include heavy metals, back to seawater. A second mechanism of exchange with the overlying seawater, which appears to be at least as important to heavy metal cycling as solute exchange, is sediment resuspension. This study shows that sediment resuspension contributes both solid and dissolved metals to the water column. How the Fe/S cycle interacts with anthropogenic metals depends in part on how the metals are added to the system: by deposition from the water column and, in previously contaminated sites, by mixing of contaminants into the cycling layer from below.

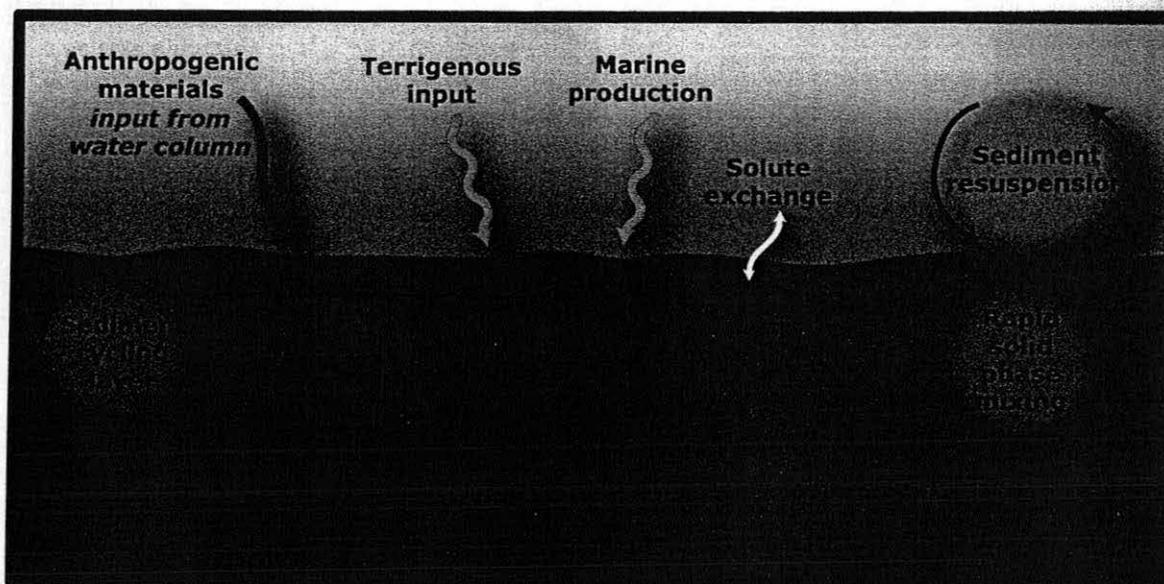


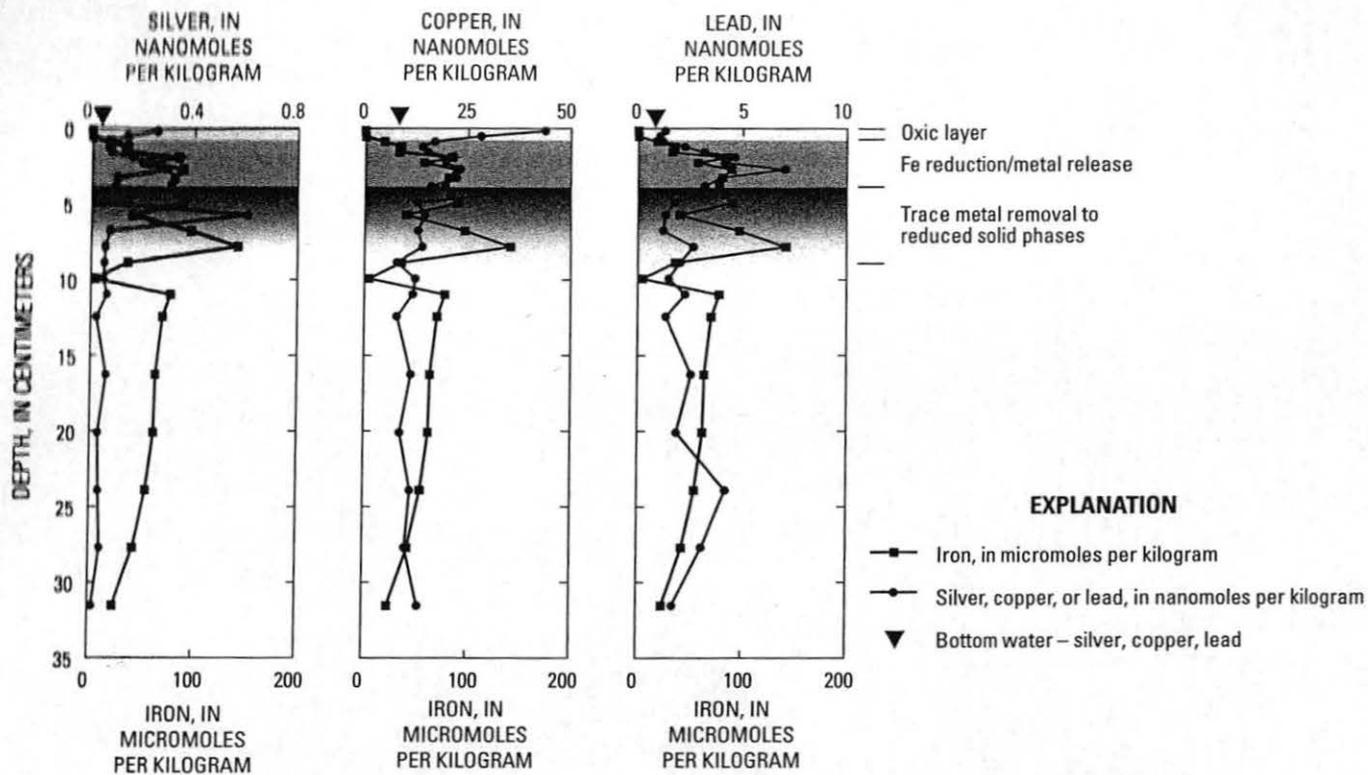
Figure 10.1. Factors influencing heavy metal cycling in coastal sediments.

### Heavy Metal Cycling and Benthic/Water-Column Exchange at the Massachusetts Bay Site

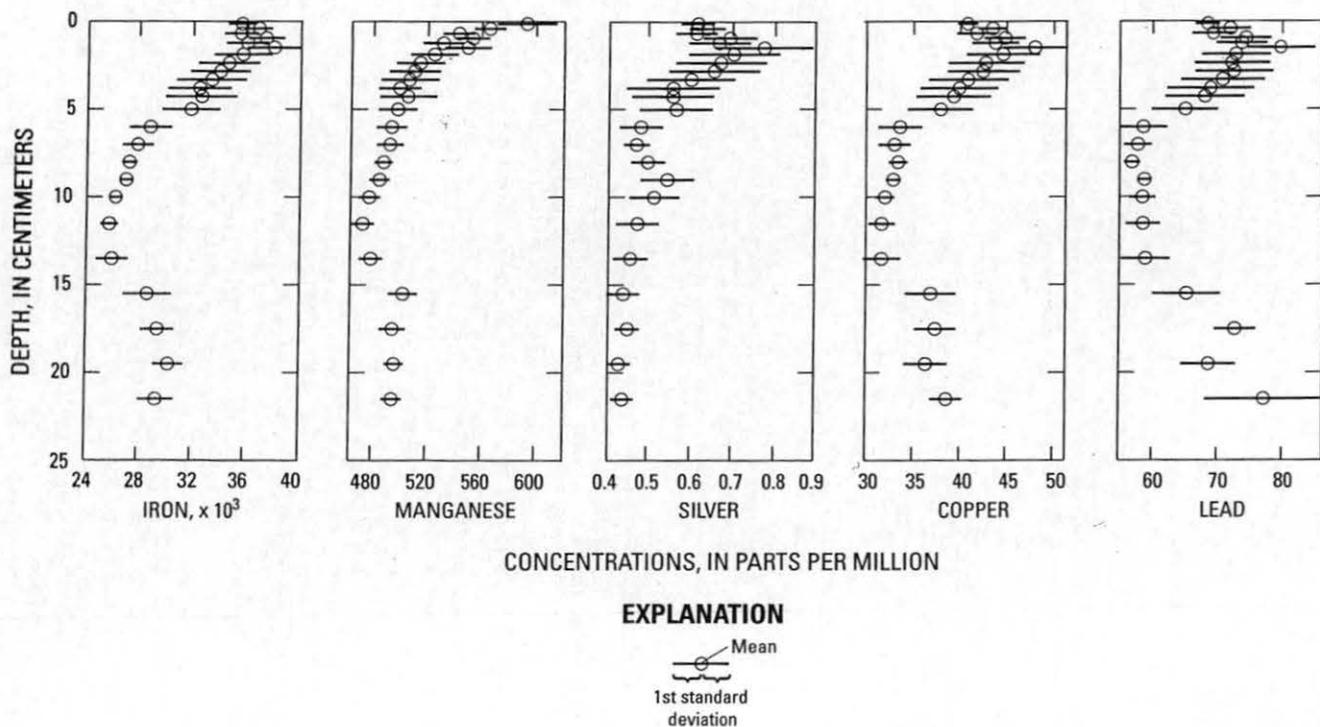
The Massachusetts Bay site is characterized by an oxic layer that is 3–5 mm thick, an Fe reduction layer that extends to about 5 cm below the interface, and an absence of  $H_2S$  in pore waters.

