Ecological Applications, 19(6), 2009, pp. 1522–1535

Influence of remediation in a mine-impacted river: metal trends over large spatial and temporal scales

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Abstract. The effectiveness of mine-waste remediation at the Clark Fork River Superfund site in western Montana, USA, was examined by monitoring metal concentrations in resident biota (caddisfly, *Hydropsyche* spp.) and bed sediment over a 19-year period. Remediation activities began in 1990 and are ongoing. In the upper 45 km, reduced Cu and Cd concentrations at some sites were coincident with remediation events. However, for a period of three years, the decline in Cu and Cd directly below the treatment ponds was offset by high arsenic concentrations, suggesting that remediation for cations (e.g., Cu and Cd) mobilized anions such as arsenic. The impact of remediation in the middle and lower reaches was confounded by a significant positive relationship between metal bioaccumulation and stream discharge. High flows did not dilute metals but redistributed contaminants throughout the river. The majority of clean-up efforts were focused on reducing metal-rich sediments in the most contaminated upstream reach, implicitly assuming that improvements upstream will positively impact the downstream stations. We tested this assumption by correlating temporal metal trends in sediment between and among stations. The strength of that association (r value) was our indicator of spatial connectivity. Connectivity for both Cu and Cd was strong at small spatial scales. Large-scale connectivity was strongest with Cu since similar temporal reductions were observed at most monitoring stations. The most upstream station, closest to remediation, had the lowest connectivity, but the next three downstream sites were strongly correlated to trends downstream. Targeted remediation in this reach would be an effective approach to positively influencing the downstream stations.

Key words: arsenic; bioaccumulation; caddisfly; cadmium; Clark Fork River Superfund site; connectivity; copper; Hydropsyche *spp.; Montana, USA; remediation.*

Introduction

Remediation activities in mine-impacted rivers are occurring all over the world, as mines close or as the wastes of abandoned mines are cleaned up. The U.S. Environmental Protection Agency has identified over 150 rivers or streams which have been heavily contaminated with metals from hard rock mining (EPA 2004). In addition to the obvious environmental impacts, there are large economic consequences associated with remediating such sites. The conservative estimated cost for mine-waste remediation in the U.S. ranges from seven to 24 billion U.S. dollars (EPA 2004). However, despite the large economic investment, very few studies address the long-term success of remediation. Existing studies are often short term (<5 years) and focus on indirect measures of success. For example, while water quality and biological assessments (Nelson and Roline 1996, Prat et al. 1999, Gale et al. 2004, Neal et al. 2005) provide information on chemical and biological changes along a contamination gradient, neither provides direct evidence of metal exposure and bioavailability. Aquatic organisms do not always respond to changes in dissolved metal exposure (Hare et al. 2003), and physical variability (e.g., habitat preferences) can influence the distribution of indicator species.

The influence of metal bioaccumulation and species-specific tolerance to metals exposure has been successfully demonstrated (e.g., Cain et al. 2004, Clark and Clements 2006) and provides a direct link between metal exposure and ecological effects. These studies support the approach of using resident organisms to determine metal bioavailability from local environmental conditions (Phillips and Rainbow 1993) and provide an appropriate measure of biological response to remediation.

Here we use a 19-year data set to evaluate the influence of remediation along a 200-km segment of the Clark Fork River (CFR) Superfund site in western Montana, USA (Fig. 1). This is part of the largest Superfund complex in the United States and has been severely impacted by mining activities for more than a

Manuscript received 16 August 2008; revised 20 January 2009; accepted 29 January 2009. Corresponding Editor: J. S. Baron.
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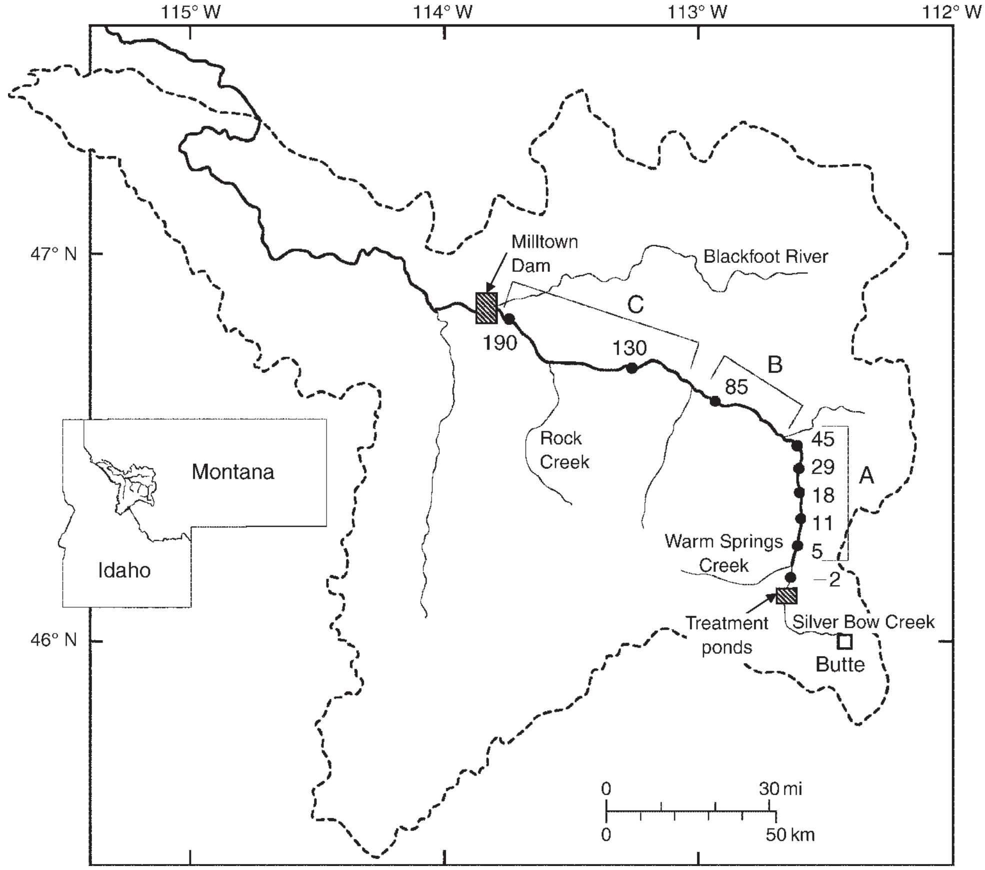

Fig. 1. Site location map of the Clark Fork River, Montana, USA, Station kilometers are marked as solid circles and indicate distance (km) from the confluence of Warm Springs and Silver Bow Creeks. Upper Reach (A), Middle Reach (B), and Lower Reach (C) are designated stream reaches.

century (Moore and Luoma 1990). Annual concentrations of Cu and Cd were measured in fine-grained surface sediments and resident aquatic organisms. Sediments are the largest source of metals in the river and reflect contaminant inputs (Moore and Luoma 1990). Metals in insects reflect bioavailable metal in the system (Hare 1992, Phillips and Rainbow 1993, Cain and Luoma 1998, Rainbow 2002, Solà and Prat 2006). Together, both indicators reveal trends of environmental change over time and space.

