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Effect of Tributary Inflows on the Distribution of Trace Metals in Fine-Grained Bed Sediments and Benthic Insects of the Clark Fork River, Montana

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The effect of tributary inflows on metal concentrations in <63-μm sediments and benthic insects was examined on two scales (380 km and <2 km) in a river impacted by mining. A dilution−mixing model effectively described large-scale dispersion of Cd, Cu, and Pb in the sediments of the river. Input of metal from contaminated flood plains may introduce additional contamination in the middle reaches of the river. Intensive sampling around the confluences of two tributaries showed that there were significant, localized decreases in some metal concentrations immediately downstream of the inflows. Sediment metal concentrations 1 km below the inflows returned to values within the range predicted by the dilution−mixing model. Metal concentrations in benthic insects exhibited spatial patterns similar to those of the sediments, indicating that biological exposures to metals are at least partially dependent on the physical processes controlling the dispersion of sediment-bound metals. Tributary inflows introduce variability in metal contamination on different spatial scales that must be considered when assessing ecological risks in contaminated rivers. In addition to large-scale dilution of contaminants, smaller areas of reduced metal exposure occur near tributary inflows. These may shelter metal-sensitive taxa from severe metal contamination in the mainstem.

Introduction

Mining and smelting practices have resulted in metal contamination of rivers. Uncontained waste from mines located in the headwaters of a large river system can be transported downstream for hundreds of kilometers, eventually contaminating extensive areas of the river, its flood plain, and aquatic organisms (*1*−*5*). Understanding the processes that control the extent and dispersion of contamination away from a source could help reduce adverse effects of future mining and aid the remediation of contamination from historical mining activities.

Simple exponential models describe the downstream distribution of metals in sediments of many rivers contaminated by mine wastes (*6*−*9*). These models can empirically describe the downstream dilution of contaminated sediments by uncontaminated sediments at a point in time, but they do not specifically account for factors that can cause the contamination concentration gradient to change, such as sediment inputs from tributaries or metal and sediment inputs from multiple sources (*7*). Marcus (*7*) used a dilution−mixing model that employed drainage basin areas (as a surrogate for sediment yield) to predict metal concentrations in ephemeral stream bed sediments below tributary confluences as well as suspended sediment metal loads in unmonitored tributaries (*10*). Both studies were conducted in rivers with small (several hundred square kilometers) drainage areas. A similar model was used to predict the dispersion of metal-rich sediment away from ore bodies both before and after mining in larger systems (*11*, *12*). These basin area dilution−mixing models could also provide a context for studying variability, multi-scale spatial trends, or influences of secondary and tertiary sources of contamination (*2*) within larger contamination gradients. Few studies have considered these topics.

In contaminated rivers, metal exposures of biota, determined by tissue residues in organisms such as benthic insects, can follow the downstream contamination trend observed in fine-grained bed sediments (*4*). Thus, bioaccumulation appears to be linked to some of the same processes that control the distribution of sediment-bound metals, even if sediments are not necessarily a direct pathway of exposure. The physical processes that influence metal dispersal in mine-impacted rivers are rarely considered in assessments of biological exposures or toxicity. Understanding how physical processes affect biological exposures might improve the basis for predicting biological risks from contaminants.

In the Clark Fork River, Montana (Figure 1), bed sediments, flood plain sediments, and benthic insects have been extensively contaminated with Cd, Cu, Pb, and other elements by mining and smelting at Butte and Anaconda, near the river's headwaters (*2*, *4*, *9*, *13*−*19*). Mine wastes are no longer discharged directly into the river, but contaminated bed sediments extend at least 380 km downstream of the headwaters (*9*). Contaminated tailings also are stored in the flood plain for at least 180 km downstream (*9*). These flood plain deposits could be a secondary source of contamination to the river (*2*, *9*, *19*).

In this paper, we use intensive sampling and a basin area dilution−mixing model (*7*) to examine the roles of upstream contamination and tributary inflows in controlling the metal concentrations in both fine-grained bed sediments and benthic insects of the Clark Fork River. Our study examines changes in sediment and aquatic insect metal concentrations on spatial scales ranging from <1 to 380 km. The dilution−mixing model also provides a context to assess, indirectly, how input from the contaminated flood plain might affect metal distributions in sediments.

Materials and Methods

Sampling Strategy. Metal concentrations in the <63-μm fraction of bed sediment and in benthic insects were sampled simultaneously at sites along a 380-km reach of the Clark Fork River and in five tributaries (Figure 1) during low flow conditions. Bed sediments in the Clark Fork River range in size from large cobble to clays. The <63-μm fraction was chosen to reduce grain-size bias in metal concentrations among sites. For the large-scale sampling, sites were located approximately 30 km from one another. This sampling intensity is adequate to resolve the large-scale contamination gradient (*9*). For the small-scale sampling, six mainstem sites were sampled within a 2-km reach bordering the confluence of each tributary. The insect taxa we sampled inhabit riffles. Thus, the specific location of sampling sites was determined by habitat and accessibility to the river.

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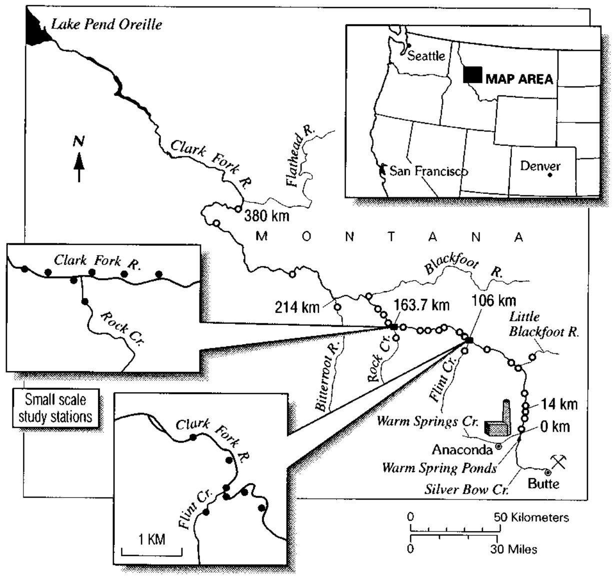

FIGURE 1. Map of study area showing the location of sediment sampling sites (○) on the Clark Fork River and its tributaries for 1986−1992. Insets show confluences of Rock Creek and Flint Creek with the Clark Fork River and sampling locations (●) for 1989 study within 2 km of tributary confluences.