Differences between the behavior of the Ag, Cu, and Pb in the oxic layer reflect their differing affinities for attachment to Fe oxides. Pb is most strongly removed when Fe oxides precipitate from pore waters, and its concentration in the pore waters of the oxic layer of the sediments rarely rises above its concentration in bottom water. In contrast, for the data in different seasons, Ag is often present and Cu is generally present at higher concentrations in pore waters of the oxic layer than in bottom water. These characteristics of the three metals are illustrated in figure 10.2 with results from a core taken in May 2002. All three metals are clearly released in conjunction with the reduction of Fe oxides in the 1–3 cm depth interval. Once in solution, they diffuse upwards toward the sediment-water interface, where they may be removed when Fe oxides precipitate,

and downwards, where they are removed to the solid phase. At the Massachusetts Bay site, where sulfate reduction is slow enough that dissolved  $H_2S$  is not observed, upward diffusion is dominant, resulting in enrichment of the metals in the solid phase at the sediment surface (fig. 10.3). Thus, although the results of this study and that of Bothner and others (Section 7) show that there has been no increase in metal loading since the new outfall opened in Massachusetts Bay in September 2000, diagenetic processes have generated an enrichment of metal concentrations in surface, relative to deeper, sediments. Particles that are enriched in Ag, Cu, and Pb are eroded preferentially when bottom currents are sufficient to resuspend particles; the first particles eroded are enriched over surface sediments by up to 40 times for Ag, 8 times for Cu, and 4.5 times for Pb. Thus, resuspension is an important source of particulate metals in the water column. In addition, the resuspended particles release Ag and Cu to solution; both solute exchange and resuspension are sources of dissolved metals to the water column. One goal of the ongoing study is to quantify the relative importance of these processes by examining bottom current records to determine the frequency and strength of resuspension events in the study area.



**Figure 10.2.** Concentrations of iron (Fe in micromoles/kg), silver (Ag in nanomoles/kg), copper (Cu in nanomoles/kg), and lead (Pb in nanomoles/kg) in pore waters from a core taken at the Massachusetts Bay site (Station 3, figure 7.1) in May 2002.



