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Statistical comparisons of heavy-metal concentrations in river sediments

Received: 18 July 1995 / Accepted: 31 July 1995

Abstract Statistical *t* tests were used to determine lead, copper, and chromium enrichment in sediments from the Lower Branch of the Rouge River in southeast Michigan, USA. Both absolute metal concentrations and ratios of trace metal to conservative metal concentrations were used to compare sampled sites along the Lower Branch of the Rouge River to background sites in the headwaters region. Concentration ratios were used to reduce the effects of certain chemical and physical characteristics on the level of metal contained in a given sediment. Results from the comparison of sample sites to the background reveal metal enrichment at several sites, particularly along the highly urbanized, downstream section of the river. This section of the Lower Branch of the Rouge River exhibits significant lead and copper contamination, as well as measurable chromium enrichment when using either concentrations alone or ratios as methods of comparison. The areas of metal enrichment appear to coincide closely with areas of known anthropogenic activities. Of particular interest, however, is the enrichment of lead and copper at two upstream sites where the statistical tests suggest an anthropogenic source for the enrichment, but where no previously known cultural activities existed. These data prompted a historical search of records, which discovered several abandoned landfills immediately upstream of the metal enrichment sites.

Key words Heavy metals · Statistics · River sediments

Introduction

Contaminated river sediments are a concern not only because they act as a continuing source of potential problems for water quality and the biota in the waterway, but

because they may represent a means to quantify the relationship between sources of urban runoff and water quality degradation. The Rouge River, the major urban drainage for the metropolitan Detroit, Michigan, USA, area (Fig. 1), has historically suffered and continues to suffer from the combined stress of pollutant loadings from various sources. Although the majority of continuous point sources have been eliminated through the issuance and enforcement of National Pollution Discharge Elimination System (NPDES) permits for municipal and industrial dischargers, the river remains polluted (MDNR 1994). Sediment contamination, contributed from nonpoint sources including urban runoff, groundwater discharge, and atmospheric deposition, is the most likely cause of this continued pollution. Heavy-metal contamination, derived from 80 years of industrial activity, represents a significant percentage of the total pollutant loadings to the Rouge River. In contrast to most organic pollutants, trace metals are not usually eliminated from aquatic ecosystems by natural processes due to their nonbiodegradability. Both toxic and nontoxic heavy metals tend to accumulate in bottom sediments, from which they may be released by various processes of remobilization. Frequently, these metals can move up the biological chain, eventually reaching humans, where they can cause chronic and acute ailments (Forstner and Wittmann 1979; Ankley and others 1993, 1994).

The determination of metal levels in sediments may play a key role in detecting sources of pollution in aquatic systems (Forstner and Wittman 1979; White and Tittlebaum 1984, 1985; Allen and Polls 1993). Although sediment analyses alone are insufficient to evaluate the degree of toxicity in an aquatic system, they can be used semi-quantitatively to identify areas prone to environmental impacts from anthropogenic activities and to trace the sources of pollution. White and Tittlebaum (1984), for example, have shown that under favorable conditions, pollution sources may even be detected long after input has taken place.

Although current analytical techniques have greatly simplified the analysis of heavy metals in sediment, the determination of whether significant contamination exists

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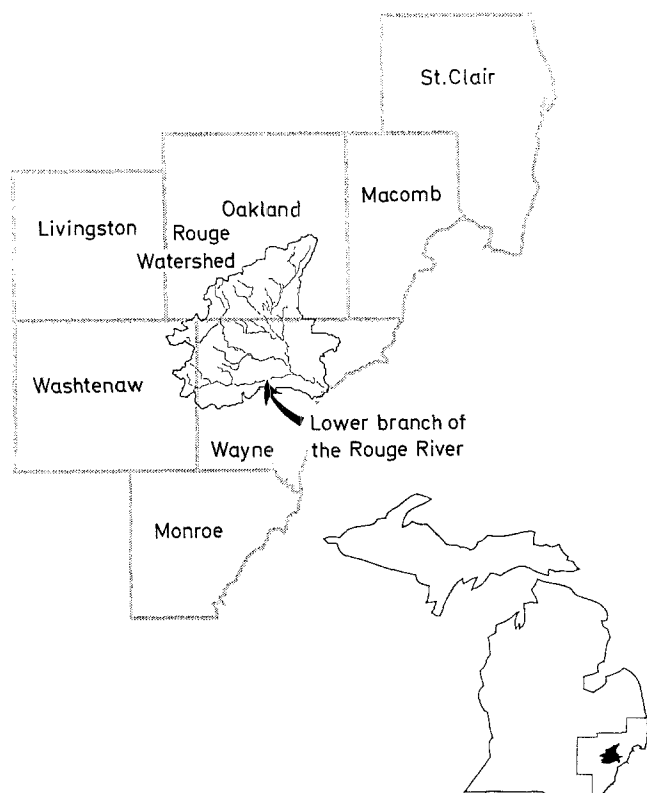