Sediment Procedures. Triplicate bed sediment samples were collected at each site. Each sample was composited from the surface of several deposits of fine-grained material that collected in slow waters along the river's edge (*9*) adjacent to the riffles. Where possible, samples were collected on both sides of the river, or from the perimeter of island bars in the river. The sediments were immediately sieved in ambient river water, through a 63-μm nylon-mesh sieve, transported on ice back to the lab, and dried in a 60 °C oven. After being dried, the samples were ground in a ceramic mortar and pestle.

Sediment samples collected during 1986−1988 and 1990−1992 were digested in a hot, 16 N HNO_3 reflux (*20*) (1986−1988 data reported by Axtmann and Luoma, *9*). In 1989, the sediments were digested with a concentrated aqua-regia-HF microwave digestion (*21*). Results from the two methods are comparable. Cu, Cd, and Pb concentrations were determined in 1986−1987 samples by flame atomic absorption spectrometry (AAS) and in 1989−1992 samples by inductively coupled argon plasma emission spectrometry (ICAPES).

Recoveries for routinely conducted analyses of National Bureau of Standards (NBS) Reference Material 1645 (river sediment) ranged from 70 to 97% for both digestion and analytical methods (AAS and ICAPES). Measured Cu concentrations (104 $\pm$ 3 μg/g, $n = 25$) were within the 95% confidence interval reported by NBS (109 $\pm$ 19 μg/g). Both Pb and Cd concentrations (675 $\pm$ 13 and 8.0 $\pm$ 0.3 μg/g, respectively; $n = 25$) were below the 95% confidence interval reported by NBS (714 $\pm$ 28 and 10.2 $\pm$ 1.5 μg/g, respectively); however, recoveries were consistent among years. Metal concentrations reported here do not necessarily represent total sediment metal concentration but rather an acid-extractable fraction of metal associated with the sediment.

Insect Procedures. The immature form (larva and nymph) of six insect taxa from two orders (Trichoptera and Plecoptera) were collected in our studies of the Clark Fork River and its major tributaries (*4, 18*). For this study, data are reported for four taxa that are common in much of the river: *Hydropsyche* spp. (Trichoptera), *Arctopsyche grandis* (Trichoptera), *Pteronarcys californica* (Plecoptera), and *Claassenia sabulosa* (Plecoptera). Insect samples have been collected annually since 1986. Insect metal concentrations appear to vary with annual river discharge, in contrast to sediment metal concentrations which show no consistent variation with discharge (Hornberger et al., unpublished data). To reduce year-to-year variation from our spatial analysis, data for insects are reported for 2 years of similar river discharge, 1989 and 1990. Insects were randomly sampled from wadable (depth <0.6 m) riffles. Cross-channel sampling was possible at some upstream sites (see below). At other sites, samples were collected from only one side of the river, depending on accessibility. Samples were collected with kick nets and removed from rocks by hand. Individuals were sorted on site to order or family as they were collected. The sample was then transferred to sealable plastic bags filled with ambient river water, held in an iced cooler for 4−6 h to allow time for depuration of the digestive tract content, and then frozen. Complete depuration is difficult to achieve by this procedure, and it was not verified in these samples. The presence of gut content has been shown to positively bias the absolute metal concentrations of the whole insect, but it does not compromise the relative comparisons of bioaccumulation among stations, which is of greater importance to this study (*22*). Before analysis, specimens were thawed in the laboratory and rinsed with deionized water to remove contaminating particles (*4*). Taxa were identified to either genus or species (*23, 24*) and separated. Individuals within taxa were composited into one to five subsamples, depending on the total number of specimens collected at a site, with each subsample having a minimum total dry weight of 50 mg. Samples were dried at 80 °C, weighed, and then digested by hot 16 N HNO_3 reflux. The acid was evaporated, and the dry residue was reconstituted in 0.6 N HCl. Samples were filtered (0.4 μm) and then analyzed by ICAPES.

Data quality assurance was checked by analyzing procedural blanks and standard reference materials (NBS Standard Reference Material 1577a, bovine liver). Measured concentrations of Cd and Cu in the reference material were 0.38 $\pm$ 0.07 and 138 $\pm$ 2 μg/g, respectively, representing recoveries of 86% for Cd and 87% for Cu. Measured Cd concentrations were within the range of certified values, but Cu concentrations were slightly lower than the certified value of 158 $\pm$ 7 μg/g. The reliability of the method could not be verified for Pb because concentrations in NBS reference material were below analytical detection limits.

Intensive Sampling around Tributary Confluences. Fine-grained sediments and benthic insects were sampled in the Clark Fork River at distances of approximately 0.1, 0.5, 1.0, and 10 km upstream and downstream of the confluences of two tributaries (Flint Creek and Rock Creek) in August 1989 during low flow to assess site-specific variability in metal concentrations on small spatial scales (Figure 1). The choices of specific sample sites could influence the small-scale signature of the tributaries in the mainstem, because mixing at tributary confluences is not instantaneous. The Clark Fork River was wadable both above and below Flint Creek, so both sediments and insects could be sampled at mid-channel (Figure 1). However, the mainstem was not wadable near Rock Creek. Therefore, both insect and sediment samples from the mainstem below Rock Creek were collected only from the tributary side of the river at the site 0.1 km below the confluence and from the opposite side of the river at the site at 0.5 km below the confluence. It is unlikely that either water or sediment was well-mixed across the channel at these points (*25*). The samples collected at 1.0 km below Rock Creek, where the channel was ~45 m wide, were taken from along the perimeter of a mid-channel island bar. Cross-channel surface conductivity measurements made at this site in 1995 (at a somewhat lower discharge of ~650 cfs in 1995, compared with ~750 cfs in 1989) indicated that the water was well-mixed (Axtmann, unpublished data).