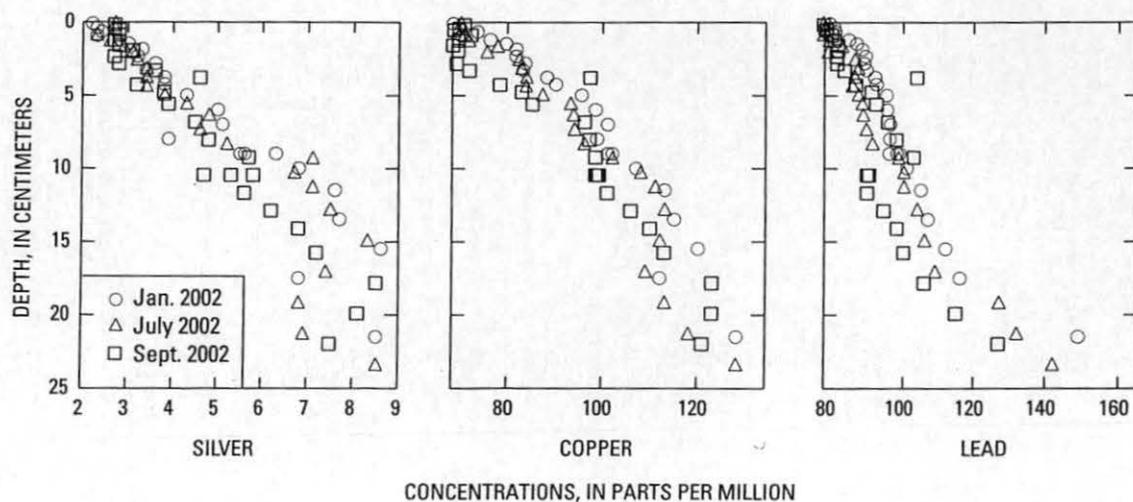
**Figure 10.3.** Concentrations of five solid-phase metals in sediments at the Massachusetts Bay site (Station 3, figure 7.1). The data are average values at each depth from a total of nine cores taken during the period from February 2001 to October 2002.