The influence of remediation was assessed by applying a novel approach: using contaminants as a spatial transport marker (that is, a measure of contaminant movement from upstream to downstream), we quantified the strength of spatial connectivity throughout the study reach and identified site-specific zones that influenced contaminant loads to downstream stations. Because it is not generally feasible to remove all waste material, remediation often targets only the most contaminated river segments. The implicit assumption with this approach is that improvements upstream will positively impact downstream stations. However, it is not clear that this assumption has been tested. Spatial connectivity allows us to examine that premise. Three specific objectives are addressed: (1) describe spatial and temporal trends of Cu and Cd in surface sediment and resident biota; (2) using sediment metal concentrations as a spatial marker of downstream transport, test the assumption that site-specific upstream remediation will impact downstream stations; and (3) quantify the strength of local (small-scale) and regional (large-scale) connectivity to identify reach-specific zones that influence downstream stations.

Background

Mining and processing of metal ores began in the 1850s in headwaters of Silver Bow Creek and the upper Clark Fork River (CFR) in western Montana, USA (CFR; Fig. 1). For more than a century, large quantities of waste rock, tailings, and slag (hereafter referred to as tailings) rich in heavy metals were produced. Andrews (1987) estimated that 100 million tons of tailings were disposed of in Silver Bow Creek and the upper CFR between 1880 and 1982. Erosion, runoff, and large floods during the 20th century transported and dispersed tailings over extensive distances in the channel and

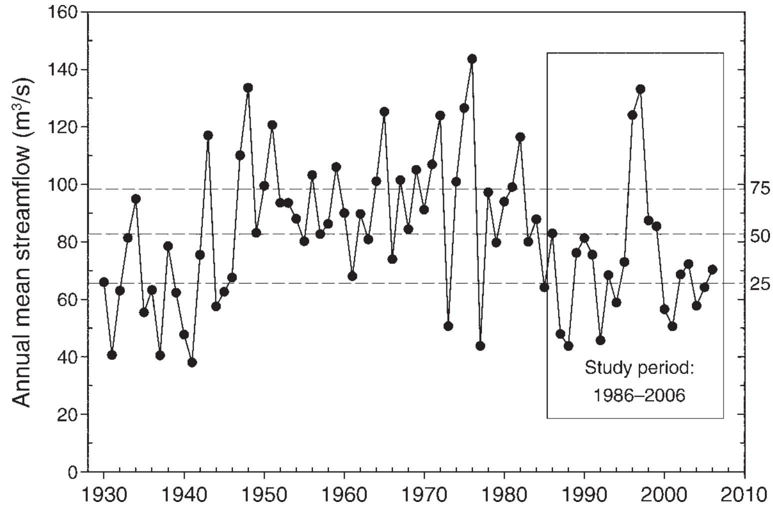

FIG. 2. Annual mean streamflow at a station with the longest period of record (1930–2007) in the Clark Fork River (⟨http://waterdata.usgs.gov/mt/nwis⟩). The magnitude of variability is representative of flow conditions at most monitoring stations. High flow, mean flow, and low flow conditions are represented by the 75th, 50th, and 25th percentiles (dashed lines; right-hand axis).

floodplain of the CFR. Although the disposal practices that contributed to the greatest dispersion of tailings have been discontinued, metal contamination of sediments, floodplains, and biota presently extends >400 km downstream, with the highest levels of contamination in the upper 45 km (Reach A, Fig. 1; Andrews 1987, Moore and Luoma 1990, Axtmann and Luoma 1991, Hornberger et al. 1997).

The CFR was declared a Superfund site in 1989 and remediation efforts were initiated to mitigate some of the most severe metal inputs (Pioneer Technical Services 2002). To reduce the amount of tailings deposited into the river, large berms were constructed in the upper 45 km between 1989 and 1990. Small-scale demonstration projects have also been conducted, which focused on in situ treatment of soils in the riparian zone and bank stabilization (Pioneer Technical Services 2002). Remediation is ongoing, but to date, all activities have been spatially restricted to the upper 45 km of the CFR.

Because discharge is the primary mechanism of contaminant transport in this system, hydrologic conditions during the study period were compared to historical conditions at a site with a long continuous streamflow record (Fig. 2). Since 1986, most streamflow values fell between the 25th and 50th percentiles, however high-discharge events exceeded the 75th percentile in 1996 and 1997 (Fig. 2). Annual mean streamflow conditions prior to remediation were generally higher than those observed during the study period.

METHODS

Field collection

Metal concentrations in aquatic macroinvertebrates and streambed sediment at nine mainstem stations in the Clark Fork River (CFR) were studied from 1986 to 1987 and from 1990 to 2006 (Axtmann and Luoma 1991, Cain et al. 1995, Hornberger et al. 1997, Dodge et al. 2006). Most stations were sampled in consecutive years although the period of record (10–19 years) depends on when the station was added to the monitoring network. Since 1993, dissolved Cu concentrations (and other water-quality parameters) have been measured at six of the nine long-term monitoring stations (see Dodge et al. 2006 for specific details on sampling protocols). Dissolved Cd concentrations in the CFR are near or below detection limits and are not discussed here. Sampling sites were located adjacent to USGS gauging stations where possible, beginning on Silver Bow Creek, 2 km above the confluence of Silver Bow and Warm Springs Creeks. Stations extended ~200 km downstream to Milltown Dam (Fig. 1). The six sites closest to remediation activities are located in the upper 45 km (Reach A, Fig. 1). Three additional sites were sampled at a broader spatial scale to evaluate changes in the middle (Reach B, 85 km) and lower river segments (Reach C, 130 and 189 km; Fig. 1).

Bed sediment was collected from the surface of small deposits in slack waters at the edge of the river using an acid-washed polypropylene scoop (Axtmann and Luoma 1991). Three replicate composite samples were collected from each station, and samples were collected from both sides of the river wherever possible. Particle-size distribution can influence metal concentrations (Salomons and Forstner 1984). Thus, accurate detection of spatial and temporal trends can only be made if grain-size bias is considered. Because grain size in the CFR varies from cobbles to clays, composite samples were wet sieved in ambient river water using a trace-metal-clean 64-μm nylon-mesh sieve (one per site). The fine-grained (<64-μm) fraction was collected in acid-washed 500-mL polyethylene bottles and transported to the laboratory on ice.

