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Trace-Metal and Organochlorine Residues in Sediments of the Upper Rockaway River, New Jersey

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As part of a larger study performed in cooperation with the New Jersey Department of Environmental Protection, the U.S. Geological Survey has investigated the sediment quality of the upper Rockaway River in New Jersey's Morris County. Much of the physiography of the upper Rockaway River basin is dominated by northeast-southwest trending valleys and ridges. As a result of glaciation, the valleys are filled with thick sequences of glacial deposits. The course of the Rockaway River (Fig. 1) follows these valley fill deposits. Headwaters originate in Berkshire Valley and flow southwest parallel to the trend of the valley until reaching the main west-to-east Rockaway valley. The river eventually empties into Boonton Reservoir, which separates the upper and lower sections of the Rockaway River. Boonton Reservoir is a drinking-water supply for more than 225,000 residents of the area, and therefore, the sediment and water quality of the reservoir and upper reaches of the river is extremely important.

This paper presents the results of a study to determine whether trace metals (of anthropogenic origins), polychlorinated biphenyls (PCBs), and/or chlorinated insecticides have been deposited in the sediments of the upper Rockaway River, and whether variations in the spatial contamination of the river's sediment correspond to changes in the basin's land use.

MATERIALS AND METHODS

Sediment samples were collected from seven locations of the upper Rockaway River. The locations of the sampling stations are indicated in Figure 1. For each of the seven sites, samples were collected from the top 2 centimeters of the undisturbed bottom material using either an acid-rinsed polyurethane scoop (for samples requiring metal analysis) or an acetone-rinsed stainless steel scoop (for samples requiring organic analysis). Immediately after collection, the sediment samples were passed through a 63-micron sieve by continuous flushing with river water. A stainless-steel sieve was used for samples scheduled for organic analysis, whereas a plastic/nylon sieve was used for samples scheduled for

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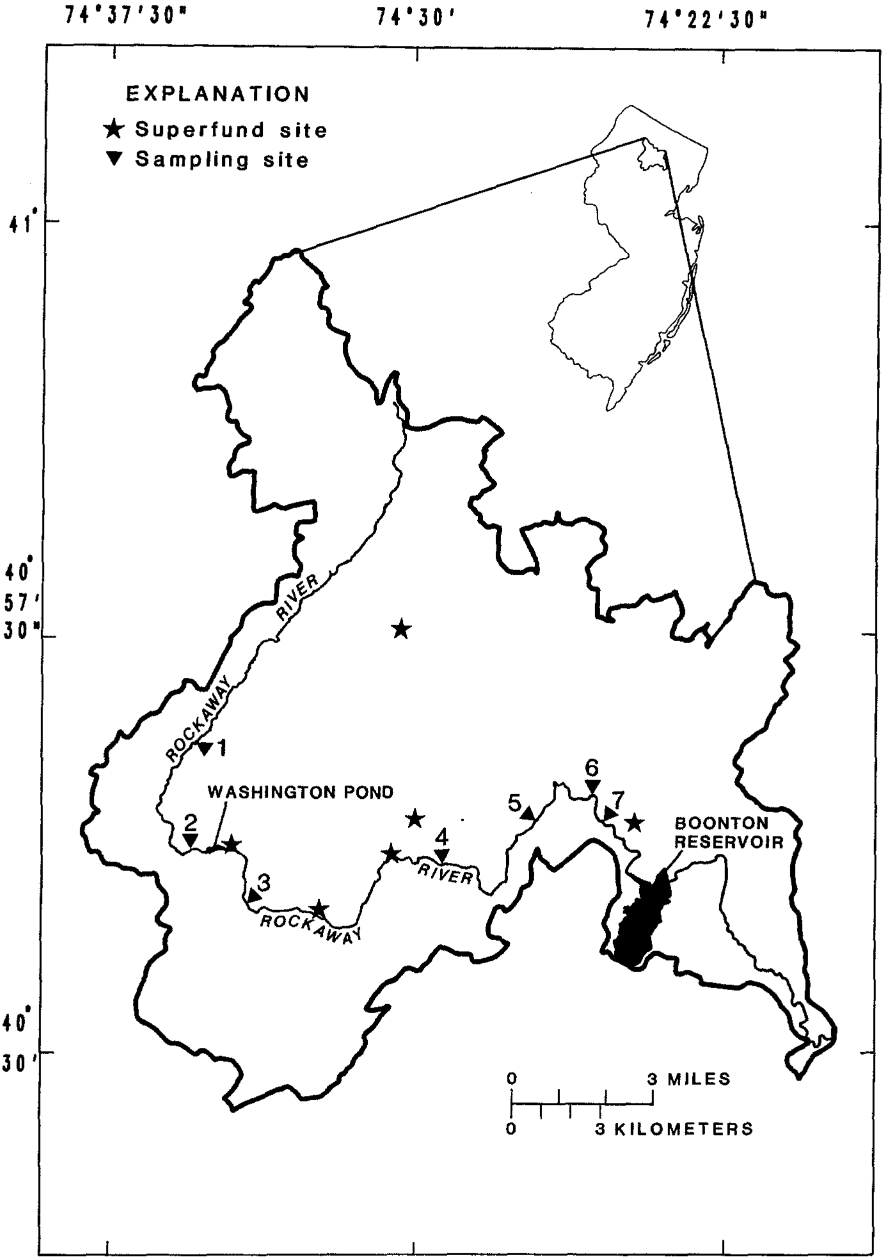