## Heavy Metal Cycling and Benthic/Water-Column Exchange at the Hingham Bay Site

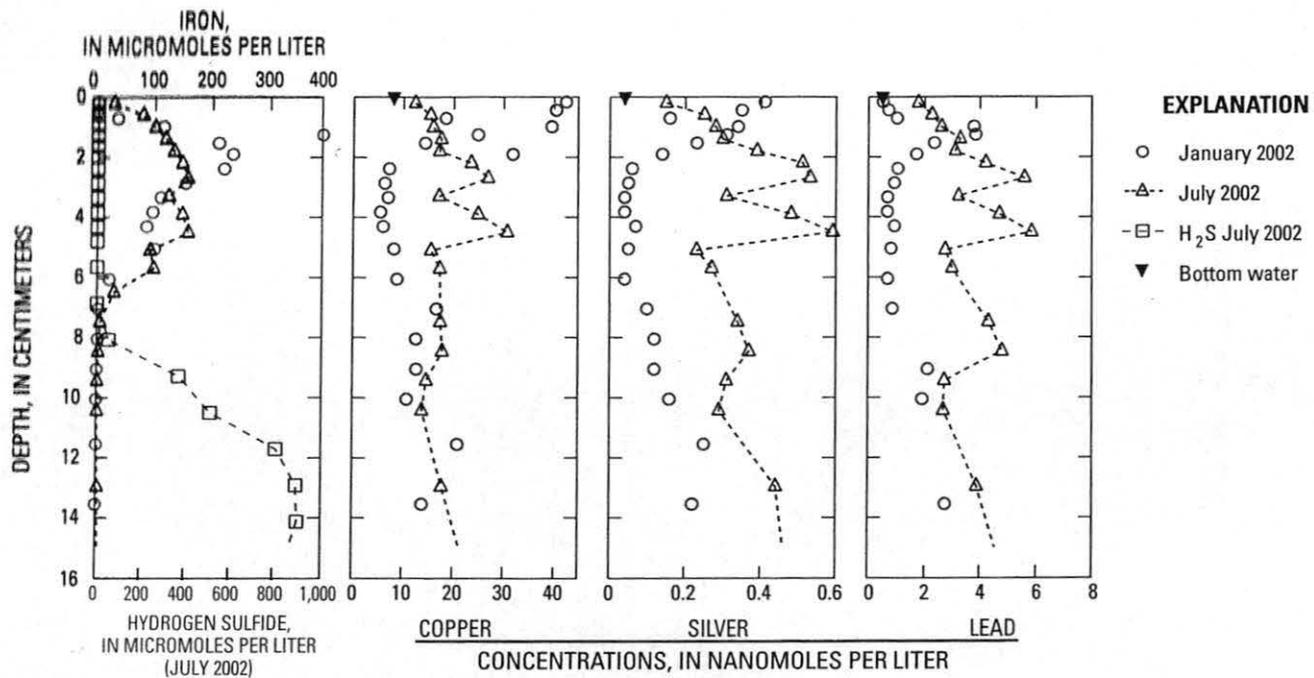
The oxic layer is significantly thinner at the Hingham Bay site in the summer than at the Massachusetts Bay site. The sulfate reduction rate is high enough so that all  $\text{Fe}^{2+}$  is removed by precipitation of  $\text{FeS}$  and concentrations of  $\text{H}_2\text{S}$  are measurable in pore waters within 6 cm of the sediment-water interface. In addition, solid phase profiles of Ag, Cu, and Pb (fig. 10.4) show that the primary source of the metals to the cycling layer is upward mixing from previously deposited contaminated sediments. At this site, the cycling layer has distinct seasonal characteristics (fig. 10.5). During the winter, the cycling system is charged by the downward migration of the oxic layer and upward mixing of sulfides. These processes result in the oxidation of Fe, Ag, Cu, and Pb sulfides. The released Fe then precipitates as Fe oxides, to which trace metals adsorb readily. Ag and Cu become enriched in pore waters at the sediment-water interface in winter, but the less soluble Pb does not. The source of the enrichment may be the oxidation of sedimentary sulfides; another possible source is the decomposition of particles that have been deposited recently from the water column. During early summer, the trace metals are released to pore waters when Fe oxides are reduced. These dissolved metals can diffuse both upward and downward, but downward transport is dominant because of rapid removal by the formation of highly insoluble sulfide minerals. Thus, as the summer progresses, the

recycled Fe oxides release less sorbed Ag, Cu, and Pb when they are reduced. These metals are no longer enriched in surface pore waters, and there is no longer a correlation between  $\text{Fe}^{2+}$  and the metals in pore waters. The largest fluxes of dissolved Cu and Ag from sediments to the water column occur in winter, during the charging phase of the seasonal cycle.

Sediment resuspension is also an important mechanism of sediment/water column exchange of metals. Controlled erosion experiments using an experimental chamber of the EROMES design (Tolhurst, 2000) demonstrated three ways in which resuspension transfers metals from sediments to the water column. (1) Erosion results in significant release of particulate metals to the water column (fig. 10.6A). The critical shear stress, at which erosion begins, was 0.12–0.14  $\text{N/m}^2$  at both the Hingham and Massachusetts Bay sites. The quantity of particulate Cu in the water overlying the sediment in the erosion chamber increased continuously until a shear stress of 0.25  $\text{N/m}^2$  at the Massachusetts Bay site and 0.3  $\text{N/m}^2$  at the Hingham site. (2) Short-term reactions lead to the release of dissolved metals from the eroded particles (fig. 10.6B). Once the critical shear stress was exceeded, the concentration of dissolved Cu in the water overlying the sediments in the erosion chamber increased sharply. This increase was much larger than could be explained by simple expulsion of pore waters during erosion. Therefore, the observed increase in the dissolved Cu concentration must have resulted from the release of Cu from suspended particles. (3) The fine-grained



**Figure 10.4.** Concentrations of three solid-phase metals in sediments at the Hingham Bay site (Station 8, figure 7.1). Metal concentrations at a depth of about 15 cm are similar to surface concentrations that were measured at the same site in 1978 (Bothner and others, 1998).