Interpretations of bioaccumulation data in this analysis were restricted to the genus *Hydropsyche* spp. (Order Trichoptera), a metal-tolerant, filter-feeding caddisfly that is widespread in the Clark Fork (Cain and Luoma 1998). *Hydropsyche* are "fortuitous feeders" (Mecom 1972). Detritus (both organic and inorganic), diatoms, and animal material make up the greatest portion of food ingested (Benke and Wallace 1980, Boon 1985, Voelz and Ward 1996). Ingested particles are dependent on life stage but late-instar *Hydropsyche* ingest a range of particle sizes, from 75 μm (diatoms; Wallace et al. 1977, Fuller et al. 1983, Voelz and Ward 1996) to 75–250 μm (detritus; Voelz and Ward 1996). Late-instar *Hydropsyche* can become predaceous (Tajmrová and Helesic 2007). *Hydropsyche* are univoltine (one-year life cycle) and relatively sessile, thus they are useful indicators of site-specific bioavailable concentrations of metals.

Hydropsyche collected in the CFR grow rapidly in the summer and emerge in late summer and early fall (Hauer and Stanford 1982). Sample collections took place in late summer in all years (early-mid August), so most *Hydropsyche* were late instar (IV–V). Metal analyses on a range of *Hydropsyche* sizes were not significantly different (M. Hornberger, *unpublished data*), thus we assumed that metal exposure was not necessarily due to the life-stage of the organism but rather the exposure conditions at a site. The influence of seasonality was not examined, and exposure variables do change throughout the year. However, annual collections during low-flow conditions provided temporal consistency. Metal bioaccumulation patterns in the CFR do not systematically differ between the two dominant *Hydropsyche* species (*H. occidentalis* and *H. cockerelli*; Hornberger et al. 1997, Cain and Luoma 1998), thus data for both species were combined in our analysis.

Hydropsyche were collected from riffles simultaneously with bed sediment. A trace-metal-clean nylon mesh kick net was used to sample until ~200–300 individuals were collected. Insects were frozen in the field and transported back to the laboratory where they were thawed and rinsed with ultra-pure deionized water to remove any surface particulate material. Samples were sorted to the lowest possible taxonomic level, usually to species (Schefter and Wiggins 1986, Merritt and Cummins 1996). Sample mass was usually sufficient to analyze 3–6 subsamples from each station. Each subsample was composed of ~40–70 individuals (third or fourth instar) of the same species. *Hydropsyche* were not depurated after collection. An earlier study by Cain et al. (1995) reported that while *Hydropsyche* gut content contributed 32–46% toward the whole body Cu and Cd concentration, there was no statistical difference among stations. The authors concluded that the influence of gut content does not confound trends or conclusions about spatial distributions (Cain et al. 1995).

Regional background metal concentrations were determined in each year using data from the Blackfoot River and Rock Creek, two reference tributaries within the watershed (Fig. 1). Metal concentrations in these regional reference stations were not temporally variable (Dodge et al. 2006). Mean concentrations in background bed sediment ranged from 10 to 30 μg/g Cu and 0.5 to 2.0 μg/g Cd (dry mass). Regional reference concentrations in *Hydropsyche* (also reported in dry mass) ranged from 10 to 20 μg/g Cu and 0.2 to 0.5 μg/g Cd.

Sample preparation and analysis

Bed-sediment samples were dried at 60°C and ground using an acid-washed ceramic mortar and pestle. Replicate aliquots of ~0.6 g of sediment were digested using a hot, concentrated HNO_3 reflux digest (Luoma and Bryan 1981). After a digestion period of 2 weeks, samples were evaporated to dryness and re-dissolved with 20 mL of 0.6 mol/L HCl. The reconstituted samples were filtered through an in-line disposable 0.45-μm syringe filter. The filtrate was diluted 1:5 or 1:10 with 0.6 mol/L HCl, and analyzed for metals using inductively coupled argon plasma emission spectroscopy (ICAPES).

Macroinvertebrate samples were placed in a tared scintillation vial and dried at 60°C. After a final dry mass was obtained, samples were digested by reflux using concentrated HNO_3 then evaporated to dryness. The dried residue was reconstituted in 0.6 mol/L HCl, filtered through a 0.45-μm filter, and analyzed for metals using ICAPES. Concentrations for bed sediment and *Hydropsyche* are reported in ug/g dry mass.

Quality assurance

Non-metallic nets and acid-washed sampling equipment were used throughout the study. Cross contamination between sites was avoided by frequent gear changes and collecting sequentially from downstream to upstream (low to high contamination). Procedural blanks were analyzed with each sample batch and recovery efficiency for each metal was determined using standard reference materials for both bed sediment (SRM 2711; National Institute of Standards and Technology, Gaithersburg, Maryland, USA) and biota (SRM 1566a [National Institute of Standards and Technology], NRC Tort-2 [National Research Council Canada, Ottawa, Ontario, Canada]). Annual reports published by the USGS describe specific QA/QC results for each year (Dodge et al. 2006). Over the course of the study, mean recoveries (±SD) for SRM 1566a (oyster tissue) were 99.8% ± 1.3% Cu and 101% ± 4% Cd; for NRC Tort-2 (lobster hepatopancreas), recoveries for Cu and Cd were 93.2% ± 4.0% and 94.6% ± 6.0%, respectively. The measured concentrations were within ranges of reported uncertainty. Standards analyzed for bed sediment were also within acceptable certified ranges. Mean percentage recoveries for SRM 2711 (Montana soil) were 92.5% ± 8% for Cu and 103% ± 3.6% for Cd.