Statistical Analysis of Insect Data. Concordance between metal concentrations in *Hydropsyche* spp. and in fine-grained sediment over the broad (380-km) scale was analyzed by

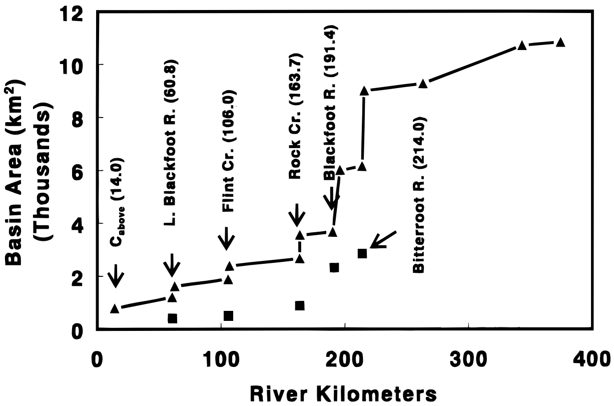

FIGURE 2. Basin area (thousands of km²) of the Clark Fork River (▲) and its major tributaries (■) as a function of river kilometer.

correlation. *Hydropsyche* spp. are best suited for this analysis because they are widely distributed in the river.

Effects of tributary inflows on small-scale changes in insect metal concentrations were tested by either ANOVA or the Kruskall–Wallis test. Data were log-transformed for ANOVA if they were heteroscedastic. If log-transformation did not correct heteroscedasticity, the Kruskall–Wallis test was performed. Metal concentrations in samples collected near the confluences of each tributary were analyzed separately. Data for *Hydropsyche* spp. were analyzed by a mixed-model, two-factor ANOVA. Site location, either upstream or downstream of a tributary, was the first fixed factor, and site distance from the tributary was the second random factor. Interaction between factors was examined with the Tukey Honest Significant Difference test. Other taxa were tested with a single-factor (upstream vs downstream) ANOVA because the availability of specimens either prevented collection of samples or severely limited sample size ($n = 1$) at some sites. Differences in metal concentrations were determined to be significant if $\alpha \leq 0.05$.

Dilution–Mixing Model. In river systems where sediment-bound metals behave relatively conservatively (i.e., streamwater pH is near-neutral and there are no drastic changes in pH or redox conditions at tributary confluences), the metal concentration in sediments below tributary confluences can be estimated from

$$C_{\mathrm{below}} = \frac{C_{\mathrm{above}}A_{\mathrm{above}}}{A_{\mathrm{above}} + A_{\mathrm{trib}}} + \frac{C_{\mathrm{trib}}A_{\mathrm{trib}}}{A_{\mathrm{above}} + A_{\mathrm{trib}}}$$

where C_{below} is the sediment metal concentration (μg/g) in the mainstem below the tributary confluence, C_{above} is the metal concentration (μg/g) in the mainstem sediments immediately above the confluence, C_{trib} is the metal concentration (μg/g) in the tributary sediment, A_{above} is the summed area (km²) of the drainage basin above the confluence, and A_{trib} is the area (km²) of the tributary drainage basin (*7*).

The River Mile Index (*26*) was used to obtain basin areas for the Clark Fork River and its tributaries (in our study, 0 km begins at the confluence of Warm Springs and Silver Bow Creeks, immediately downstream of the Warm Springs Tailings Ponds, Figure 1). Model predictions for the Clark Fork River (C_{below}) were constrained to locations where basin areas were known (generally above and below the confluences of major tributaries) (Figure 2). The first site on the mainstem that had a published basin size was at ~21 km (*26*). Measured sediment metal concentrations from our site closest to that location (at 14.0 km) were used for the boundary condition (C_{above}) in model calculations.

The predicted magnitude of contamination, particularly in the 214-km reach upstream of the confluence of the Bitterroot River, is greatly influenced by the metal concentration chosen for the boundary condition (C_{above} at 14 km). Measured sediment metal concentrations in the upstream most contaminated reaches of the Clark Fork River were highly variable within a given site and over short distances (*9*). Thus both the high and low measured sediment metal concentrations at 14 km were used for the boundary condition (C_{above}), and a range of downstream values was predicted in order to fully illustrate the uncertainty of predictions at any specific location (Figure 3).