Fig. 1 Location map

is an unresolved problem (Allen and Polls 1993). Metal distribution in sediments is influenced by several sediment characteristics, principally grain size and organic content. Because of these influences, dissimilar sediment types within the same river system can have significantly different levels of contamination. Currently, the acceptable method of determining heavy-metal contamination in sediments involves the comparison of metal concentration values with some established standard or threshold criteria (Allen and Polls 1993). However, in some cases, this method can be influenced by a sediment's physical and chemical composition. Although concentrations alone are a proven means of identifying contamination at sites where extremely high levels are present, various parameters, including sediment type, grain size, and analytical methods, make comparisons between sites difficult.

This paper uses a statistical method employed successfully by White and Tittlebaum (1984) to identify sites and potential sources of contamination in both river and lake sediments. The method relies on the use of concentration ratios of pairs of metals, alone or in conjunction with absolute concentration values, to identify areas of metal enrichment caused by anthropogenic activities. Several researchers (Kemp and others 1976; Allan and Brunskill 1976; Forstner 1976; White and Tittlebaum 1984, 1985) have advocated using metal concentration ratios in order to reduce the effect of grain size, organic content, and other sediment characteristics resulting from samples obtained from different locations.

It has been reasoned that the ratio of an element under

consideration to another element of low variability, such as an element of "conservative behavior," e.g., iron or aluminum, can determine whether metal enrichment, i.e., contamination, has taken place. Conservative metals are unlikely to experience enhanced concentrations in sediments due to anthropogenic activities. In addition, because of their high initial concentrations, they are less likely than trace metals to be influenced by anthropogenic activities. Trace metals, however, are naturally present in small initial concentrations and are far more susceptible to change, particularly from anthropogenic sources. Thus, ratios of trace metals to conservative metals may reveal geochemical imbalances due to elevated trace metal concentrations normally associated with anthropogenic activities (Forstner 1976; Forstner and Wittmann 1979; White and Tittlebaum 1984).

Values of background concentrations of heavy metals in sediment samples collected along the heavily urbanized Lower Branch of the Rouge River were used to calculate metal pair ratios for comparison to metal pair ratios of sediment collected from the headwater region. Results of these comparisons indicate striking similarities to background ratios from other nonpolluted aquatic systems. For example, background ratios for lead/iron obtained by Kemp and others (1976) in Lake Erie sediments averaged 1.4 for several locations, while background ratios obtained by White and Tittlebaum (1984) from a deep core off the mouth of the Mississippi River in Louisiana averaged 1.6. Similarly, background ratios obtained for the headwater region of the Lower Branch of the Rouge River averaged 1.6. Nearly identical results were also obtained for copper/iron and chromium/iron, suggesting the applicability of the ratio method and the acceptability of the headwater sediment samples as background.

This study attempts to identify the location of heavy-metal contamination in sediments along the Lower Branch of the Rouge River. Statistical *t* tests were used to compare both trace metal-to-conservative metal concentration ratios and absolute metal concentrations from along the Lower Branch of the Rouge River to sediment collected from the headwater region of the river.

Sampling program and experimental procedures

Sediment samples were collected at approximately 1-km intervals along the Lower Branch of the Rouge River using a Ponar grab sampler. The background samples consisted of 16 discrete samples obtained from four separate locations along two tributaries to the Lower Branch of the Rouge River at its headwaters near the Wayne-Washtenaw County line (Fig. 2). The four locations are in a rural, typically wetlands environment, isolated from urban development. Element concentrations for the background samples are reported in Table 1.

The first sampling area was located adjacent to the confluence of the Lower and Main Branch of the Rouge River (Fig. 2). Downstream of this confluence, the river

