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# INFLUENCE OF FLOW-RELATED EVENTS ON CONCENTRATION AND PHASE DISTRIBUTION OF METALS IN THE LOWER FRASER RIVER AND A SMALL TRIBUTARY STREAM IN BRITISH COLUMBIA, CANADA

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Abstract—A substantial portion of the total copper, nickel and zinc in bottom sediments of the lower Fraser River and a tributary, Still Creek were in reactive forms. Particulate rather than dissolved components were responsible for the bulk of the metal interactions within all of the sediments examined. Increased flow generally resulted in a loss of reactive copper, nickel and zinc from sediments of Still Creek and of reactive copper and zinc from sediments of the Fraser River. Decreased flow was accompanied by an increase in the levels of the reactive copper, nickel and zinc fractions in both systems. Flow-related processes appeared to influence concentration and phase distribution of the metals in these lotic environments.

## INTRODUCTION

Over the last decade considerable effort has been made to develop an understanding of the fate of trace metals and other potential pollutants following their discharge into aquatic environments. The bulk of evidence indicates that heavy metals react readily with suspended particulate matter and, through sedimentation processes, accumulate in bottom deposits (Williams *et al.*, 1978; Bewers and Yeats, 1978; Eaton, 1979). Diagenesis of metals can be delayed, however, by physical or chemical disturbances (Duke *et al.*, 1978).

Spring freshet, an annual phenomenon in western Canada and the northwestern United States, can substantially modify river and stream beds. Drainages such as the Fraser River in British Columbia, Canada, which transports an estimated $1.2 \times 10^{13}$ g suspended sediment during freshet from May to July (Thomas and Grill, 1977), are thus likely to mobilize considerable quantities of heavy metals which accumulate in bottom sediments of polluted regions during low flow periods.

While the literature contains numerous reports of the geochemical partitioning of heavy metals in various hydrosoils (Jenne, 1968; Rashid, 1971; Guy *et al.*, 1975), there have been few reports which describe the impact of flow-related processes on the concentration and phase distribution of metals in river bed sediments. We report here the effects of seasonal water flow variations on the concentrations of reactive and non-reactive copper, nickel, and zinc in surficial bottom deposits of the lower Fraser River and one of its more polluted tributaries, Still Creek.

## METHODS

### *Sampling sites*

Three sampling locations were used in the study; two sites on Still Creek, in the Brunette drainage basin, and one site on the Fraser River at New Westminster (Fig. 1). Still Creek drains a highly urban-industrialized area within the municipalities of Burnaby and Vancouver, B.C. and has been classified as a storm sewer by the Greater Vancouver Regional District. Most reaches of the creek, however, are uncovered. A more detailed description of the Brunette basin is presented elsewhere (Hall *et al.*, 1976). Samples were collected from the west side of the Gilmore Avenue (49°15′45″N, 123°00′48″W) and Douglas Road (49°15′35″N, 122°58′59″W) bridges, two areas of intense industrial development. Sediments at Gilmore Avenue were composed of coarse sand and decaying plant material while those at Douglas Road consisted of loosely packed, fine clay. Samples from the Fraser River were collected at the marina in New

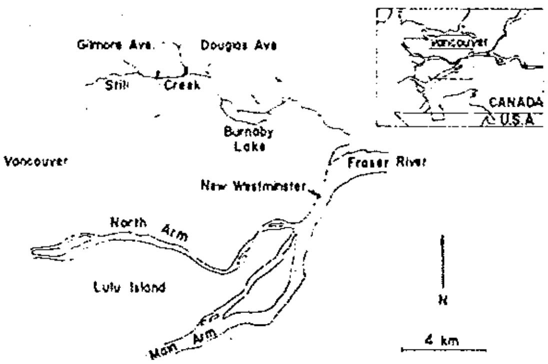

Fig. 1 Lower Fraser River drainage. ● denotes sampling locations.

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Westminster (49°12'20"N, 122°52'56"W). Sediments at this site were composed of compacted clay and silt. This region of the river was under tidal influence but sediments were never exposed during low tide and were upstream from the salt wedge. Additional sediment characteristics have been reported elsewhere (Bindra and Hall, 1979, Chapman *et al.*, 1979).