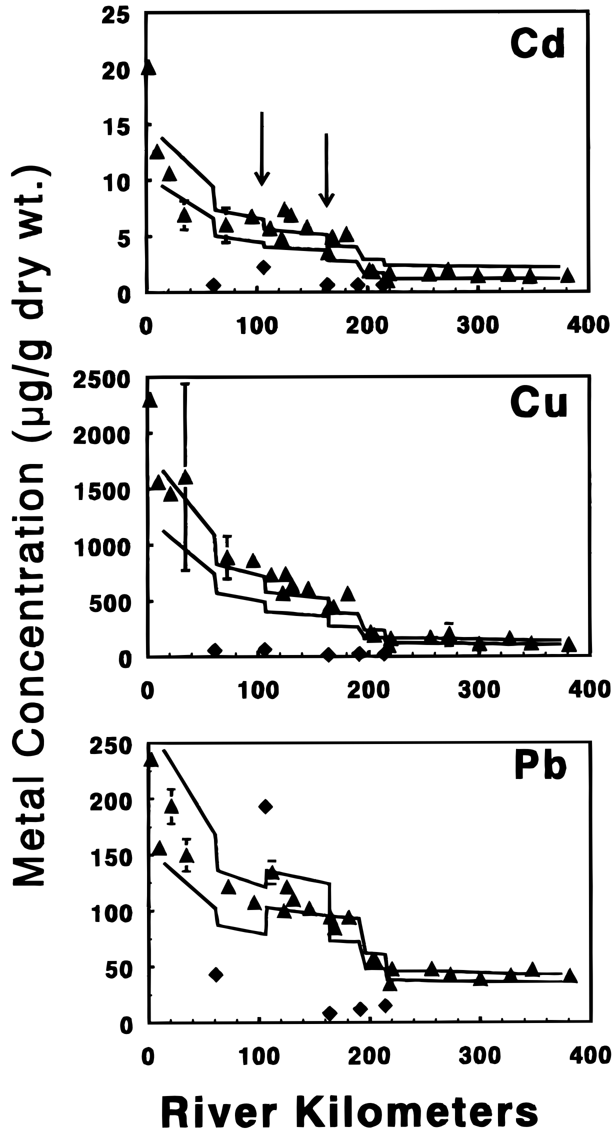

FIGURE 3. Metal concentrations (mean ± 1 standard deviation) in the <63-μm bed sediments in the Clark Fork River (▲) and its major tributaries (♦). Data are for mainstem samples collected in 1986, 1987, 1988, and 1990 and for tributary samples collected during 1986–1992 (not all sites were sampled all years). Distance downstream is measured as river kilometers downstream from the confluence of Warm Springs and Silver Bow Creeks. Solid lines represent the high and low ranges of metal concentrations predicted by the dilution–mixing model. Arrows in the Cd plot indicate locations of the confluences of Flint Creek (106 km) and of Rock Creek (163.7 km).

Where tributary sediment metal concentrations (C_{trib}) were known, these data were used in the calculation (Table 1). Numerous small, unsampled tributaries enter the Clark Fork between the major tributaries indicated in Figure 2. Although not treated as separate subbasins, their basin areas are included in the basin area increases that occur between the major tributaries (Figure 2). An area-weighted mean metal concentration (using all sampled tributaries) was calculated

TABLE 1. Location (River Kilometer of Confluence with Clark Fork River), Basin Area (km^2), and Sediment Metal Concentrations (μg/g dry wt) for Tributaries Used in Dilution−Mixing Model[a]

site	river km	area (km^2)	Cd (μg/g)	Cu (μg/g)	Pb (μg/g)
CF (C_{above})	14.0	782	9.5−13.81	1125−1661	143−244
Little Blackfoot River	60.8	407	≤1.2	54	43
Flint Creek	106.0	499	2.2	61	193
Rock Creek	163.7	855	≤1.2	11	8
Blackfoot River	191.4	2330	≤1.2	21	12
Bitterroot River	214.0	2851	≤1.2	20	15
unsampled tributaries (area-weighted mean)			1.3[b]	24.2	27.6

[a] The range of metal concentrations used for the boundary condition (C_{above}) at 14 km (used in the 380-km prediction), and the area-weighted mean metal concentrations (all tributaries) used for C_{trib} for unsampled tributaries are also given. [b] Area-weighted mean for Cd calculated assuming that below detection limit values are equal to 1.2 μg/g.

and used for C_{trib} (Table 1) for these unsampled tributaries.

Results

Tributary Characteristics. Table 1 shows metal concentrations in the major tributaries of the Clark Fork River (used as C_{trib}) and the area-weighted mean metal concentrations used in the dilution−mixing model for the unsampled tributaries. The two tributaries chosen for the small-scale study of tributary influences on mainstem metal concentrations had the high and low extremes of metal concentrations of any tributary that was sampled. Concentrations of some metals, notably Pb and Cd, were enriched in Flint Creek sediments due to mining in the headwaters. Concentrations of Pb in Flint Creek sediments exceeded those in Clark Fork River sediments collected above the confluence, making Flint Creek a potential source of Pb to the mainstem.

Because Cd concentrations in most tributary sediments were at or below the analytical detection limit ($Cd_{det\ lim}$ = 1.2 μg/g), we used both the value of the detection limit and a value equal to one-tenth the detection limit (approximately the Cd concentration in crustal rock) for C_{trib}. For the model predictions, the high measured C_{above} was used in conjunction with C_{trib} = 1.2 μg/g, and the low measured C_{above} was used with C_{trib} = 0.12 μg/g, in order to represent the broadest range of values.

Model Predictions: 380-km Scale. Metal concentrations observed in mainstem sediments generally were within the range of concentrations predicted by the dilution−mixing model below each tributary and over the 380 km of the Clark Fork River that were studied (Figure 3). The model accurately predicted the ~50% decline in metal concentrations between 14 and 100 km, where the basin area more than doubles due to the inflow of the Little Blackfoot River as well as numerous other small tributaries. The model also accurately predicted metal concentrations downstream from the Bitterroot River (below 214 km). For example, the model predicted Cd, Cu, and Pb concentrations of 1.2−2.2, 104−142, and 36−43 μg/g, respectively, at 380 km; the mean concentrations observed were 1.4, 117, and 41 μg/g (Cd, Cu, and Pb). In contrast, concentrations of Cd and Cu determined in sediments often exceeded concentrations predicted by the model in the middle reaches (60−200 km) of the river, while Pb concentrations in the sediments conformed with model predictions (Figure 3).

Metal concentrations in *Hydropsyche* spp. sampled within the 380-km contamination gradient correlated significantly with metal concentrations in sediments (Figure 4). Relative to sediment metal concentrations, bioaccumulation of Pb was more variable than for either Cd or Cu. For example, high Pb concentrations occurred in insects collected in 1989 from sites in the mid-range of the sediment contamination gradient (70−110 μg/g).