**Figure 10.5.** Concentrations of dissolved iron and hydrogen sulfide (in micromoles per liter) and silver, copper, and lead (in nanomoles per liter) in pore waters from cores taken at the Hingham Bay site (Station 8, figure 7.1).

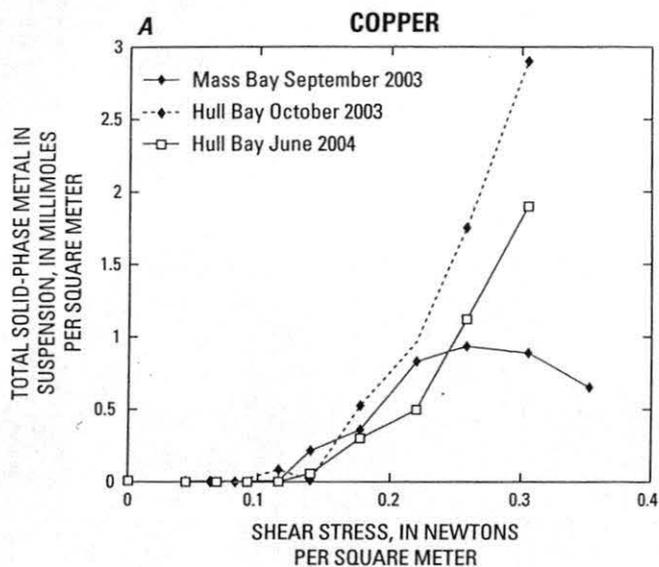
particles that may remain in suspension for hours to days continue to release up to 6 percent of their metal loading to the water column during a 90-hour period (fig. 10.6C). This percentage is calculated by comparing the observed increase in dissolved Cu in 90-hour-long incubations of resuspended particles to the initial Cu concentrations in the resuspended particles.

### Benthic Exchange and the Budget of Cu in Boston Harbor

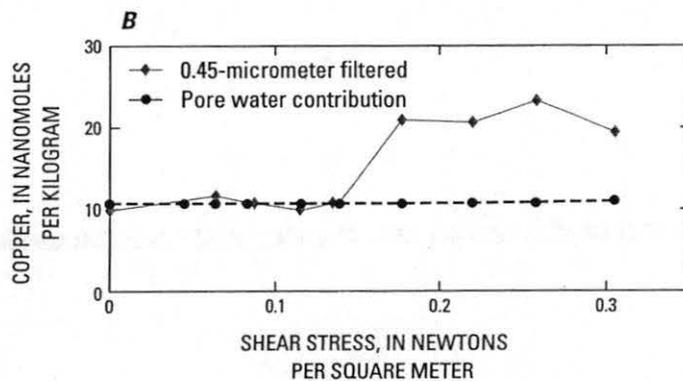
L. Kalnejais (WHOI) and R. Signell (USGS) used wind and tidal records to show that bottom currents at the Boston Harbor site were sufficient to erode sediments on the order of every 2 weeks, and that storm events could cause large erosion events on an annual basis (Kalnejais, 2005). With this information, Kalnejais (2005) and Kalnejais and others (in press) were able to show that sedimentary processes are a major part of the Cu cycle in Boston Harbor (fig. 10.7). The erosion tests indicated that release of particulate Pb is important, but dissolved Pb release was not; nonetheless, instantaneous release after erosion was the only sedimentary source of dissolved Pb to the water column. No data on inputs of Ag to the harbor were available.

The release of dissolved Cu from sediments (by erosion and diffusive flux) to harbor waters was shown to be larger than the loading from any other individual source except rivers (the river flux includes both dissolved and particulate Cu). The input of dissolved Cu from sediments was 60 percent of the input from rivers, and 30 percent of the sum of all other inputs. The total annual input from sediments to harbor waters was about 80 percent of that from all other sources. The flux of solid Cu from sediments to harbor waters via erosion includes particles that are repeatedly resuspended and redeposited, so that the ultimate significance of this source is difficult to establish. However, a fraction of the eroded particles may remain in the water column for enough time to disperse significantly. Eight hours after the completion of erosion experiments, 9 percent of the initially eroded mass remained in suspension. The particles that remained in suspension after this time were enriched in trace metals, so that 19 percent of the total particulate Ag, 15 percent of Cu, and 34 percent of Pb remained in suspension.