Figure 1. Map of the Rockaway River Basin showing the location of sampling stations and U.S. Environmental Protection Agency Superfund sites.

metal analysis. The less than 63-micron sediment fraction was then collected in glass mason jars with Teflon[1]-lined lids, and the greater than 63-micron sediment fraction was discarded. Once collected, samples were packed in ice and shipped to the U.S. Geological Survey's Central Laboratory for organic and metal analyses.

Analytical methods used to quantify metal and organochlorine residues in sediment samples have been described in detail by Fishman and Friedman (1985) and Wershaw et al. (1983), respectively. Briefly, the inorganic analysis consisted of a total recoverable metals analysis in which the sediments were dried, ground, and homogenized. The samples were then digested with a combination of hydrofluoric, nitric, and perchloric acids in a Teflon beaker, and heated on a hot plate at 200°C. The resulting salts were dissolved in hydrochloric acid and demineralized water for analysis by atomic-absorption spectrometry. Sediment samples requiring organochlorine analysis were extracted with acetone and hexane. The extracts were then purified using adsorption chromatography on an alumina column. To analyze for the presence of PCBs, the extracts were further purified using a silica gel column. The organochlorine compounds were then quantified by gas chromatography using an electron-capture detector.

RESULTS AND DISCUSSION

The reach of the Rockaway River upstream from Washington Pond (fig. 1), which includes sampling stations 1 and 2, drains primarily forested areas of the upper Rockaway basin. Therefore, the effect of anthropogenic inputs on these locations is expected to be small. By contrast, the section of the Rockaway River between Washington Pond and Boonton Reservoir, which includes sampling stations 3 through 7, drains an area consisting primarily of residential, commercial, and industrial land usage. Included in this drainage area are six U.S. Environmental Protection Agency Superfund sites. As a result, the sediments at sites 3 through 7 are expected to be strongly effected by anthropogenic trace metals and organic compounds.

Results of the sediment trace metal and total Fe and Al analyses are presented in Table 1. The concentration of each trace metal at each sampling site is given in units of mg/kg (milligrams per kilogram). Total Fe and Al concentrations are given in units of mg/g (milligrams per gram). The value beneath each trace metal concentration is the ratio of the concentration of the trace metal (mg/kg) to the total concentration of Fe (mg/g) in the same sediment sample. Likewise, the second value beneath each metal concentration is the ratio of the concentration of the trace metal (mg/kg) to the total concentration of Al (mg/g) in the same

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[1] Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 1. Concentrations of trace metals (mg/kg), total Fe (mg/g), and total Al (mg/g) and ratios of trace metal concentrations to both Fe and Al concentrations for sediment samples from seven locations of the upper Rockaway River.

	Station						
Metal	1	2	3	4	5	6	7
Fe	30	33	39	22	28	21	22
Al	15	17	11	13	14	13	10
As	13	18	17	9	11	9	10
As/Fe	.4	.5	.4	.4	.4	.4	.5
As/Al	.9	1.1	1.5	.7	.8	.7	1.0
Cd	1	<1	16	6	6	15	9
Cd/Fe	.03	< .03	.4	.3	.2	.7	.4
Cd/Al	.07	< .06	1.6	.5	.4	1.2	.9
Cr	160	300	550	400	420	500	420
Cr/Fe	5.3	9.1	14	18	15	24	19
Cr/Al	11	18	50	31	30	38	42
Cu	41	32	110	110	110	170	120
Cu/Fe	1.4	1.0	2.8	5.0	3.9	8.1	5.5
Cu/Al	2.7	1.9	10	8.5	7.9	13	12
Pb	50	50	270	280	330	420	360
Pb/Fe	1.7	1.5	6.9	13	12	20	16
Pb/Al	3.3	2.9	25	22	24	32	36
Hg	.2	.2	.8	.6	.6	.9	.8
Hg/Fe	.007	.006	.02	.03	.02	.04	.04
Hg/Al	.013	.012	.07	.05	.04	.07	.08
Ni	30	20	40	50	40	50	40
Ni/Fe	1.0	.6	1.0	2.3	1.4	2.4	1.8
Ni/Al	2.0	1.2	3.6	3.8	2.9	3.8	4.0
Zn	110	130	510	350	320	490	380
Ni/Fe	3.7	3.9	13	16	11	23	17
Ni/Al	7.3	7.6	46	27	23	38	38

sediment sample.

