Particle Size and Chemical Control of Heavy Metals in Bed Sediment from the Rouge River, Southeast Michigan

KENT S. MURRAY,* DOUGLAS CAUVET, MARK LYBEER, AND JOHN C. THOMAS
Department of Natural Sciences, University of Michigan—Dearborn, 4901 Evergreen, Road, Dearborn, Michigan 48128

Anthropogenic activities related to 100 years of industrialization in the metropolitan Detroit area have significantly enriched the bed sediment of the lower reaches of the Rouge River in Cr, Cu, Fe, Ni, Pb, and Zn. These enriched elements, which may represent a threat to biota, are predominantly present in sequentially extracted reducible and oxidizable chemical phases with small contributions from residual phases. In size-fractionated samples (>300, 300–75, 75–38, 38–17, and 17 μm) trace metal concentrations generally increase with decreasing particle size, with the greatest contribution to this increase from the oxidizable phase. Experimental results obtained on replicate samples of river sediment demonstrate that the accuracy of the sequential extraction procedure, evaluated by comparing the sums of the three individual fractions, is generally better than 10%. Oxidizable and reducible phases therefore constitute important sources of potentially available heavy metals that need to be explicitly considered when evaluating sediment and water quality impacts on biota.

Introduction

River sediments are both carriers and potential sources of contaminants in aquatic systems. During the last decade the major objectives of research on metal-polluted waters have changed from the initial surveys of sources and pathways to more detailed investigations of the mechanisms controlling the mobility and bioavailability of different metal species (1–3). Unfortunately, many studies dealing with particulate metals in aquatic environments rely on total metal concentrations (4–6). The use of total concentration as a criterion to assess the potential effects of sediment contamination on aquatic biota implies that all forms of a given metal have an equal impact on the ecosystem. Such an assumption has recently been shown to be suspect (1, 2). Studies of metal speciation (1–3) within different particle-size classes can provide further detailed information about processes influencing the metal content of sediments. The Rouge River of southeastern Michigan has historically suffered from the combined stress of pollutant loadings from a variety of sources including atmospheric deposition, hazardous waste from manufacturing facilities and abandoned dumps, sewage from combined sewer overflows, dredged materials, urban runoff, and contaminated groundwater (4–8).

* Corresponding author phone: (313)593-5277; fax: (313)593-4937; e-mail: kmurray@umich.edu.

FIGURE 1. Location of the study area and the Rouge River watershed.

The Rouge River catchment is a fan-shaped basin draining a land area of approximately 1139 km² in Wayne and portions of Oakland and Washtenaw Counties (Figure 1). Overall, more than 50% of the land use in the basin is residential, commercial, or industrial. The remaining land use is primarily farmland or is undeveloped. The eastern portion of the catchment is intensely urbanized and includes the cities of Detroit (Figure 1). Flood plain and river sediments throughout the lower reaches of all four branches of the river contain significant levels of a wide range of both organic and inorganic constituents including PCBs, PNAAs, and heavy metals (4–8). Results from an earlier study indicated that six heavy metals, Cr, Cu, Fe, Ni, Pb, and Zn occur in these sediments at concentrations which frequently exceed toxicity based guidelines (4, 7, 8). In fact, this stretch of the Rouge River has been classified as a “Site of Environmental Concern” by the Michigan Department of Environmental Quality because of heavy metal and PCB contamination of the bed sediment. The International Joint Commission, established by the United States and Canada in part to resolve air and water quality problems, considers the Rouge River one of the 42 areas of greatest concern with the Great Lakes Basin (6).

This study focuses on the southern half of the main branch of the Rouge River where some of the highest metal concentrations can be found in the bed sediment. In the study area, the Rouge River ranges from a relatively shallow stream to a moderately deep and channelized river with a gentle gradient of approximately 20 m km⁻¹. In 1996, instantaneous streamflow varied from 0.33 to 1.01 m³ s⁻¹ in Southfield to 0.73–10.31 m³ s⁻¹ in Dearborn, near the U-M campus (Figure 2). The Rouge River is an effluent stream with nearly 100% of its base flow derived from groundwater (9). Most of the sediment transported and deposited by the river consists of fine to medium grained sand. Less than 25% of the bed sediment consists of coarse sand and gravel (>300 μm) and typically less than 10% of the sediment is in the silt
and clay size fraction (<17 μm). Grain size generally decreases downstream along the main branch of the river, resulting in progressively higher concentrations of silt and clay (10–12%) by the time it passes the U-M campus.

Previous work within the drainage basin concentrated on the role of particle-size in controlling heavy metal concentrations in bed and floodplain sediment along the lower branch of the Rouge River (4, 7). Along this branch heavy metal concentrations in the bed sediment increase with decreasing grain size. Most notable are increases in Cr, Cu, and Pb. Both Cu and Pb, for example, are found in the clay and silt size fractions in concentrations that are 10–100 times the EPA criteria for the Protection of Surface Water Quality (7).