Small-Scale Tributary Effects. The same dilution−mixing model used to predict sediment metal concentrations over 380 km of the river was used, over a short (several kilometer) distance, to predict metal concentrations directly below the confluences of Flint Creek and Rock Creek. The range of metal concentrations in sediments collected in 1989 at the

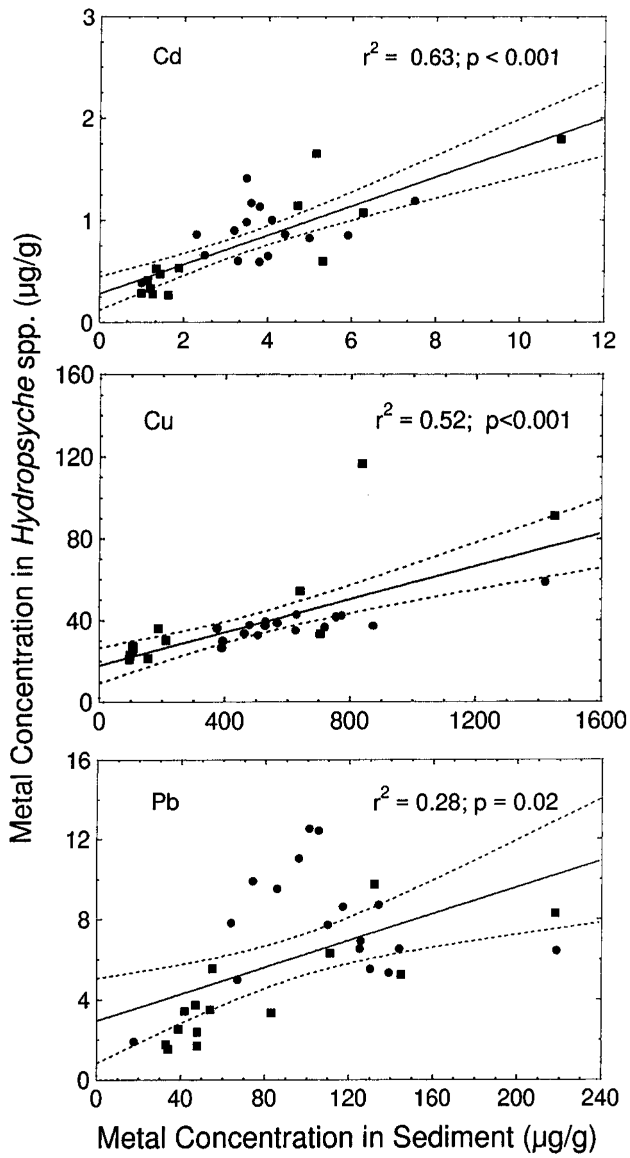

FIGURE 4. Correlation between Cd, Cu, and Pb concentrations in fine-grained bed sediments (<63 μm) and in the caddisfly *Hydropsyche* spp. for years of similar annual discharge in the Clark Fork River. Data from 1989 (●) and 1990 (■) are shown. Data are fit by linear regression. Dashed lines are the 95% confidence interval. The coefficient of determination (r^2) and the significance level of the correlation are shown for each metal.

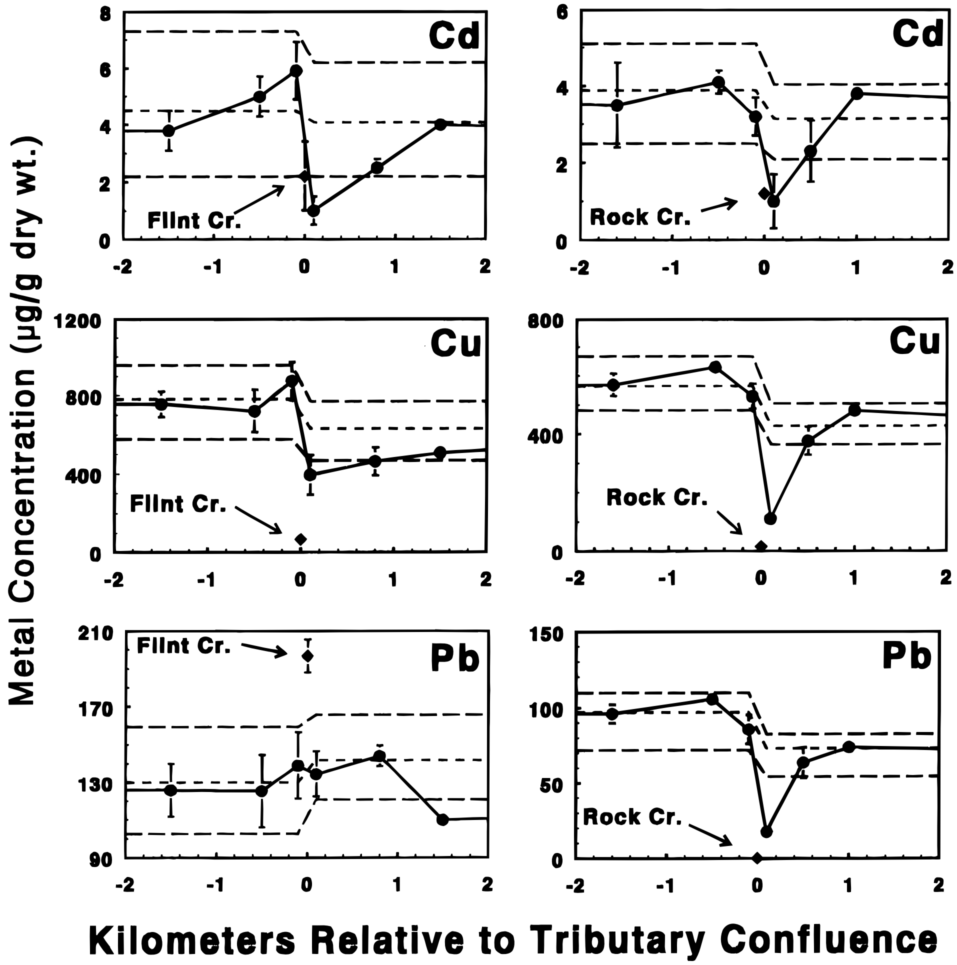

FIGURE 5. Metal concentrations (mean ± 1 standard deviation) in the <63-μm bed sediments collected in 1989 within 2 km of the confluences with Flint Creek (river km 106) and Rock Creek (river km 163.7). Metal concentrations in samples collected ~10 km above and below the confluence are indicated but not include in these plots. Metal concentrations in tributary sediment are indicated. For Cd, Rock Creek sediment had a concentration less than or equal to the analytical detection limit of 1.2 μg/g. Dashed lines represent high, low, and average dilution mixing model predictions for tributary confluences. Model calculation used the high, low, and average measured values for the four upstream sites within 10 km of confluence for C_{above}.

four sites above the confluences was used for C_{above} in each case.