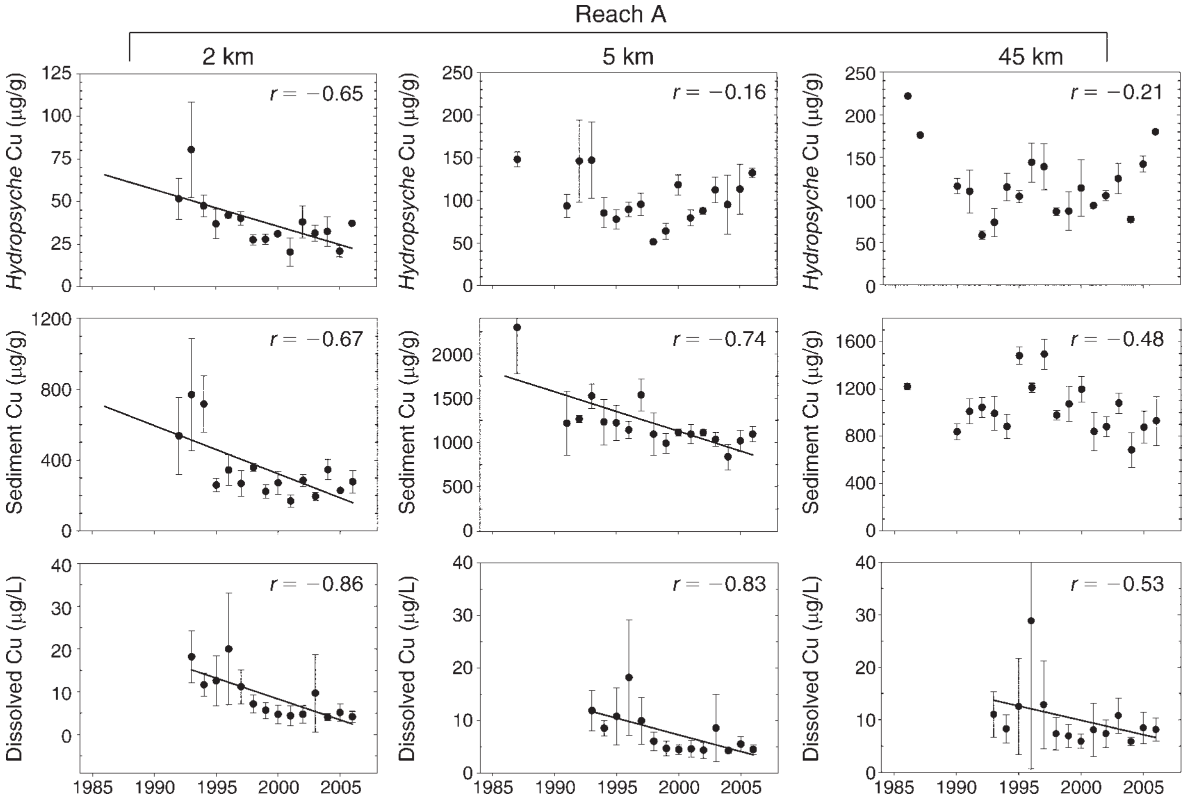

FIG. 3. Annual Cu concentrations (mean ± SE) in caddisflies (*Hydropsyche* spp.) and in bed sediment (both in μg/g dry mass), and dissolved Cu (μg/L) plotted against year. Data are shown for the six sites with the longest period of record. Note that the *y*-axis scales vary by Cu source and site. A Pearson correlation (*r*) was calculated at each site. Significant temporal relationships ($P < 0.05$) are represented by solid lines.

Statistical analysis

Statistical analysis was conducted using Statistica (StatSoft, Tulsa, Oklahoma, USA). Pearson correlations between metal concentration and year were used to describe temporal patterns. Correlations were also used to identify spatial similarities in temporal metal trends between and among stations (spatial connectivity, described next). Correlation coefficients with $P < 0.05$ were considered to be statistically significant.

Because contaminant transport is primarily driven by streamflow, linear regression was used to identify relationships between Cu and Cd bioaccumulation (dependent variable) and total annual discharge (independent variable). The difference in slopes was determined using a homogeneity-of-slopes model with a Tukey hsd post hoc test. In order to assess the impact that earlier discharge events may leave remnants of contaminated deposits behind (that is, flow events may not flush the system each year), metal concentrations in *Hydropsyche* for each year were regressed against total annual discharge from one year previous. Except where noted, a significant relationship driven by a single year was not considered relevant. Because sample size varied among years, all analyses were conducted on annual mean values (±SE).

Spatial connectivity was examined by considering metal concentration as a spatial contaminant marker (e.g., the downstream transport of contaminated material, hereafter called spatial connectivity). Correlations in temporal metal concentrations between and among stations were used as an indicator for spatial connectivity. Local-scale connectivity (temporal relationships between station pairs) and regional-scale connectivity (temporal relationships among all stations) were evaluated. The strength of that connectivity is reflected in the correlation coefficient.

RESULTS

Metal trends: remediated reach

In the last 15 years, Cu concentrations in sediment, water, and *Hydropsyche* declined by more than 50% at the most upstream station (–2 km, Fig. 3). The highest Cu concentrations occurred in 1993 (*Hydropsyche*, 80.4 ± 28 μg/g; sediment, 769 ± 317 μg/g; water = 18.2 ± 6.0 μg/L; mean ± SE for all data). By 2005, Cu concentrations declined to 20.8 ± 3.3 μg/g in *Hydropsyche* and 229 ± 11 μg/g in sediment and 5.1 ± 1.9 μg/L in water. All three indicators were significantly reduced over time (Fig. 3). Cadmium concentrations in *Hydropsyche* also decreased, though the relationship was

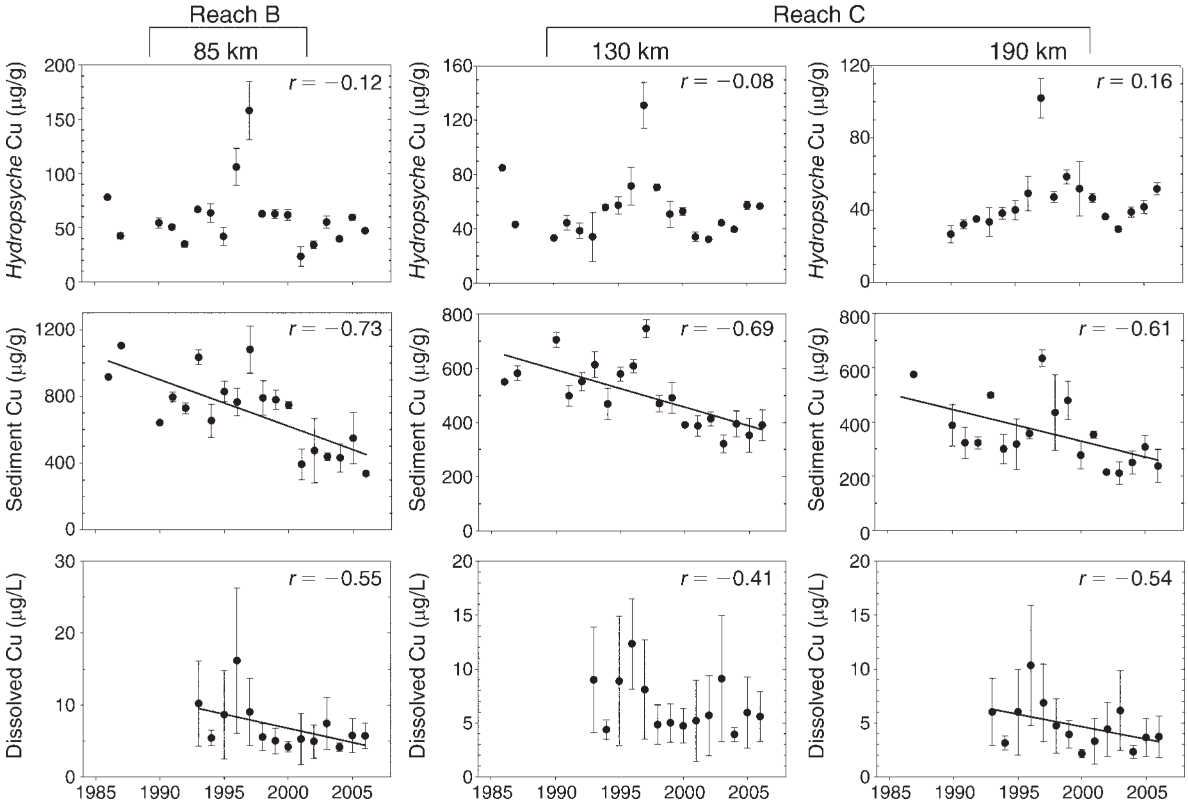

FIG. 3. Continued.