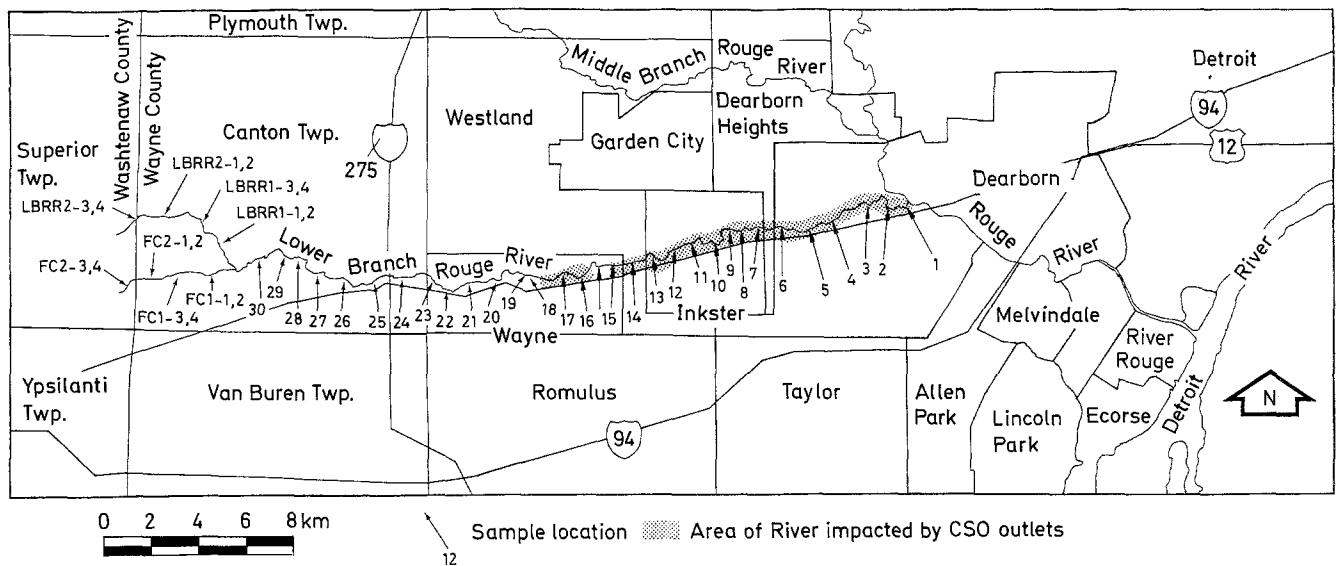


Fig. 2 Location of sampling sites along the lower branch of the Rouge River

Table 1 Concentrations of lead, copper, chromium, and iron in background samples

Sample	Wt. (g)	Pb (ppm)	Cu (ppm)	Cr (ppm)	Fe (%)
LBRR1-1	2.005	38	153	18	3.6
LBRR1-2	2.012	59	129	16	1.8
LBRR1-3	2.031	49	135	17	2.5
LBRR1-4	2.002	23	163	17	1.9
LBRR2-1	2.012	55	148	19	2.0
LBRR2-2	1.995	53	175	16	1.9
LBRR2-3	2.043	54	139	15	1.8
LBRR2-4	2.007	61	153	17	2.2
FC1-1	1.992	53	152	15	1.9
FC1-2	1.994	60	190	18	2.8
FC1-3	2.003	58	159	17	2.3
FC1-4	2.023	42	132	19	1.9
FC2-1	1.996	59	160	20	3.2
FC2-2	2.013	57	149	17	2.3
FC2-3	2.005	23	156	18	2.1
FC2-4	2.002	73	148	19	1.7

is channelized for most of its remaining length until it reaches the Detroit River. The remainder of the collection sites extend westward from the confluence and were selected to coincide with bridge crossings to facilitate river access and sample collection. Four or five discrete samples were collected at each sample site. Once collected, each sample was transferred into a clean, wide-mouth, 0.5-l glass jar and transported to the laboratory for analysis.

One sample from each site was analyzed for total organic carbon (TOC) by EPA Method 415.2. While TOC is not itself a contaminant, it may be used to identify sites where elevated organic contamination might exist. Alternatively, studies by Allen and Polls (1993) and Horowitz (1991) have shown that a correlation of grain size with TOC may also be unrelated to organic contamination. A comparison of TOC content to site location along

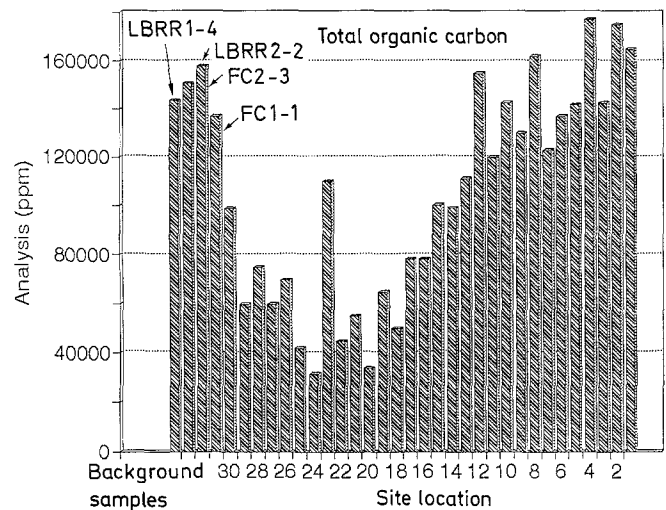


Fig. 3 Variation of TOC content with sample locations

the Lower Branch of the Rouge River shows a distinct bimodal distribution (Fig. 3). High TOC content in the headwater region is probably related to the higher percentage of silt and clay at this location (Fig. 4), while the increase in TOC content at downstream sample sites, which have progressively lower percentages of silt and clay, may indeed be related to an increase in organic contamination.