Metal concentrations in sediment samples collected 0.8–1.0 km below both confluences were within the range of concentrations predicted by the dilution mixing model (Figure 5). Where there was a large difference in metal concentration between a tributary (C_{trib}) and the mainstem above the confluence (C_{above}) (e.g., Cd, Cu, and Pb at Rock Creek and Cu at Flint Creek), metal concentrations in sediments collected immediately below the confluence (0.1 km) were well below the ranges predicted by the model. Thus immediately below the confluence of each tributary, sediment metal concentrations were more characteristic of the tributary than of the mixture of the mainstem and tributary. This effect could be exaggerated along the bank of the mainstem receiving the tributary input, where mixing would be less complete. For example, metal concentrations in the samples collected from the Rock Creek side of the Clark Fork River, 0.1 km below the confluence, appeared to have much greater tributary influence than samples collected 0.1 km below Flint Creek from a mid-channel island. If the sediments collected immediately below Rock Creek had been collected from mid-channel or the opposite bank, no effect of the tributary might have been observed.

When the difference between tributary and mainstem sediment metal concentrations was small, the influence of tributary inflow on mainstem metal concentrations was not as obvious. Lead concentrations in Flint Creek sediments exceeded those in Clark Fork sediments collected above the confluence by 50% (197 ± 9 vs 130 ± 18 μg/g, respectively). The model predicted approximately a 9% increase in Pb concentrations below the confluence. Although Pb concentrations in samples collected within 1 km of the confluence were within the model predictions, the mean Pb concentration at 0.1 km below the confluence actually decreased slightly. Lead concentrations decreased to values outside of the predicted range by 1.5 km below the confluence of Flint Creek. The high spatial variability in metal concentrations inherent in the system may have partly obscured the small tributary input of Pb. For the other metals and for Pb below Rock Creek, the predicted differences in metal concentrations above and below the confluence were at least 20%, because $C_{above} \gg C_{trib}$.

Metal concentrations in insects collected near the tributaries exhibited spatial patterns similar to those observed in sediments. Metal concentrations in samples immediately downstream of the confluences tended to reflect tributary input (Figure 6). This general pattern was observed in all four taxa for at least one metal (e.g., Cd concentrations at Flint Creek, Figure 6), and it was most consistently displayed by the caddisflies, *Hydropsyche* spp., and *A. grandis*. In *Hydropsyche* spp., metal concentrations at sites upstream of the tributaries were relatively stable (significant differences occurred only at 0.5 km upstream of Rock Creek where concentrations of Cu and Pb were greater than either one or both of the adjacent upstream sites). Concentrations of all

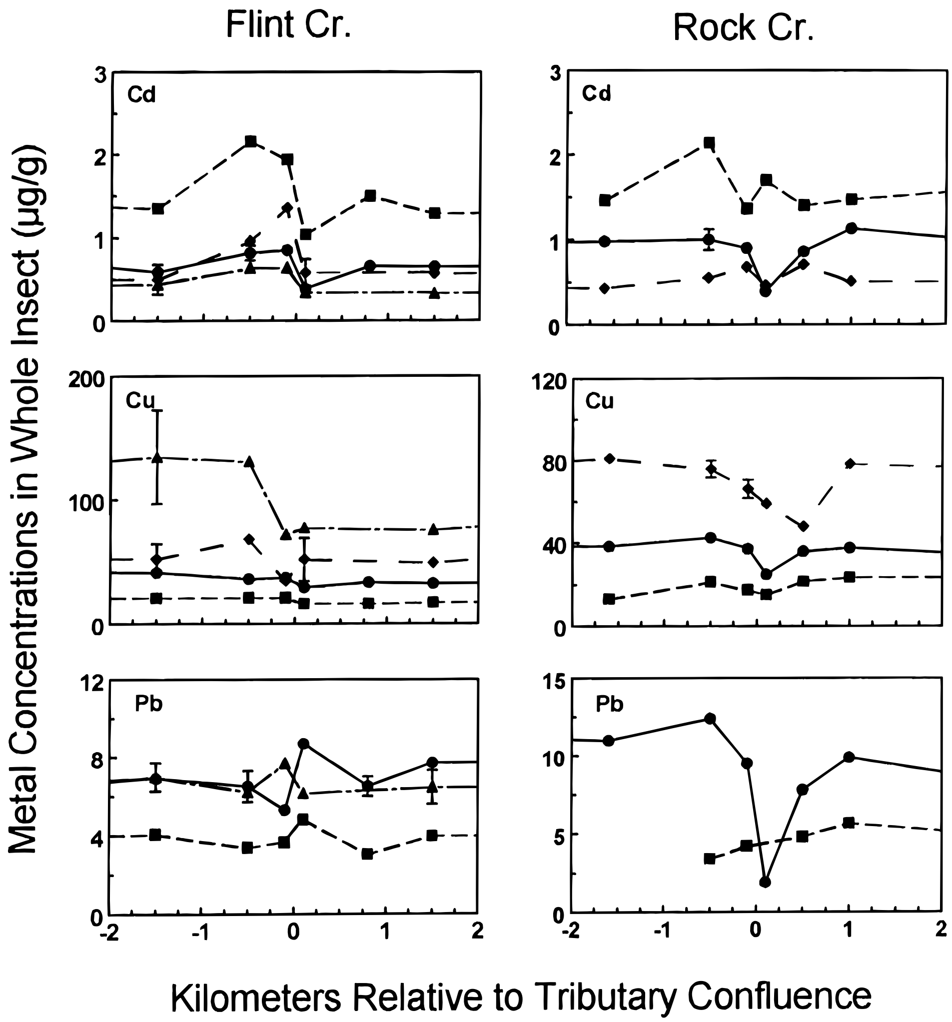

FIGURE 6. Metal concentrations (mean ± 1 standard deviation where *n* > 1) in insects sampled in the mainstem of the Clark Fork River within 2 km of the confluences with Flint Creek (river km 106) and Rock Creek (river km 163.7). Metal concentrations in samples collected ∼10 km above and below the confluence are indicated but not included in these plots. Lead data for *Claassenia sabulosa* are not shown because concentrations in many samples were below analytical detection limits. *Hydropsyche* spp. (●); *Arctopsyche grandis* (■); *Pteronarcys californica* (▲); *Claassenia sabulosa* (♦). Standard deviations for samples of *Hydropsyche* spp. are sometimes smaller than the symbol size.