weaker than for Cu ($P = 0.05$). Cadmium in sediment declined 10–40% since 1992 but was not statistically significant over the course of the time series (Fig. 4). Like Cu, the highest Cd concentrations were observed in 1993 for both indicators (*Hydropsyche*, 2.1 ± 0.2 μg/g; sediment, 12.2 ± 6.0 μg/g).

Sediment and dissolved Cu concentrations at the next downstream station also decreased with time (5 km, Fig. 3; $P < 0.01$ in both cases), but Cu bioaccumulation was more variable. Cadmium concentrations were significantly reduced over time (Fig. 4; $P < 0.01$ in both cases). *Hydropsyche* concentrations ranged from a high 3.0 ± 0.4 μg/g in 1987 to a low of <1.0 μg/g in recent years (Fig. 4). Concentrations of Cd in sediment declined from the highest measured concentration of 20.1 ± 7.2 μg/g in 1987 to <10 μg/g by the mid-1990s.

Metal concentrations were temporally variable at the last four downstream stations in Reach A. Sediment Cu concentrations at the three upstream stations with a shorter period of record were strongly related to changes over time ($P \leq 0.02$), but temporal trends in Cu bioaccumulation were weaker and not significant (Table 1). Cadmium sediment concentrations decreased significantly over time at 18 and 29 km ($P < 0.01$), but weaker at 11 km ($P > 0.12$). No unidirectional trend was observed in Cd bioaccumulation at 11 or 18 km, but Cd in *Hydropsyche* did decrease at 29 km ($P < 0.01$). Copper and Cd concentrations in sediment and *Hydropsyche* were highly variable at the most downstream Reach A station (45 km, Figs. 3 and 4). Concentrations in recent years remain largely unchanged from the early years of the study. Dissolved Cu concentrations were weakly significant over time ($P = 0.05$), but the trend is largely driven by high values from 1995 to 1997 (Fig. 3).

Metal trends: unremediated reach

Copper concentrations in sediment significantly decreased over time in Reaches B and C (Fig. 3), but Cu bioaccumulation was temporally variable. For example, Cu concentrations in *Hydropsyche* varied more than a factor of six at 85 km (e.g., 158 ± 27 μg/g in 1997 to 23.4 ± 8.9 μg/g in 2001). High concentrations in dissolved Cu concentrations were observed from 1995 to 1997, but have remained relatively constant since 1998 (Fig. 3). Cadmium in sediment decreased significantly over time ($P < 0.01$) but Cd bioaccumulation varied five-fold, ranging from 0.5 to 2.5 μg/g (Fig. 4).

In Reaches B and C, high bioaccumulation values were coincident with years of high flow. Total annual discharge accounted for 72% of the Cu bioaccumulation pattern at 85 km, 58% at 130 km, and 43% at 190 km (although this relationship is driven by the value in 1997) (Fig. 5A). Discharge accounted for 23% of the Cd bioaccumulation pattern at 85 km, 46% at 130 km, and 72% at 190 (Fig. 5B). Dissolved Cu concentrations also increased during periods of high flow, but there was no