With the exception of As, the data in Table 1 suggest that the sediment concentrations of trace metals downstream from Washington Pond have been enriched above natural levels. To test this hypothesis, the nonparametric, one-tailed, Mann-Whitney statistical test was applied to the trace-metal data of Table 1. The Mann-Whitney test was chosen primarily because it is free of the assumption that the data are normally distributed. The test only assumes that both samples are random samples from their respective populations, that there is mutual independence between the two samples, and that the measurement scale is at least ordinal (Conover 1980). The test's null hypothesis states that the distribution of the concentration of a given trace metal in the sediment upstream from Washington Pond is identical to the trace-metal concentration distribution in the sediments downstream from Washington Pond. This implies that the means and medians of the two populations are also equal. The alternative hypothesis states that the two populations have different distributions, and, therefore, the means and medians of the two populations are different.

Results of the statistical test indicate that the concentrations of Cd, Cr, Cu, Pb, Hg, Ni, and Zn at stations 3 through 7 are significantly higher than their respective concentrations at stations 1 and 2 at the 95-percent confidence level. Given the nature of the statistical test and the relatively small amount of data, this is the highest confidence level attainable for these seven metals, inasmuch as their concentrations at stations 1 and 2 are lower than any of their concentrations at stations 3 through 7. Only the concentration of As was not significantly higher at the downstream stations than at the two upstream stations.

All of the trace metals listed in Table 1 are found naturally in sediment and soil samples, and, therefore, it commonly is difficult to determine whether or not their concentrations have been increased by anthropogenic activities. For example, the elevated trace-metal concentrations at stations 3 through 7 relative to concentrations at stations 1 and 2 may be attributable only to natural variations in concentration. It has been demonstrated that ratios of trace-metal concentrations to conservative-metal concentrations can help determine if trace-metal enrichment has occurred by eliminating much of the variability associated with differences in grain-size distribution and organic matter content of different sediment samples (White and Tittlebaum 1984). Because of their relatively high concentrations, conservative metals such as iron or aluminum exhibit small percentage variations in their concentrations as a result of anthropogenic activities; by contrast, trace metals present in sediments at relatively low concentrations can exhibit large percentage variations. Therefore, ratios of trace-metal concentrations to conservative-metal concentrations can be expected to increase as a result of anthropogenic inputs to a surface-water system.

Before proceeding, it should be noted that Fe is not classically defined as a conservative metal. However, for the purposes of this paper, the description of both Fe and Al as conservative metals implies only that their sediment concentrations are high relative to the sediment concentrations of trace metals such as Pb or Ni, and as a result, their concentrations exhibit only small percentage variations due to anthropogenic activities.

To determine further whether trace-metal concentrations downstream from Washington Pond have been enriched as a result of anthropogenic activities, the Mann-Whitney test was applied to the trace/conservative-metal concentration ratios in Table 1. For each trace metal, the ratio of the trace-metal concentration to the Fe concentration at stations 1 and 2 was compared to the same ratio at stations 3 through 7. At a 95-percent confidence level, the ratios for Cd/Fe, Cr/Fe, Cu/Fe, Pb/Fe, Hg/Fe, and Zn/Fe at the two upstream stations (stations 1 and 2) were significanly lower than their respective ratios at the five downstream stations (stations 3 through 7). In addition, the Ni/Fe ratio at stations 1 and 2 was significantly lower than the same ratio at stations 3 through 7 at a 90-percent confidence level. As/Fe ratios for the upstream sites were not significantly different from the downstream ratios.

These same statistical comparisons were applied to the trace/conservative-metal-concentration ratios using Al as the conservative metal. At a 95-percent confidence level, the ratios of Cd/Al, Cr/Al, Cu/Al, Pb/Al, Hg/Al, Ni/Al, and Zn/Al at stations 3 through 7 were significantly greater than the same ratios at stations 1 and 2. No significant difference was observed for the As/Al ratios between the upstream and downstream stations. These results are in good agreement with the statistical-test results of both the trace-metal-concentration data and the trace/Fe-metal-concentration ratios and indicate that the trace metal concentrations in the Rockaway River sediments downstream of Washington Pond have been increased by anthropogenic activities.