metals decreased significantly at 0.1 km below the confluences of both tributaries, except Pb at Flint Creek which increased significantly (Figure 6). Thus, the direction and the relative magnitude of change in metal concentrations were consistent with the inputs of sediment-bound metals from the tributaries.

The influence of the tributaries on insect metal concentrations was generally less distinct at sites located >0.5 km downstream of the tributaries, as metal concentrations tended to return to upstream values (Figure 6). In *Hydropsyche* spp., metal concentrations in the samples collected at 1.5 and 1.0 km downstream of Flint Creek and Rock Creek, respectively, were usually statistically indistinguishable from sites at ≥0.5 km upstream of the respective tributary. Only Cu and Pb concentrations at 1.5 km downstream of Flint Creek remained slightly lower and higher, respectively, than one or more upstream sites. However, at both tributaries the mean metal concentrations from all three downstream sites (as a group) were never significantly different than those at the upstream sites. This was usually observed in other taxa also. Significant differences between upstream and downstream sites (one-way ANOVA) occurred only at Flint Creek where Cd in *A. grandis* and *P. californica* and Cu in *A. grandis* were less downstream than upstream. Thus, the effect of tributary inflows on insect metal concentrations was typically restricted to the site immediately downstream of the tributary.

Tributary inputs did not appear to uniformly affect metal bioaccumulation in all taxa however. At Flint Creek, Cu and Pb concentrations in *P. californica* changed—in a manner consistent with tributary inputs—at the site 0.1 km upstream of the confluence (Figure 6) instead of downstream of the confluence as in the caddisflies, *Hydropsyche* spp., and *A. grandis*. Copper concentrations in *C. sabulosa* showed a similar pattern. At Rock Creek, Cd concentrations in *A. grandis* were highly variable upstream and downstream of the confluence (Figure 6), and no clear tributary signal was observed. Similarly, the effect of tributary inputs was not obvious on Cu concentrations in *C. sabulosa*. Copper concentrations decreased gradually from 0.5 km upstream to 0.5 km downstream of the confluence. The lowest Cu concentrations occurred at 0.1 and 0.5 km below the confluence of the tributary.

Discussion

The dilution−mixing model predicted the downstream dispersion of sediment metal concentrations reasonably well over a 380-km reach of the Clark Fork River. The first-order controls on contamination at any point in the river appeared to be the watershed area (as a surrogate for sediment input) upstream from that point and the metal concentration in the upstream-most watershed (C_{above}). Where these are the major factors controlling contamination in mine-impacted rivers, reducing contaminant concentrations in the most upstream sediments could be the most effective strategy for remediating downstream contamination. The dilution−mixing model predicts that reducing Cu concentrations in the upstream stretch of the Clark Fork River (C_{above}) to 100 μg/g would result in concentrations of approximately 30 μg/g below the confluence of the Bitterroot River (at 214 km). Reducing C_{above} for Pb to 50 μg/g would result in concentrations of approximately 30 μg/g below the confluence of the Bitterroot. For Cd, reducing C_{above} by one-half (to 6 μg/g) would result in concentrations below the detection limit ($\sim$0.8 μg/g) just below 214 km (if $C_{trib} = 0.12$ μg/g).

The model predicted contamination changes accurately in the upstream- and downstream-most reaches. Cadmium and Cu concentrations were consistently underpredicted in the middle reaches (approximately 60−200 km) of the river however. One explanation for the low predicted concentrations in this area is local input of metals from the contaminated flood plain sediments. Elevated metal concentrations in eroding banks of the river occur as far downstream as 180 km from the headwaters (*9*). Slumping of contaminated river banks and/or influx of groundwater that has passed through contaminated flood plain could reduce the effectiveness of tributary inflows in diluting contamination in mine-impacted rivers (*27*). These secondary sources are not taken into account in the model predictions, although an estimate of the sediment contribution from eroding banks would certainly increase the predictive capability of the model. The variability in sediment metal concentrations typical of the contaminated upper reaches of the Clark Fork River also adds uncertainty to the downstream predictions. Thus, quantitative determinations of the influence of the secondary inputs based on deviations from the dilution−mixing model are not feasible. Nevertheless, the significance of the secondary sources is indicated by the fact that observed concentrations exceeded predictions based upon the highest measured concentrations at 14 km. If upstream metal concentrations were drastically reduced, the additional contaminant sources in the middle reaches of the river might become a more important factor controlling sediment metal contamination in that area.

The model more accurately predicted Pb concentrations in the middle reach than it did Cu and Cd concentrations. Unlike Cd and Cu, there is a well-defined secondary source of Pb (Flint Creek) in this reach of the river. Because this input is known, it may have improved the predictive capability of the model. Where tributaries are a source of contamination in a mining-impacted river, tributary remediation is probably necessary for remediation of the mainstem. Again, however, inputs from other secondary sources (erosion of contaminated banks, for example) could mitigate the diluting effect of the tributary, as seen with Cd and Cu. The dilution−mixing model assumes that sediments behave conservatively and that mixing occurs instantaneously below tributary confluences. The model predicts clear step decreases (or increases, in the case of Pb below Flint Creek) below tributaries. In large river systems such as the Mississippi, complete mixing of water parcels below large tributary confluences may not occur for 200−300 km downstream, based on cross-channel specific conductance measurements of surface waters below the confluence of the Ohio and Mississippi Rivers (*28*). For rivers with smaller channel widths (on the order of 5−15 m) complete mixing of waters can occur within 25 channel widths downstream from a confluence, depending on bed morphology (*29*). Johnsson et al. (*25*) reported essentially complete mixing of bedload within 100 km downstream of a triple confluence in the Orinoco River. Clearly, mixing of both water and bedload is not instantaneous. In the Clark Fork River, we have shown that one result of incomplete mixing is high variability in contamination around tributaries, with mainstem metal concentrations immediately below the confluences that more closely reflect tributary values than a mixture of tributary and mainstem.