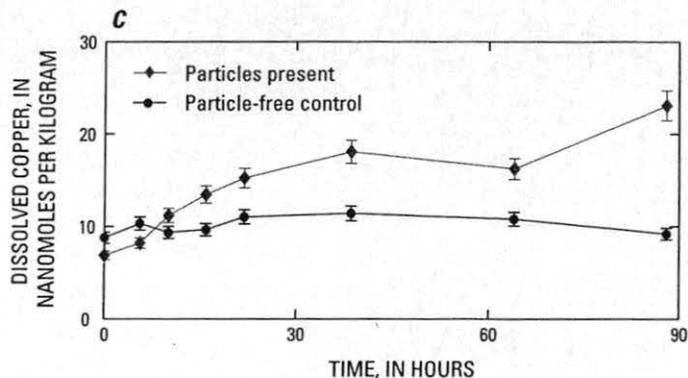
The importance of the sedimentary source will increase as contamination control reduces the loadings from other sources. Thus, the legacy of contaminated sediments from earlier activities will be increasingly important to the cycles of contaminants in Boston Harbor.



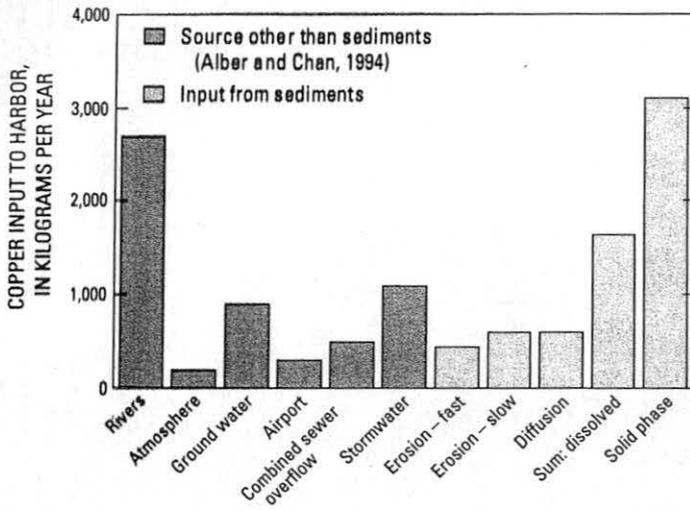
**Figure 10.6 (A).** The release of solid-phase copper as a function of bottom shear stress during a controlled erosion experiment on sediments (test area = 90 cm<sup>2</sup>) from the Hingham Bay and Massachusetts Bay sites.



**Figure 10.6 (B).** Concentration of dissolved copper in the overlying water of a controlled erosion experiment on Hingham Bay sediments. Blue symbols indicate the measured concentrations, and black symbols indicate the concentrations that would have been observed if Cu release resulted only from the expulsion of pore waters during resuspension.