Because heavy metal constituents have an affinity for the finer grain sizes, Murray (4) normalized the bed sediment chemistry data by comparing the potentially polluting heavy metal analyses with a conservative metal to reduce grain size effects. The resulting trend along the main branch of the Rouge River indicated an anthropogenic source for the metal enrichment in the bed sediment. The results of this initial study also indicated that the heavy metal enrichment was undoubtedly related to 100 years of industrialization and urbanization in the metropolitan Detroit area. In particular, the discharge of heavy metals to the environment used in the automobile manufacturing, including Fe in steel, Cr used in electroplating operations, Cu in wiring, Pb in fuels and paints, and Ni in ceramics, paints, and dyes. More recently, it has been suggested that contaminated groundwater, a significant nonpoint source of contamination within the Rouge River Watershed, plays a substantial role in the transportation and deposition of heavy metals in stream sediments of urban river systems (10, 11).

The work presented here was undertaken to obtain more information about the role of particle size as a control of heavy metal concentrations in bed sediment of stressed urban streams, and the chemical speciation of large excess concentrations of heavy metals such as Cu and Pb, in these systems.

Methods

Sample Collection, Separation, and Size Analysis. Surface sediment was collected in the summers of 1995 and 1996 at 1 km intervals along all four branches of the Rouge River. At all sample locations, the bed sediment was collected using a Ponar Grab Sampler to obtain a large amount of surface sediment (upper 3–4 cm) in areas of low flow velocity. Ten of the sample sites (Figure 2) were selected for detailed analysis during this study. Each sediment sample was split in the laboratory into two identical subsamples for bulk chemical and particle-size analysis. The samples were stored at 4 °C for 3–4 days and then separated into the following size effects. The resulting trend along the main branch of the Rouge River.

The work presented here was undertaken to obtain more information about the role of particle size as a control of heavy metal concentrations in bed sediment of stressed urban streams, and the chemical speciation of large excess concentrations of heavy metals such as Cu and Pb, in these systems.

FIGURE 2. Location of sample sites along the main branch of the Rouge River.
sulfides and organic material. The double potassium chlorate extraction has been used successfully (3) to dissolve galena (PbS), chalcopyrite (CuFeS₂), cinnabar (HgS), orpiment (As₂S₃), stibnite (Sb₂S₃), sphalerite (ZnS), and pyrite (FeS₂), all of which are likely present in southern Michigan soils (13).

The residual fraction of the oxidizable extraction step was rinsed in 10 mL of deionized water, dried overnight, and digested with the total digestion procedure described above. All bulk sediment samples and sediment extracts were analyzed for Cr, Cu, Fe, Ni, Pb, and Zn. Bulk (not size-separated) samples from each of the 10 sample sites went through the chemical separation procedure, and splits of those samples were completely digested by the methodology discussed above. The sum of the concentrations in the individual extraction steps were generally within 10% of the measured total concentration for all elements analyzed, although precision suffered where individual metal concentrations were near the detection level. Total Organic Carbon (TOC) was also determined for both the bulk and all size fractions at Thermo Analytical, Inc., laboratory in Ypsilanti, MI using EPA Method 9060.

Results and Discussion

Metal Enrichment. Total metal concentrations of the bulk samples from each location are shown in Figure 3. Most heavy metals are enriched in the bed sediment in the study area relative to concentrations found in the sediment of either the headwaters region of the river or tributary streams. Particle size analysis (Table 1) shows that most of these samples are composed of medium sand (75–300μm). Total metal concentrations in size-fractionated sediment samples (Figure 4) display trends similar to those found in the bulk samples. The particle-size data, however, suggests that although the highest metal concentration typically occur in the <17μm size fraction, the medium sand fraction contributes the largest percentage to the total metal concentrations of these samples.

Sequential extractions of bulk river sediment samples (Figure 5) show that concentrations for reducible Ni are by far lower than the reducible phase for the remaining metals. Fe, Cr, Cu, Pb, and Zn progressively increase their concentration in this phase. These results are in contrast to prior studies on the extraction of reducible metals from stream sediments or suspended solids (1, 3, 15, 16). For example, in rural watersheds where heavy metals are introduced to streams as a result of mining activities, reducible Cu, Pb, and Zn are generally found to represent a minor fraction of the total metal concentration of the solid (12, 15, 16). Along the main branch of the Rouge River however, reducible Cu, Pb, and Zn were found at concentrations representing 40, 40, and 50% respectively, of the total concentration of that metal present in the sediment. Jaagumagi (14) has suggested that Cu, Pb, and Zn under aerobic conditions and near neutral pH can complex with organic ligands, oxides, and clay. Moreover these metals may also coprecipitate with hydrated Fe and be deposited in river sediments, all as a result of changing conditions that naturally occur in an urban river system on a seasonal basis.