### *Sampling*

Three sediment cores (top 5 cm) were collected from each sampling site by hand in alcohol-rinsed Plexiglas coring tubes (5 × 30 cm). Water samples were collected in glass-stoppered bottles which were prewashed in 5% nitric acid for at least 48 h and then rinsed in double-distilled, deionized water (d-$H_2O$). Sediment cores were stored intact in the Plexiglas tubes with the overlying water present and sealed at each end with neoprene stoppers. Cores were maintained on ice during transport and stored at 5°C prior to processing (which occurred within 3–4 days of collection).

### *Water and ash determinations*

The overlying water was siphoned from 1 core and 3 subsamples from the surface sediment were transferred to preweighed crucibles. Dry weights were determined after drying for 48 h at 90°C. Ash content was determined from the subsamples of 1 core following combustion at 500°C for 7 h.

### *Sediment fractionation*

An extra core was collected from each site on 19 February 1979. The top 4 cm of the core was transferred to an interstitial water recovery apparatus (Reeburgh, 1967) and the interstitial water (IW) squeezed from the core by positive nitrogen pressure through a nylon mesh filter (Millipore Corp.) into prewashed, sterile polypropylene vials. The filtrate was filtered through a 0.2 μm pore size membrane (Nuclepore Corp.) mounted in a sweenex adaptor on a 5 ml plastic syringe.

### *Metal determinations*

Three subsamples of surface sediment from 1 core were transferred to 15 ml Corex centrifuge tubes by means of a Teflon-tipped spatula and dried for 48 h at 90°C. After adjusting the sediment dry weight to 0.1–0.2 g, 10 ml of hydrogen peroxide (acidified to pH 2.0 with concentrated nitric acid) was added slowly while the mixture was maintained at 90–95°C. Additional acidified peroxide was added until no more fumes evolved from the reaction mixture. Membranes containing IW particulate materials were transferred directly to Corex centrifuge tubes and treated as above. After oxidation was complete, 0.5 ml of 3 N hydrochloric acid (Aristar) was added and diluted immediately with 5 ml d-$H_2O$, and the reaction continued for an additional 30 min at 90–95°C. The mixture was centrifuged at 6800 *g* for 10 min and the pellet washed one time with d-$H_2O$, dried and weighed. The supernatant fractions were pooled, evaporated to dryness and resuspended in 1.5 N hydrochloric acid. The pooled material contained metals that were associated with organic, sulfur and easily acid-extractable components of the sediment and will be referred to as the reactive metal fraction.

The dried pellet from above was transferred to Teflon beakers. 10 ml hydrofluoric acid (49%) was added and the mixture evaporated to dryness at 180°C in a sand bath. Five ml concentrated nitric acid and 5 ml perchloric acid (70–72%) were added and the mixture was again evaporated to dryness. The flocculent residue was suspended in 1.5 N hydrochloric acid, centrifuged and the supernatant fraction was retained for subsequent analysis. The metal recovered by this extraction procedure represents the non-reactive metal associated with the sediment.

Aqueous samples were evaporated to dryness and resuspended in 1.5 N hydrochloric acid prior to estimation of total metal concentration.

All glassware and materials were precleaned in 5% nitric acid for at least 48 h prior to use. All fractions for metal analysis were stored in new metal-free polyethylene centrifuge tubes (Eppendorf) prior to determination of copper, nickel and zinc by flameless atomic absorption spectrometry using a Varian Techtron Model 63 carbon atomizer. Standards were prepared by dissolving elemental metals in concentrated nitric acid and diluting to the appropriate concentration with 1.5 N hydrochloric acid. Although recovery of a metal spike gives little information about the recovery of the metal naturally present in the sample (Martin *et al.*, 1980), known quantities of each metal were added to subsamples to compare metal extraction from the same sediment sites at different sampling times.

### *Organic carbon*

Three subsamples (approx. 0.2 g wet weight surface sediment) from the remaining core were transferred to tared, acid-washed tubes, dried at 90°C, and weighed before addition of 5 ml of 0.01 or 0.05 M potassium dichromate and 10 ml of concentrated sulfuric acid. The oxidation reaction was conducted for 3 h at 90°C, after which the contents of the tubes were cooled to room temperature, the particulate material pelleted by centrifugation at 6800 *g* for 10 min, and the optical density of the supernatant fraction measured at 480 and 520 nm in a Bausch and Lomb Spectronic 20 colorimeter. Organic carbon determined by wet oxidation was estimated from a standard curve in which potassium biphthalate was used as a standard. Organic carbon analysis of aqueous samples was conducted by initially evaporating the solution to dryness at 90°C prior to resuspension in the above reagents. The procedure for organic carbon determination by combustion was similar to that described above for ash determination. All glassware was washed in chromic acid solution and rinsed in d-$H_2O$ before use.