An additional sample from each site location was dried and mechanically sieved to determine the grain-size distribution at each site (Fig. 4). If no variability in grain size exists along a river, then metal concentration alone would be sufficient to identify sites of metal enrichment. However, in most river systems, some variability in grain size is to be expected (Allen and Polls 1993). Knowledge of this variability is essential in a comparison of sample sites to background since trace metals as well as organic contaminants often concentrate in the finer-grained sediments (Horowitz 1991). Figure 4 indicates a general decrease in the percentage of fine-grained sediments downstream

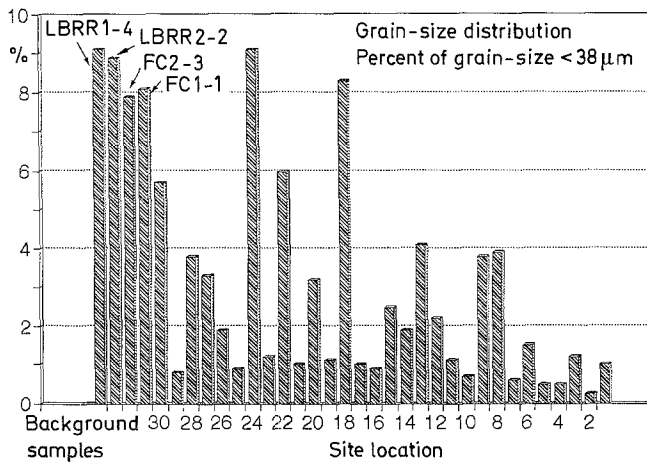


Fig. 4 Variation of grain-size distribution with sample location

from the headwater region, suggesting that metal concentrations alone may not be sufficient to identify sites of metal enrichment.

The remaining samples collected from each sample site were dried at 100°C and ground to a composite powder, from which representative samples of approximately 2 g were taken. A modified EPA 3050 method was followed for the complete digestion of the sample utilizing nitric and hydrochloric acid. Metal concentrations were then determined by air-acetylene flame atomic absorption spectrophotometry. Using the obtained metal concentration values, trace metal/conservative metal concentration ratios were determined for each sample analyzed. In all cases, iron was used as the conservative metal species because of its relative abundance in the Earth's crust. It is thus less likely to be affected by anthropogenic activities. Copper, lead, and chromium were chosen as trace metal species to be studied due to their relative abundance in the surface water of the Rouge River (Czack and others 1995).

Results

The statistical *t* test as used by White and Tittlebaum (1984) in their analysis of lake and river sediments evaluates the null hypothesis, i.e., that the mean of one data set is equal to the mean of another set of data. Fundamental to this procedure is the incorporation of variances of each set of data. In this study the statistical *t* test was used to determine the existence of any significant concentration and/or ratio differences ($P < 0.05$) between each sample location and the background samples.

Table 1 lists the variations in element concentrations with location in the background samples. An example of the results obtained from the application of the statistical *t* test are presented for lead concentration values in Table 2. Sites found to have metal concentrations or ratios significantly different from the background are actually rejecting the null hypothesis and are indicated in Table 2. The mean standard deviation (SD), and the number of

Table 2 Comparison of lead concentrations at each site to background

Site	N	Mean (ppm)	SD	Significantly different from background?
Bkg	16	51.0	10.8	
1	4	141.2	31.5	Yes
2	4	299.1	41.1	Yes
3	4	98.4	.84	Yes
4	5	162.2	7.1	Yes
5	4	271.1	13.5	Yes
6	4	89.1	17.3	Yes
7	5	138.2	10.4	Yes
8	4	99.2	23.5	Yes
9	4	81.2	43.5	Yes
10	4	332.4	33.5	Yes
11	4	120.2	22.8	Yes
12	4	81.2	12.3	Yes
13	4	37.6	7.8	No
14	5	36.7	10.4	No
15	4	48.2	11.5	No
16	4	43.6	18.7	No
17	4	23.8	12.5	No
18	4	18.1	46.4	No
19	4	33.3	32.6	No
20	4	24.6	12.2	No
21	5	78.5	8.4	Yes
22	5	46.3	111.2	No
23	4	96.5	10.7	Yes
24	4	21.1	61.0	No
25	4	60.6	24.3	No
26	4	30.2	12.4	No
27	4	23.0	45.3	No
28	4	23.2	56.8	No
29	4	49.2	12.6	No
30	4	21.0	29.7	No