With the exception of Cu and Zn, the trace metals are all higher, and in some instances substantially higher, in the oxidizable phase than the reducible phase, and the oxidizable phase represents the largest fraction of the total metal concentration. This suggests that oxide coatings may well be the most effective scavengers of trace metals in Rouge River sediment. Cu and Zn have their largest concentration in the reducible phase, and with the exception of Fe, nine of the metals studied have greater than 20% of their
FIGURE 4. Total metal concentrations in five size-fractions of bed sediment samples collected from each of the 10 sample sites.
FIGURE 5. Sequential extractions of bulk bed sediment samples collected from each of the 10 sample sites.
concentration in the residual phase. These results are in contrast to Tessier and others (1) who found that the residual fraction accounted for more than 50% of the total metal concentration. In both studies, the residual phase is believed to consist mainly of primary and secondary minerals, which hold metals within their crystalline structure.

The percentage of the total metal concentration represented by the residual fraction is important when attempting to distinguish between background and anomalous levels of trace metals in bed sediment. Because metals in reducible or oxidizable form may become soluble under the natural changing conditions in an urban river system there will consequently be a greater impact on surface water quality and biota where these phases are present in higher percentages of the total metal concentrations. Conversely, metals held within the crystalline structure of primary and secondary minerals will not solubilize under normal river conditions and therefore can neither impact surface water quality nor become biologically available.

**Chemical Speciation and Particle-Size Effects.** Sequential extraction of size-separated river sediments shows chemical speciation trends consistent with the bulk sample analysis; see Supporting Information. Results of the particle-size analysis show that these samples are composed of predominantly fine to medium sand, although grain-size decreases slightly downstream. The sequential extraction of individual size fractions provided more information about particle-size control of metal concentrations in the sediments.

Metal concentrations in the reducible phase are strongly dependent on particle size with concentrations of Cr, Fe, Ni, Pb, and Zn showing significantly higher concentrations in the < 38 µm size fraction than in coarser fractions combined. As discussed above, the acetic acid-hydroxylamine extraction is designed to liberate metals bound in non- or partly crystalline Fe and Mn oxides or hydrous oxides, carbonate associated metals, and exchangeable metals (1, 2). The oxide coatings are probably the most effective scavengers of trace metals in river sediments and should be present predominantly as coatings on particle surfaces or as small particulates (2, 3, 16, 17). Metals in the reducible phase should be present predominantly as diagenetic or detrital sulfides and chemically bound with organic material. Although the sediment sampling was intended to collect only oxidized, surface sediment, the oxidized layer was often quite thin (2–3 cm), allowing the possibility that some reduced sediments containing diagenetic sulfides may have been collected. As in all three phases, metal concentrations in this chemical phase tend to increase with decreasing grain size. Although this trend is most noticeable in the oxidized phase, it is still evident in the residual phase. There are, however, notable exceptions to this trend. For example, Cu concentrations are typically nonlinear across all three phases. Where Cu does show an increase in concentration with decreasing particle size, as in the residual phases at R25, R9, R13, and L1, the increases are generally not of the same magnitude as increases in the residual phase of other metals.

The two important phases of the oxidizable metal concentrations evaluated by Tessier and others (18–20), metals bound to Fe–Mn oxides and metals bound to organic matter, cannot be easily distinguished by the methodology employed in this study. Total organic carbon data, however, shows trends that are quite similar to trends of metal concentrations in the oxidizable phase. Organic carbon should be found concentrated in the smaller size fractions (21, 22). The relative proportions of metals in the oxidizable fraction of the bulk samples suggest that a significant fraction of the metals in the oxidizable phase is bound by organic matter. This is particularly true for Cr. Jaagumagi (14) has documented that Cr(VI) can react strongly with oxidizable, usually organic molecules with the resultant formation of insoluble Cr(III). Cr(III) can be transported to the bed sediments through sorption to organic particles and coprecipitation with hydrous Fe–Mn oxides. When considered a fraction of the nonresidual phase, this proportion generally decreases in the order Cr ≥ Pb ≥ Zn ≥ Ni ≥ Cu. With the exception of Cr, this sequence resembles field observations of trends of metal binding by natural organic material (22). It is also similar to the sequence of minerals found in the oxidized phase of bed sediment from the Clark Fork River, MN, an area with elevated concentrations of metals derived from precious metal mining of a large sulfide ore body in the Boulder Batholith (3).

Metals in the residual fraction should come primarily from silicate and other resistant minerals. Residual concentrations are similar to bulk concentration measured along the lower branch of the Rouge River (4, 6). These background concentrations are in turn similar to but slightly lower than global concentrations in shale (3). As suggested by Brook and Moore (3), the shale values are, in general, slightly higher than appropriate background concentrations for river sediment, and this seems to be the case for the Rouge River as well. Since these minerals are present typically in lattice positions in primary and secondary minerals, there is little particle-size control of residual metal concentrations.

**Acknowledgments**

The authors wish to thank the Michigan Department of Environmental Quality-Surface Water Quality Division, the Wayne County Department of Environment, and the University of Michigan.

**Supporting Information Available**

Figure of sequential extractions of size fractionated bed sediment samples collected from each of the 10 sample sites. This material is available free of charge via the Internet at http://pubs.acs.org.

**Literature Cited**


Received for review August 4, 1998. Revised manuscript received November 30, 1998. Accepted December 15, 1998.

ES980794E