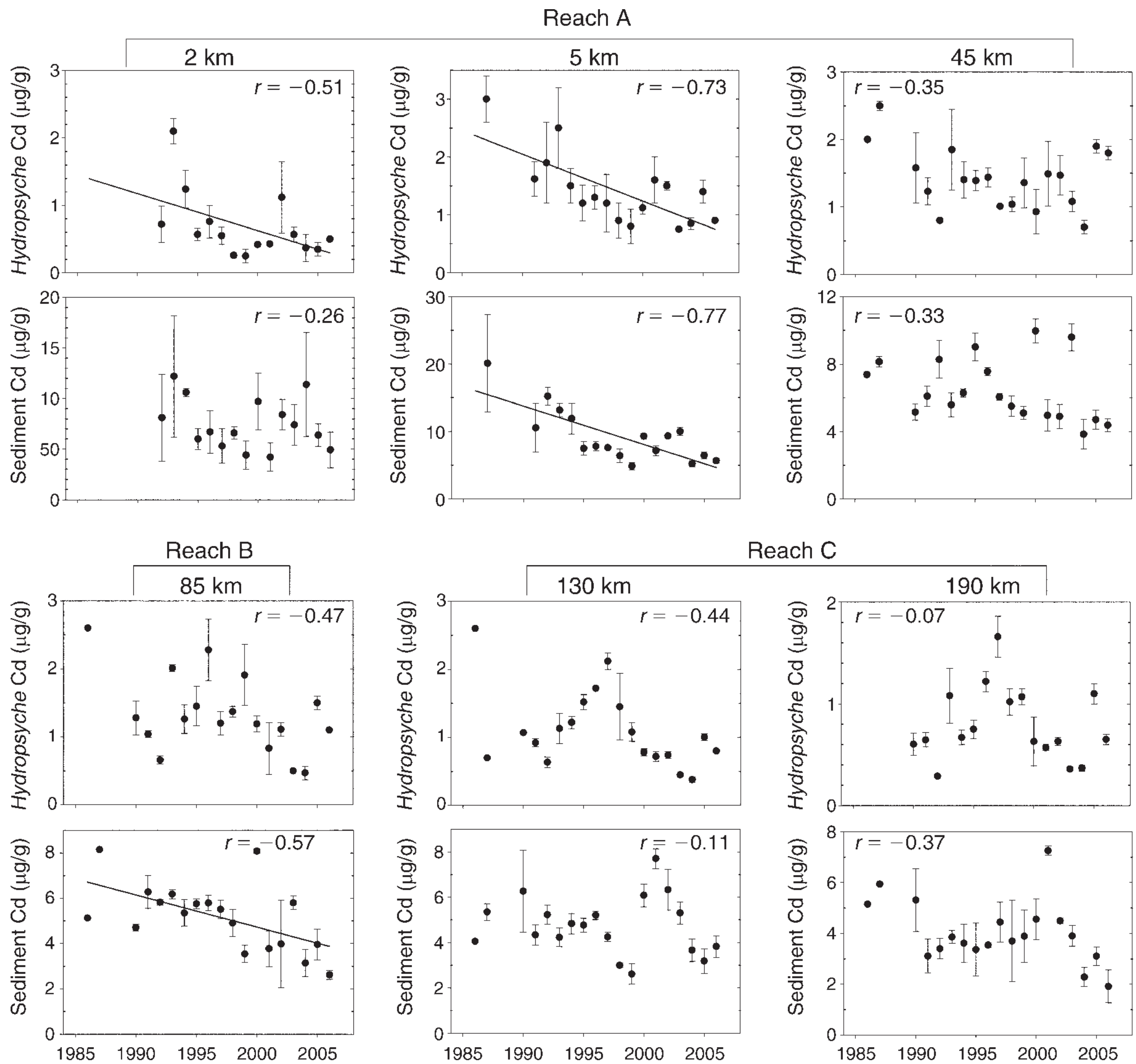

FIG. 4. Annual Cd concentrations (mean ± SE) in *Hydropsyche* and bed sediment (µg/g dry mass) plotted against year. Data are shown for the six sites with the longest period of record. Note that the *y*-axis scales vary by Cd source and site. A Pearson correlation (r) was calculated at each site. Significant temporal relationships ($P < 0.05$) are represented by solid lines.

association between Cu and Cd in sediment concentrations and stream discharge. While there was no significant difference between slopes for either metal at 85 and 130 km, the most downstream station was statistically different from the upstream stations ($P < 0.01$).

Earlier discharge events also influenced metal bioaccumulation. Significant one-year lag regressions between Cu concentrations in *Hydropsyche* and total annual discharge occurred at all three downstream stations (85 km, $r^2 = 0.22$, $P = 0.04$; 130 km, $r^2 = 0.30$, $P = 0.02$; 190 km, $r^2 = 0.41$, $P < 0.01$). Cadmium bioaccumulation was impacted mostly by flow conditions in a current year but a weakly significant one-year lag regression occurred at the most downstream station (190 km, $r^2 = 0.25$, $P = 0.04$).

Unintended consequences of remediation

While Cu and Cd concentrations declined at the most upstream station, arsenic concentrations in *Hydropsyche* increased during a three-year period (Fig. 6). Prior to 2002, mean *Hydropsyche* arsenic concentrations below the ponds were 8.8 ± 2.8 µg/g. However, arsenic increased nearly threefold from 2002 to 2004 (Fig. 6). Coincident with the increase in bioaccumulated arsenic was an increase in dissolved arsenic (Gammons et al. 2007). Arsenic in sediment did not increase (or decrease) during the course of the time series (Dodge et al. 2006).

Spatial connectivity

The influence of upstream remediation activities on downstream stations was examined by evaluating simi-

TABLE 1. Annual concentrations of copper and cadmium in caddisflies and sediment (μg/g dry mass) at the three upstream stations in Reach A of the Clark Fork River Superfund site (Montana, USA).

Element and year	11 km		18 km		29 km	
	Hydropsyche	Sediment	*Hydropsyche*	Sediment	*Hydropsyche*	Sediment
Cu						
1986					185 ± 6	1591
1987			157 ± 7	1558		1352
1988						
1989						
1990					96.3 ± 14.2	1451 ± 82
1991					87.9 ± 1.2	1356
1992						
1993						
1994						
1995			69.0 ± 1.8			
1996	129 ± 12	1727 ± 84	90.4 ± 14.1	1429 ± 88	108 ± 16	1283 ± 42
1997	141 ± 13	2053 ± 600	134 ± 27	1607 ± 119	149 ± 12	1552 ± 105
1998	60.4 ± 5.6	1362 ± 389	61.6 ± 7.5	946 ± 90	82.7 ± 5.4	842 ± 74
1999	83.9 ± 24.7	1422 ± 191	59.4 ± 9.3	1411 ± 273	88.3 ± 3.4	810 ± 205
2000	97.2 ± 1.2	1652 ± 357	97.4 ± 23.3	932 ± 72	80.9 ± 15.1	1105 ± 63
2001	81.6	1422 ± 145	63.7 ± 2.3	1097 ± 72	78.0 ± 1.7	882 ± 53
2002	89.7 ± 3.5	1350 ± 349	74.1	1236 ± 241	70.1 ± 9.6	1024 ± 81
2003	107 ± 8.5	1603 ± 44	118 ± 20	1314 ± 68	214 ± 34	1091 ± 91
2004	116 ± 17	1148 ± 112	136 ± 73	940 ± 139	90.2 ± 2.5	721 ± 162
2005	124 ± 7	1353 ± 49	118 ± 4	1098 ± 53	98.5 ± 11.0	967 ± 65
2006	274 ± 78	1283 ± 67	151 ± 35	1121 ± 106	164 ± 39	992 ± 98
Cd						
1986					2.7 ± 0.1	10.2
1987			3.0 ± 0.1	12.6		10.0
1988						
1989						
1990					2.0 ± 0.5	11.0 ± 2.4
1991					2.1 ± 0.6	11.7
1992						
1993						
1994						
1995			1.6 ± 0.6			
1996	1.9 ± 0.5	9.0 ± 0.8	1.3 ± 0.2	8.9 ± 1.1	1.4 ± 0.3	8.1 ± 0.4
1997	1.7 ± 0.5	8.4 ± 0.9	1.9 ± 0.2	7.5 ± 0.1	1.7 ± 0.1	6.9 ± 0.4
1998	1.1 ± 0.2	6.8 ± 2.1	1.0 ± 0.6	5.5 ± 0.6	0.9 ± 0.1	4.8 ± 0.5
1999	1.2 ± 0.2	4.5 ± 1.2	0.8 ± 0.1	5.0 ± 1.0	1.0 ± 0.2	4.3 ± 1.8
2000	1.5 ± 0.1	10.5 ± 0.3	1.2 ± 0.2	8.6 ± 0.7	1.0 ± 0.3	10.3 ± 0.4
2001	2.2	7.3 ± 0.5	1.2 ± 0.3	6.4 ± 0.5	1.4 ± 0.2	5.8 ± 0.4
2002	1.9 ± 0.3	8.1 ± 1.5	1.5	8.1 ± 1.0	1.4 ± 0.1	8.4 ± 0.4
2003	1.3 ± 0.2	9.4 ± 0.2	1.9 ± 0.5	8.7 ± 0.7	1.6 ± 0.4	9.0 ± 1.0
2004	1.5 ± 0.1	5.8 ± 0.2	1.0 ± 0.3	5.2 ± 1.0	1.0 ± 0.1	4.4 ± 1.0
2005	1.8 ± 0.0	6.3 ± 0.1	1.5 ± 0.1	6.4 ± 0.7	1.5 ± 0.3	5.7 ± 0.3
2006	1.5 ± 0.1	5.2 ± 0.4	1.4 ± 0.1	5.9 ± 0.9	1.2 ± 0.1	6.0 ± 1.2