### *Eh determinations*

A separate sediment sample was collected from the New Westminster site with a top-loading Ponar grab. An Orion 407A Ionanalyzer with a platinum electrode was used to measure oxidation-reduction potentials in the top centimeter of the sediment.

## RESULTS

Seasonal water discharge characteristics of the lower Fraser River differed greatly from those of smaller tributaries in the lower Fraser River drainage (Fig. 2). During the transition from the wet to dry season (May–July) tributaries such as Still Creek exhibited reductions in flow, whereas freshet con-

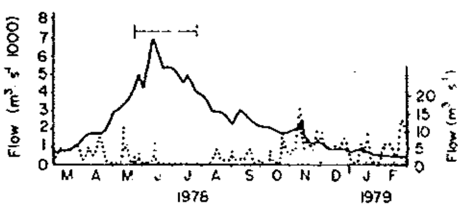

Fig. 2. Seasonal flow pattern of the Fraser River and Still Creek. Fraser River data (solid line, flow units on left vertical axis) were obtained at Hope B.C. by Water Survey of Canada. Still Creek flow (dotted line, units on right vertical axis) was estimated from rainfall data obtained from the Greater Vancouver Sewerage and Drainage District using the procedure described in their Technical Report on Still Creek, 1979.

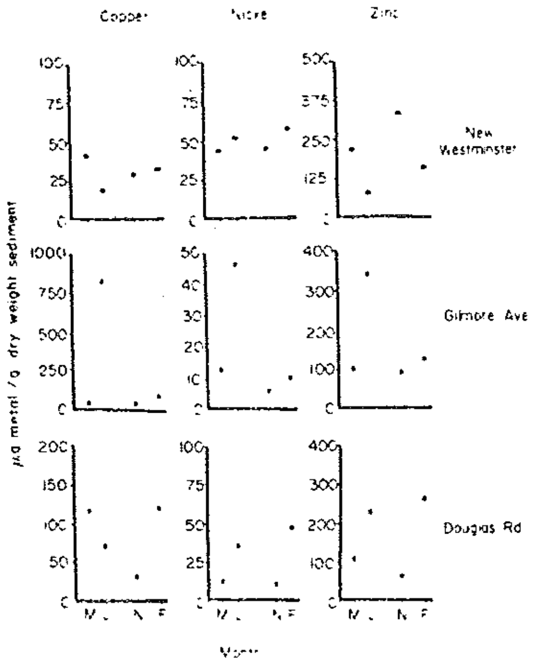

Fig. 3. Seasonal reactive metal concentrations in the Fraser River and Still Creek. Bar represents ±1 SD of 3 replicate sample

ditions, resulting from snowmelt in the distant mountains, produced annual peak discharge in the Fraser River at this time.

Metal concentrations in the sediments appeared to vary with flow conditions. As the flow decreased from May to July reactive nickel and zinc increased dramatically in the middle reaches of Still Creek (Fig. 3). Reactive copper also increased at Gilmore Avenue but decreased at Douglas Road. As flow increased with the onset of the wet season (September–November), the reactive metal concentrations decreased to levels similar to those observed at the end of the previous wet season. At the Gilmore Avenue site, the metal concentrations remained low during the wet season (November–February), whereas they increased at Douglas Avenue.

Reactive copper and zinc decreased in sediments of the Fraser River (New Westminster) during freshet (Fig. 3). Following peak discharge, the metal increased as flow decreased. Zinc concentrations fluctuated more than copper and, in fact, decreased again between November and February. Reactive nickel concentrations remained relatively constant throughout the year.

Reactive zinc accounted for the bulk of the total zinc in the sediments of Still Creek (Table 1). Further studies revealed that reactive zinc increased in relation to non-reactive zinc as flow decreased during the dry season. A similar pattern was observed for reactive nickel, although its relative contribution to total sediment nickel was less than that of zinc (Table 2). Reactive copper contributed from 96 to 98% of the total sediment copper in Still Creek (Table 3). No changes in the relative contribution of reactive to total copper were observed, however.