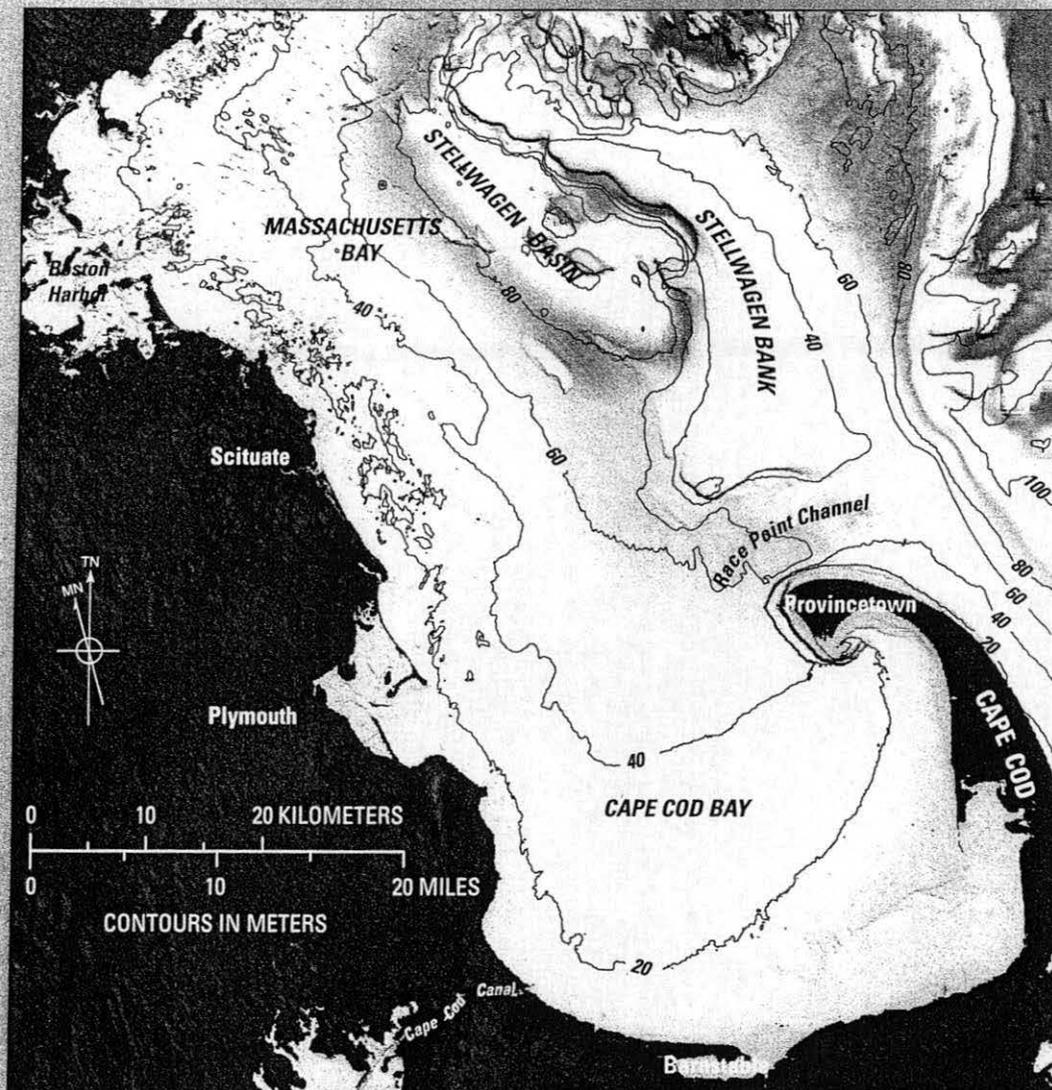
**Figure 10.6 (C).** Concentrations of dissolved copper as a function of time during the incubation of fine-grained particles that were resuspended at a shear stress of 0.3 N/m<sup>2</sup> during a Hingham Bay experiment. The blue curve shows the concentrations measured when particles were present at a concentration of 100 mg/L. The black curve shows the concentrations in a filtered control sample.



**Figure 10.7.** A comparison of inputs of Cu to Boston Harbor from sources other than sediments (in gray, from Alber and Chan, 1994) to input from sediments (in blue). The sediment inputs include three contributions from the erosion of sedimentary particles: (1) "Erosion—fast": short-term release, on a time scale of minutes; (2) "Erosion—slow": longer-term release, on a time scale of hours to days; and (3) "Solid phase": the release of particulate Cu. The "Sum: dissolved" bar is the sum of the two inputs of dissolved metal from erosion and the diffusive flux across the sediment-water interface. The "Combined sewer overflow" bar is a discharge point (usually at the harbor's edge) carrying street runoff during heavy rains combined with raw sewage, which would flow into the sewage-treatment plant during dry periods.

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# Processes Influencing the Transport and Fate of Contaminated Sediments in the Coastal Ocean— Boston Harbor and Massachusetts Bay



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U.S. Department of the Interior  
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