The results of the organic analyses for sediment samples from the seven stations in the upper Rockaway River are given in Table 2. To account for the variability of organic matter in the different sediment samples, these concentrations have been normalized for the sediment sample's organic-carbon content. The normalized concentrations are given in parentheses in Table 2 and equal the measured concentrations of the contaminant divided by the fractional mass of organic carbon in the respective sediment samples. There is strong evidence indicating that nonionic organic compounds, in the presence of water, are sorbed to sediments by partitioning into the sediment organic matter (Witkowski et al. 1986). Adsorption of nonionic solutes such as the chlorinated insecticides and PCBs to sediments is a relatively insignificant sorption mechanism in sediment-water systems due to the ability of polar water molecules to compete successfully with nonionic solutes for mineral adsorption sites (Chiou et al. 1985; Chiou and Shoup 1985; Yaron 1978). Organic matter, therefore, appears to be the single most important indicator of a sediment's sorptive capacity and must be considered when evaluating spatial contamination patterns of organic compounds in aqueous systems.

The distribution of chlorinated insecticides and PCBs in the surficial sediments of the upper Rockaway River closely parallels the distribution of trace metals. In general, the data in Table 2 indicate that the sediments at sampling stations 3 through 7 are

Table 2. Concentrations of chlorinated organic compounds (μg/kg) and organic carbon (percent) in sediment samples taken from seven sampling stations in the upper Rockaway River. Values in parentheses equal the concentrations normalized for the sediment sample's organic carbon content.

	Station						
Compound	1	2	3	4	5	6	7
Organic carbon	4.3	4.4	7.3	6.4	6.7	7.8	5.9
Chlordane	16 (372)	<1.0 (<22.7)	26 (356)	510 (7970)	140 (2090)	170 (2180)	160 (2710)
DDD	1.9 (44.2)	2.0 (45.5)	26 (356)	74 (1160)	55 (821)	61 (782)	50 (847)
DDE	1.4 (32.6)	1.4 (31.8)	10 (137)	12 (188)	7.6 (113)	9.2 (118)	24 (407)
DDT	.1 (2.3)	< .1 (<2.3)	7.1 (97.3)	14 (219)	5.4 (80.6)	< .1 (<1.3)	7.7 (131)
Dieldrin	.2 (4.7)	.1 (2.3)	.6 (8.2)	5.2 (81.3)	.9 (13.4)	.9 (11.5)	.6 (10.2)
Mirex	< .1 (<2.3)	< .1 (<2.3)	80 (1100)	32 (500)	23 (343)	29 (372)	8.2 (139)
Heptachlor epoxide	< .1 (<2.3)	< .1 (<2.3)	.7 (9.6)	10 (156)	< .1 (<1.5)	3.3 (42.3)	3.8 (64.4)
Total PCBs	14 (326)	15 (341)	170 (2330)	340 (5310)	180 (2690)	260 (3330)	90 (1530)

highly contaminated with organochlorine compounds. By contrast, organochlorine residues at stations 1 and 2 are much lower.

Statistical analysis of the data in Table 2 using the one-tailed, Mann-Whitney test confirms the elevated contaminant concentrations at stations 3 through 7 relative to stations 1 and 2. At a 95-percent confidence level, the concentrations of chlordane, DDD, DDE, dieldrin, mirex, and PCBs are higher in the sediments downstream of Washington Pond than in the sediments upstream of Washington Pond. Concentrations of DDT and heptachlor epoxide also are significantly higher downstream from Washington Pond but only at a 90-percent confidence level. When applying the statistical test to the organic-carbon-normalized data, similar results are obtained. Normalized concentrations for DDD, DDE, dieldrin, mirex, and PCBs at the stations upstream from Washington Pond were significantly lower than their respective concentrations at the stations downstream from Washington Pond at a 95-percent confidence level. Identical results were obtained for chlordane at a 90-percent confidence level. However, statistical analysis of the normalized concentrations for DDT and heptachlor epoxide revealed no significant differences between the upstream sites and the downstream sites even at a 90-percent confidence level. With the exception of these latter two comparisons, the organic-compound data indicate that sediments downstream from Washington Pond have elevated levels of anthropogenic organochlorine compounds relative to sediments upstream from Washington Pond.

In conclusion, the data suggest that the sediments of the upper Rockaway River downstream from Washington Pond have been affected by anthropogenic activities. Significant residues of PCBs, chlorinated insecticides, and trace metals have been detected in sediment samples collected from this reach of the Rockaway River. By contrast, sediments at sampling stations upstream from Washington Pond are relatively free of trace-metal and organochlorine contaminants. The sediment quality in the Rockaway River corresponds strongly to land-use data for the area, which indicates the presence of numerous residential, commercial, and industrial areas in the vicinity of the five downstream stations, whereas the two upstream stations drain primarily forested land. Normalizing trace-metal concentrations by conservative-metal concentrations and normalizing organic compound concentrations by percent organic carbon were useful techniques for confirming spatial contamination variations in sediments of the Rockaway River.

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