The reactive forms of copper, nickel and zinc accounted for the bulk of their respective total metal concentrations in sediments of the Fraser River (Tables 1, 2 and 3). As flow increased during freshet, the

Table 1. Distribution of zinc among sediment fractions

| Site | Date | Fraction* | | % Associated with reactive fraction |
|---|---|---|---|---|
| | | Reactive† | Non-reactive‡ | |
| Douglas Road | 21 May | 99±46 | 30±11 | 77 |
| | 24 July | 228±78 | 9±1 | 96 |
| Gilmore Avenue | 21 May | 93±36 | 39±6 | 71 |
| | 24 July | 342±64 | 19±1 | 95 |
| New Westminster | 21 May | 207±45 | 90±11 | 72 |
| | 24 July | 82±13 | 29±3 | 74 |

*μg metal $g^{-1}$ dry weight sediment (mean ±1 SD of 3 replicates).
†Recovery efficiency was 100–150%.
‡Recovery efficiency was 135%.

Table 2. Distribution of nickel among sediment fractions

| Site | Date | Fraction* | | % Associated with reactive fraction |
|---|---|---|---|---|
| | | Reactive† | Non-reactive‡ | |
| Douglas Road | 21 May | 14±2 | 25±3 | 36 |
| | 24 July | 36±12 | 7±1 | 83 |
| Gilmore Avenue | 21 May | 13±1 | 17±5 | 42 |
| | 24 July | 46±3 | 16±1 | 75 |
| New Westminster | 21 May | 44±4 | 39±1 | 53 |
| | 24 July | 52±2 | 35±2 | 60 |

*μg metal $g^{-1}$ dry weight sediment (mean ±1 SD of 3 replicates).
†Recovery efficiency was 61–83%.
‡Recovery efficiency was 92 and 84% for May and July samples, respectively.

Table 3. Distribution of copper among sediment fractions

| Site | Date | Fraction* Reactive† | Non-reactive‡ | % Associated with reactive fraction |
|---|---|---|---|---|
| Douglas Road | 21 May | 118 ± 40 | 2 ± 1 | 98 |
|  | 24 July | 71 ± 12 | 3 ± 2 | 96 |
| Gilmore Avenue | 21 May | 62 ± 6 | 3 ± 1 | 96 |
|  | 24 July | 824 ± 86 | 29 ± 11 | 97 |
| New Westminster | 21 May | 41 ± 11 | 6 ± 5 | 87 |
|  | 24 July | 20 ± 6 | 9 ± 1 | 69 |

*μg metal $g^{-1}$ dry weight sediment (mean ± 1 SD of 3 replicates).
†Recovery efficiency was 51–66%.
‡Recovery was 180 and 78% for May and July samples, respectively.

relative contribution of reactive to total copper decreased while that of zinc and nickel remained relatively constant (Tables 1, 2 and 3).

Oxidation-reduction potentials in surface sediments of the Fraser River also varied with the development of freshet conditions. As flow increased to peak discharge in June of 1982, *Eh* increased from +105 to +220 mV and then decreased again as flow decreased (Fig. 4).

Essentially all of the reactive copper and nickel partitioned with the particulate phase of the sediments (Table 4). The phase distribution, defined here as the logarithm of the amount of reactive metal in 1 g dry weight sediment/amount of total metal in the interstitial water accompanying 1 g dry weight sediment ranged from 3.45–3.53 in Still Creek to 4.25 in the Fraser River for nickel and from 3.80 to 4.15 for copper at all sites (Table 5). With the exception of copper, the dissolved metal concentration in the interstitial water was similar to the total concentration of each metal in the water overlying the sediments (Table 4). The data thus demonstrate that the particle-associated reactive copper and nickel were 3–4 orders of magnitude more abundant than the total amount of the respective metal in either the interstitial or flowing water.

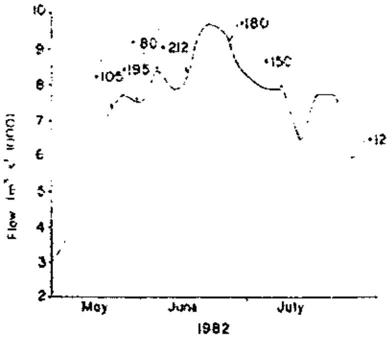

Fig. 4. Oxidation-reduction potential (*Eh*) of surface sediments in the Fraser River at New Westminster during 1982 freshet. Flow data were obtained at Hope B.C. by Water Survey of Canada.