Sediment behavior also is not strictly conservative in a river. There are areas of storage and resuspension of fine-grained material within the bed throughout a river, and this will tend to increase spatial variability in sediment metal concentrations. For example, our model effectively predicted downstream dispersion of Pb on a large (380-km) scale, but it did not predict the small-scale distribution of Pb around the confluence of Flint Creek. In fact, sediment metal concentrations are highly variable site-to-site in the Clark Fork River, even between major tributary inflows. Axtmann and Luoma (*9*) reported that when metal concentrations in the Clark Fork River were grouped into river reaches between major tributaries, concentrations were not significantly different in adjacent reaches. If one of the localized effects of tributary inflows is to introduce spatial variability in metal concentrations in mining-impacted rivers, then the complexities of sediment transport may accentuate that variability.

Our results indicate that site-specific differences in metal bioaccumulation are affected by the same physical processes controlling the dispersion of sediment-bound metals from an upstream source. Evidence of the effect of these processes was observed on both the large (380-km) and small (<2-km) spatial scales examined in the study. Changes in insect metal concentrations over the broad contamination gradient closely patterned changes in the contamination levels of bed sediments. Where physical mixing had a dramatic effect on sediment metal contamination around the confluence of tributaries, such processes had a similar effect on the metal concentrations in a variety of benthic insect taxa. Therefore, it is not surprising that downstream metal concentration gradients in stream-dwelling insects often resemble those in sediments or unfiltered water (*3*, *4*, *30*−*32*).

Although not the focus of the present study, biological and geochemical processes also affect metal concentrations in insects (*4*, *22*). The weakest overall correlations between metal concentrations in sediments and *Hydropsyche* spp. for the combined data of 1989 and 1990 occurred for Pb. In that data set, the Pb concentrations in insects collected in 1989 from mainstem stations between Flint Creek and 1.0 km below Rock Creek were notably higher than other samples relative to sediment Pb concentrations, indicating that processes specific to that time and reach enhanced the bioaccumulation of Pb. Species-specific differences in bioaccumulation is a common observation and can be affected by a number of factors including feeding habit, metal metabolism, life history, and activity patterns (*4*, *22*, *32*−*34*). These factors might also have contributed to observed inconsistencies in spatial bioaccumulation patterns among taxa. The influence of tributary input was most evident in the caddisflies, *Hydropsyche* spp., and *A. grandis*. In comparison, concentration patterns for Cu and Pb in the stoneflies, *P. californica*, and *C. sabulosa* were less indicative of tributary inputs.

Metals have been widely cited as a probable causative factor adversely affecting biological communities in the Clark Fork River (*35*−*49*). As expected, the severity of these effects is related to the distribution of metal contaminants in the river. Structural changes in the macroinvertebrate community have been documented in the upper Clark Fork River (*35*, *37*−*41*). The most significant changes coincide with high metal concentrations observed in aquatic insects in the upper 70 km of the river (*4*, this study). Taxa richness increases most dramatically after the initial rapid dilution of contamination below the first large tributary (the Little Blackfoot River) at river km 60.8. Trout populations also appear to respond to the mitigating influence of tributary inputs on metal contamination. For example, densities of brown trout increased from less than 50 fish per mile upstream of Rock Creek to about 500 fish per mile downstream of Rock Creek (*43*). Instream toxicity tests have shown that mortality of young rainbow trout is significantly reduced below Rock Creek as compared to sites upstream of Rock Creek (*44*). Although physical degradation of habitat by mine wastes is probably important in structuring biological communities in the mainstem, especially in the upper 70 km of the river, the effect of tributary dilution appears significant.

The mixing of contaminated and uncontaminated media that cause sediment metal concentrations to vary on different spatial scales probably also cause metal exposures to biota to be spatially complex. Therefore, understanding the pattern of physical dilution of contamination by tributaries inputs could be important in predicting patterns of biological effects. For example, signs of biological recovery following remediation might be observed first in mixing zones below tributary inputs. Tributaries are fundamental to the biological recovery of the mainstem, serving as refuges from contamination and as potential sources of colonists to the mainstem. Colonization by metal-sensitive taxa might occur where mixing of tributary inflows with the mainstem superimpose smaller areas of reduced metal exposure on the larger contamination gradient. The physical characteristics of mixing zones and the attendant metal exposures would be expected to vary with conditions discussed above.

In summary, the dilution mixing model effectively described large-scale (380-km) dispersion of Cd, Cu, and Pb in the fine-grained sediments of the Clark Fork River. Tributary inflows appear to control the overall downstream dilution in sediment metal concentrations, but metal concentrations of sediments are highly variable on small scales (<1 km) where tributary and mainstem flows mix. Contaminated banks may also add variability and increase metal concentrations in sediments, particularly in the middle reaches of the river. A better understanding of the geomorphologic processes in the river could increase our ability to predict perturbations in the downstream gradient. Metal concentrations in benthos resembled contamination patterns in the sediments and appear to be at least indirectly affected by the physical processes controlling the dispersion of sediment-bound metals.

Biology, hydrology, and geochemistry should all be considered when assessing the risk metals pose to biological communities in contaminated rivers. Ecological risk assessments and associated toxicology studies are often conducted outside the physical context of mining-impacted rivers (*50*). The design of such studies and the ability to interpret results might be improved by consideration of major physical processes, such as tributary inflows, that affect the transport, mixing, and deposition of contaminated media.

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