Notes: Blank cells indicate that no data were collected. Values are mean (±SE, where appropriate). When no error is listed, it means that there were no replicate samples. Pearson correlation coefficients representing the trend in Cu over time: for 11 km, *Hydropsyche* $r = 0.42$, sediment $r = -0.70$; for 18 km, *Hydropsyche* $r = -0.24$, sediment $r = -0.63$; for 29 km, *Hydropsyche* $r = 0.27$, sediment $r = -0.77$. Pearson correlation coefficients representing the trend in Cd over time: for 11 km, *Hydropsyche* $r = -0.02$, sediment $r = -0.5$; for 18 km, *Hydropsyche* $r = -0.58$, sediment $r = -0.73$; for 29 km, *Hydropsyche* $r = -0.75$, sediment $r = -0.7$.

larities in temporal metal trends between and among stations. Using annual metal concentrations in sediment as a transport marker, we assumed that similar temporal patterns among stations indicated a similar response to whatever mechanistic processes drove changes in metal concentrations. Specifically, metal trends at an upstream station were correlated to trends at each downstream station (Table 2). The strength of that association (r value) indicates the strength of station-to-station connectedness. Two connectivity patterns were identified: (1) small spatial connections (local connectivity) where temporal-trend correlations were measured between adjacent sites; (2) large, spatial connections (regional connectivity) where temporal trends at upstream stations were strongly correlated to trends at downstream stations.

Temporal metal trends were similar between most adjacent stations. Copper concentrations were significantly correlated at five of the eight station pairs; Cd concentrations were significantly correlated at seven of the eight station pairs (Table 2). The strong correlations

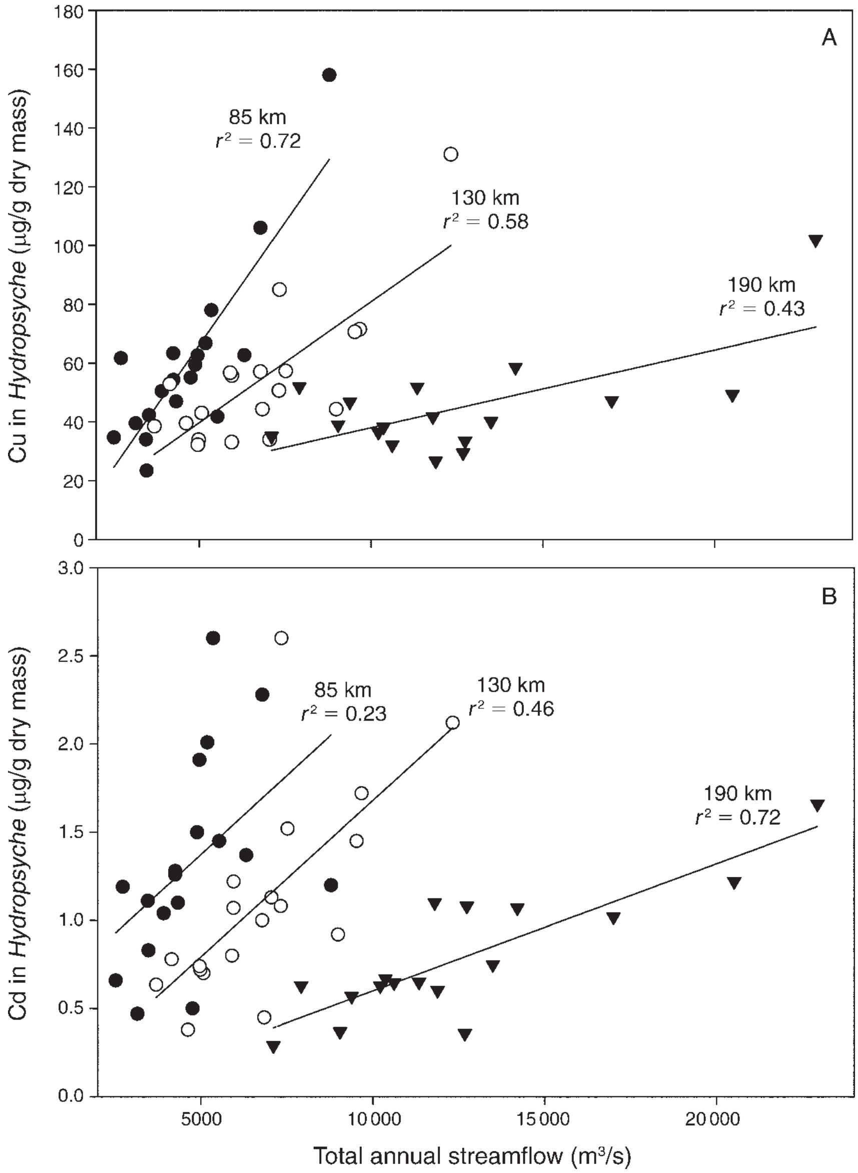

FIG. 5. Relationship between metal bioaccumulation in dry mass (µg/g) in a given year and total annual stream discharge (m^3/s) for the same year: (A) Cu; (B) Cd. Solid circles are data from 85 km downstream (Reach B); open circles are data from 130 km downstream (Reach C); triangles are data from 190 km downstream (Reach C). Solid lines identify significant ($P < 0.05$) temporal relationships from linear regressions (r^2).

($r > 0.60$) measured for both metals indicates high connectivity and suggests that temporal similarities between most adjacent stations is driven by similar mechanistic process controlling contaminant distribution in the river. Weaker connectivity ($r < 0.60$) occurred at the beginning of Reach A (–2 to 5 km, Cu and Cd; 5–11 km, Cu) and at the end of Reach A (29–45 km, Cu and Cd; Table 2).

While local-scale connectivity evaluated similarities in metal trends at small spatial scales, regional connectivity examined similarities in trends over large spatial scales. This approach was used to assess the impact of upstream metal sources on the downstream stations. Metal concentrations at one site were correlated to concentrations at each consecutive downstream station (Table 2). For example, sediment Cu at 5 km was correlated with sediment Cu at each of the seven downstream stations (Table 2). This was repeated for all stations. We consider this test a reasonable measure of remediation effectiveness because the primary sources of contamination are stream banks and floodplains in Reach A (Fig. 1) and are the areas targeted for treatment or removal as remediation progresses.