Organic content of the sediment remained relatively constant throughout the year in the Fraser River at New Westminster, contributing from 4 to 5% on the basis of weight loss following combustion (Table 6). Organic carbon determinations based on wet oxidation of sediment subsamples yielded estimates that were generally 20–30% of those obtained by combustion. The organic content of Still Creek sediments exhibited greater seasonal variability than the Fraser River. Variations in organic content were also observed between the 2 sampling sites in Still Creek.

The partitioning of dichromate-oxidizable organic carbon between the particulate and dissolved fraction of the sediments was considerably different from that of the heavy metals (Table 7). While the majority of the oxidizable organic carbon in the sediment was particle-associated, it generally contributed no more than 3 times that which was "dissolved" in the interstitial water.

## DISCUSSION

In most instances, the bulk of the total copper, nickel

Table 4. Distribution of reactive metals between particulate and dissolved phases of sediments

| Fraction | Douglas Road $Cu^{2+}$ | Douglas Road $Ni^{2+}$ | Gilmore Avenue $Cu^{2+}$ | Gilmore Avenue $Ni^{2+}$ | New Westminster $Cu^{2+}$ | New Westminster $Ni^{2+}$ |
|---|---|---|---|---|---|---|
| 1. Total reactive metal (μg $g^{-1}$ dry weight sediment) | 121 | 47 | 98 | 9.9 | 64 | 58 |
| 2. Total metal species in filtered interstitial water (ng in water accompanying 1 gram dry weight sediment) | 8.5 (5.9)* | 16.7 (11.6) | 15.4 (41) | 2.9 (7.8) | 4.6 (4.1) | 3.4 (3.0) |
| 3. Total metal species in unfiltered water overlying sediment (μg $l^{-1}$) | 1.4 | 11.3 | 3.8 | 5.3 | 1.2 | 8.9 |

*Values in parentheses represent μg metal $l^{-1}$ interstitial water.
Samples collected 19 February 1979

Table 5. Phase distribution of copper and nickel in sediments (19 February 1979)*

| Site | $Cu^{2+}$ | $Ni^{2+}$ |
|---|---|---|
| Douglas Road | 4.15 | 3.45 |
| Gilmore Avenue | 3.80 | 3.53 |
| New Westminster | 4.15 | 4.23 |

*Partition coefficients expressed as the logarithm of the amount of reactive metal in 1 g dry weight sediment/amount of total metal in the interstitial water accompanying 1 g dry weight sediment. (Interstitial water has been filtered to remove >0.2 μm diameter particles.)

Table 7. Organic carbon in interstitial water of sediments* (19 February 1979)

| Site | μg C $ml^{-1}$ IW | IWC† | TOC‡ | %§ |
|---|---|---|---|---|
| Douglas Road | 18.8 ± 3.4 | 27.1 ± 4.9 | 90 | 23 |
| Gilmore Avenue‖ | 25.0 | 9.4 | 20 | 32 |
| New Westminster | 16.9 ± 3.4 | 18.9 ± 3.8 | 32 | 37 |

*Interstitial water (IW) was squeezed from duplicate cores and filtered through a 0.2 μm pore size membrane. Organic carbon concentration was estimated by wet oxidation. Values represent mean ± 1 SD of 3 replicate samples.

†μg carbon in interstitial water accompanying 1 g dry weight sediment.

‡μg total organic carbon $g^{-1}$ dry weight sediment after IW was removed.

§Percent of TOC contributed by IWC.

‖Samples pooled to obtain sufficient IW for analysis.

and zinc in the sediments of those sites examined in the Fraser River and Still Creek consisted of the more reactive species of these metals. These results are consistent with previous findings of Bindra and Hall (1975) and others (Chapman *et al.*, 1979). Since essentially all of the reactive metal partitioned with the particulate phase, it is likely that the metals were associated with clay particle surfaces (Gibbs, 1973; Agemian and Chau, 1976), organic ligands (Guy *et al.*, 1978), sulfides (Presley *et al.*, 1972) and hydrous oxides of manganese and iron (Jenne, 1968). Determination of the relative contribution of these components to the reactive metal fraction in the sediments, however, was beyond the scope of the present study.