incremental samples (N) collected from each location are also listed for each sample site. Using concentration values alone, 14 sampling sites contain lead concentrations significantly different from the background (Table 1). The sites (1–12) are primarily associated with the highly urbanized downstream section of the Lower Rouge River, but also include two upstream sites (21 and 23). The use of lead/iron concentration ratios similarly indicates ratios significantly different from the background for the downstream sites as well as the sites 21 and 23.

Copper concentrations alone are found to be significantly different from the background in nine of the downstream sites and several upstream sites (14, 21, 23, 25, and 29). It should also be noted that although two additional downstream sites (8 and 9) were determined to have a copper concentration significantly different from the background, the mean copper concentration for these sites, was actually less than the mean background copper concentration.

In using copper/iron concentration ratios, only seven of the 12 downstream sites (1, 2, 5, 6, 7, 10, and 11) exhibited copper/iron ratios significantly different from the background ratio. As with the lead/iron ratios, the seven sites showing copper/iron ratios significantly different from the background are also the same sites showing copper concentrations alone significantly different from background. Similarly, the upstream sites 21 and 23 identified

earlier also show high copper concentrations alone and copper/iron ratios that are significantly different from background. In addition, high copper concentrations and copper/iron ratios that are significantly different from background are found at two other upstream sites (25 and 29).

Although only a couple of the sites are significantly different from the background chromium concentrations, almost all downstream sites (1–13) were found to have chromium/iron ratios that are significantly different from the background.

Discussions and conclusions

Based on the results of the statistical *t* tests, which compared sample sites along the Lower Branch of the Rouge River to background samples in the headwater region, several insights into the degree of metal enrichment in the river sediments have been gained. Both concentration values and metal pair ratios indicate that lead, copper, and chromium are present in the downstream sediments of the Rouge River at significantly higher levels than found in the background sediment; this is particularly true for lead and copper. These results indicate enrichment of these metals has occurred in the downstream part of the river at some point in the past.

The enrichment of the heavy metals along the downstream portion of the Lower Branch of the Rouge River appears to correlate very closely with the location of combined sewer overflow (CSO) outlets, which discharge urban runoff directly to the river at times of heavy rain (Rouge Program Office 1995). The observed increase in TOC along this part of the river, as shown in Fig. 3, supports this correlation since organic contaminants represent a large percentage of the discharge from CSO outlets (MDNR 1994). As a result, it appears that the use of concentration values and metal pairs may represent a means to quantify the relationship between sources of urban runoff and subsequent water-quality degradation.

The enrichment of metals at two locations upstream (sites 21 and 23) is also substantiated by statistical *t* test results. Both sites show significantly different lead/iron and copper/iron ratios than are found in background sediments, while site 21 also showed a significantly different chromium/iron ratio and sediment collected from sample site 23 contained an unusually high TOC content. Both of these sites also have lead and copper concentrations that are significantly different from background. Recent historical analysis by the Michigan Department of Natural Resources (MDNR) has identified a potential source for the contamination. Perhaps as many as six old landfills may have been located adjacent to the Lower Branch of the Rouge River in the vicinity of sites 21–23. Leachate from the landfills (transporting heavy metals and organic contaminants via the groundwater) may explain the heavy-metal enrichment at these sites and add validity to the use of both concentration values and ratio methods of analysis.

Although more work needs to be completed to verify this relationship and to determine the toxicity of the sediments at these sites, the consistency of the background samples and the fact that metal concentration ratios can be used to reduce the effects of sediment grain size and organic content may enable metal pairs and metal concentration ratios to be used to identify and distinguish between natural and anthropogenic sources of contamination. More importantly, this methodology may detect pollution long after input has taken place.

It is the conclusion of this research that heavy-metal enrichment, in the form of lead, copper, and chromium, has occurred in the sediments of downstream portion of the Lower Branch of the Rouge River at some point in the past. Initially, this metal enrichment appears to coincide with urban runoff from CSO outlets. Additionally, two upstream sites show metal enrichment when using either analysis procedure. This metal (particularly lead and copper) enrichment is also undoubtedly related to anthropogenic activities as suggested by the lead/iron and copper/iron ratios that are significantly different from background.

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