The significant increase ($P < 0.01$) in reactive copper, nickel and zinc in all but one instance in sediments of Still Creek during the period of decreased flow was likely due to a more rapid deposition of metals introduced via industry-related activities (Hall *et al.*, 1976). Interestingly, the 20–30 μg reactive nickel, 130–255 μg reactive zinc and 738 μg reactive copper (Gilmore Avenue $g^{-1}$ dry sediment which accumulated during low flow, appeared to be released from the surficial sediments as flow increased during the subsequent rainy season (August–November). The reason for the decrease in reactive copper at Douglas Road during low flow is not presently known.

Reactive copper and zinc levels in sediments of the Fraser River fluctuated with flow conditions in a manner similar to those at the Gilmore Avenue site in Still Creek. The apparent release of approx. 20 μg Cu $g^{-1}$ dry sediment at New Westminster suggests that bottom deposits serve as a source of metals for the overlying river water and may contribute to their elevated concentrations in the flowing water during periods of peak flow (Thomas and Grill, 1977). Increased flow likely caused scouring and oxidation of the bottom, processes which favor the dissolution and release of copper and zinc from the sediments (Holmes *et al.*, 1974; Lu and Chen, 1977). The increase (more positive) in *Eh* of surface sediments of the river during freshet demonstrates that the bottom, in fact, became more oxidized during increased flow. Since freshet also caused resuspension of sediments, the reactive metals may also have been released from the bottom deposits in a particulate form. The relative importance of dissolved and particulate mechanisms in the release process is difficult to determine, however, due to rapid association of the dissolved metals to particles already in suspension in the flowing water.

Table 6. Total organic carbon associated with whole sediments

| Site | Date | Organic carbon (mg C $g^{-1}$ dry weight sediment) Wet oxidation | Combustion |
|---|---|---|---|
| Douglas Road | 21 May | 13.2 ± 6.9 | 47 ± 14 |
| | 21 Nov. | 10.4 ± 3.4 | 52† |
| | 19 Feb. | 63.2 ± 21.8 | — |
| Gilmore Avenue | 21 May | 4.3 ± 0.3 | 16 ± 1 |
| | 21 Nov. | 6.0 ± 1.8 | 31 ± 18 |
| | 19 Feb. | 10.4 ± 6.0 | — |
| New Westminster | 21 May | 10.9 ± 1.1 | 40 ± 1 |
| | 21 Nov. | 10.1 ± 7.1 | 47† |
| | 19 Feb. | 12.6 ± 6.9 | — |

*Approximately 0.1 g dry weight sediment was assayed in triplicate. Values represent mean ± 1 (mean ± 1 SD of 3 replicates).

†Value obtained from 1 sample.

The 25–35 μg Ni $g^{-1}$ dry sediment that accumulated during low flow conditions in Still Creek also appeared to be released as flow increased with the onset of the local wet season. Although *Eh* was not determined for sediments of Still Creek, oxidation has also been reported to favor the release of this metal from bottom deposits (Lu and Chen, 1977). A loss of nickel was not observed in the Fraser River, however. The small seasonal variation in reactive nickel concentration and the consistent relationship between reactive and non-reactive nickel fractions at New Westminster suggest that flow-related changes in sediment chemistry were insufficient for the release of this metal.

The decrease in reactive zinc from May to July in sediments at New Westminster may also have been related to freshet conditions. The large fluctuations in concentration of this metal at other times of the year, though, indicate that factors other than flow influence zinc levels in the sediment.

The large increase in reactive metals at Douglas Road during the wet season (November–February) may have been due to changes in organic carbon concentration. Sediment organic carbon increased approx. 6-fold at the site during this period. The organic material may, therefore, have provided additional metal-binding capacity for the streambed. Since episodic changes in current patterns were observed, at the Douglas Road site, short-term accumulation of particulate organic matter in the streambed may have contributed to the observed elevated organic carbon levels.

Organo-metal associations in interstitial water have been considered key factors in regulating the release or retention of metals from sediments (Sugai and Healy, 1978). The tendency for copper and nickel to partition with the particulate phase in the presence of relatively high interstitial water dissolved organic carbon concentrations does not support a major role for dissolved organic carbon in the transport of these metals between bottom deposits and the overlying water. Instead, flow characteristics, which influenced sediment *Eh* and particle movement, appear to be more important in controlling the concentration and phase distribution of metals in these lotic environments.

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