The influence that the most upstream station (–2 km) has on all downstream stations is low since Cu and Cd trends were only weakly correlated (mean r values of

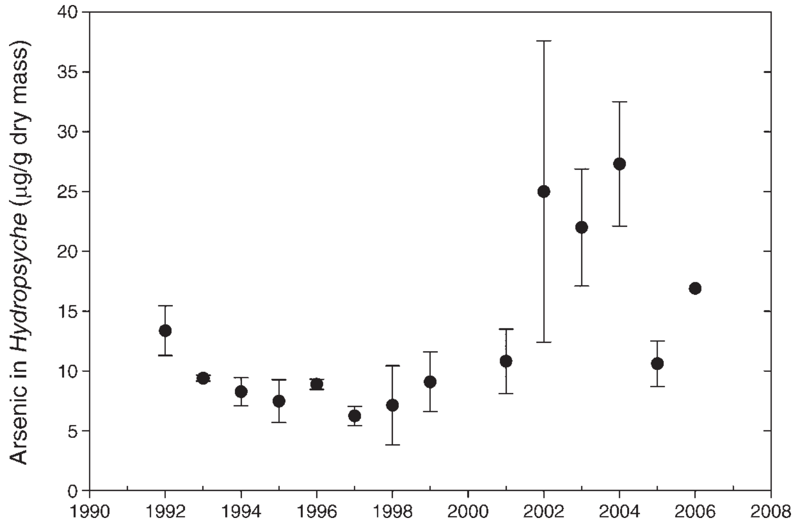

FIG. 6. Annual arsenic concentrations (mean ± SE) in *Hydropsyche* (µg/g dry mass) plotted against year at the station below the treatment ponds (–2 km, Fig. 1).

0.11 and 0.18, respectively; Table 2). However, temporal trends in Cu at the next downstream site (5 km) were highly correlated to most downstream sites, indicating a strong regional connectivity (mean *r* value 0.65) along the entire length of the study unit. Cadmium connectivity was strongest in Reaches A and B (Table 2). In general, Cd concentrations at the upstream stations were not strongly associated with stations in Reach C.

The relative importance that stations in the remediated reach (Reach A) have on stations in Reach B and C were quantified by averaging correlation coefficients listed in Table 2. The influence that a particular station has on downstream stations is represented by this mean *r* value (Fig. 7). For example, at –2 km the mean connectivity *r* value is 0.14. This low value suggests that this station is only very weakly connected to (or has limited influence on) stations downstream.

DISCUSSION

Remediation effects

Remediation activities controlled metal trends in the upper 7 km of the Clark Fork River (CFR) in western

TABLE 2. Spatial connectivity using Pearson correlations, *r*.

Element and station km	Station km									
	−2	5	11	18	29	45	85	130	190	Mean
Cu										
−2		0.52	−0.18	−0.22	0.02	−0.18	0.39	0.36	0.17	0.11
5			0.41	0.63*	0.65*	0.88*	0.73*	0.59*	0.68*	0.65
11				0.88*	0.78*	0.91*	0.76*	0.79*	0.73*	0.81
18					0.73*	0.66*	0.62*	0.75*	0.6*	0.67
29						0.44	0.63*	0.72*	0.53*	0.58
45							0.65*	0.37	0.55*	0.52
85								0.74*	0.83*	0.78
130									0.7*	
190										
Cd										
−2		0.54*	0.25	0.11	0.3	0.08	0.37	0.03	−0.25	0.18
5			0.87*	0.85*	0.7*	0.46	0.72*	0.34	0.34	0.61
11				0.88*	0.88*	0.9*	0.92*	0.56	0.43	0.76
18					0.89*	0.74*	0.81*	0.46	0.36	0.65
29						0.59*	0.69*	0.47	0.31	0.52
45							0.79*	0.28	0.15	0.41
85								0.27	0.28	0.27
130									0.66*	
190										

Notes: Station km indicates distance (km) from the confluence of Warm Springs and Silver Bow Creeks. Sediment Cu and Cd concentrations at each site were correlated to each consecutive downstream station for the respective element (see *Results: Spatial connectivity* for details). Cell values represent *r* values. Mean *r* values for stations in Reach A are listed in the far right column.
* $P < 0.05$.

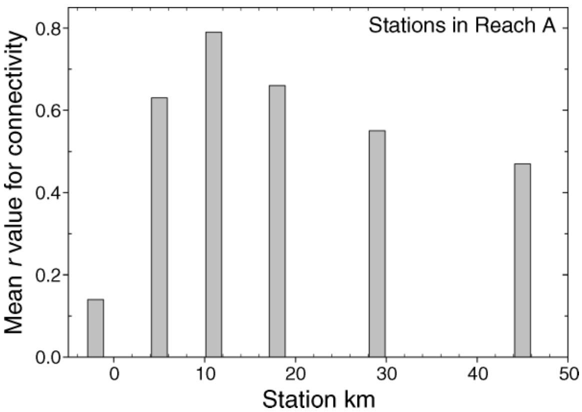

FIG. 7. Spatial connectivity demonstrating the influence of stations in Reach A (x-axis) on downstream stations. Station km indicates distance (km) from the confluence of Warm Springs and Silver Bow Creeks. On the y-axis, r values (means from Table 1) quantify the importance of Reach A stations in controlling metal trends at stations in Reaches B and C. A high r value indicates a strong spatial connection to downstream stations.

Montana, USA. Copper and Cd declined over time in both indicators. Dissolved Cu also decreased at these stations since 1996 (Fig. 3). Remediation was likely responsible for controlling metal concentrations at other Reach A stations since metals here have also declined (Table 1). However, Cu and Cd concentrations were highly variable at the most downstream site in Reach A (45 km, Fig. 3) suggesting that other site-specific factors contribute to the metal signature in this reach of the river. Similar temporal trends in sediment Cu as far downstream as 190 km suggest that removal and in-place treatment of contaminated sediment in Reach A have reduced Cu inputs in river Reaches B and C.

Natural variability can confound causal association in field data (Smith et al. 1993, Stow et al. 1998, Hornberger et al. 2000). The temporal pattern of metals in close proximity to remediation strongly suggested that removal and treatment of sediments positively influenced the aquatic system. Statistical relationships help quantify patterns associated with temporal change (e.g., see Hewitt et al. 2001), but the mechanistic processes that control these patterns can only be determined if other factors are considered. In this system, temporal decreases in Cu and Cd in bed sediment and dissolved Cu concentrations (abiotic environment), and the biomonitor (biotic environment) provide a weight of evidence that remediation is the dominant controlling factor influencing metal trends in Reach A.

Although improvements related to remediation are apparent, there were also some unintended consequences. Remediation activities may have mobilized bioavailable arsenic at the most upstream site during 2002–2004 (Fig. 6). This station is located directly below the treatment ponds where lime additions increase pH to facilitate the precipitation of cationic metals (e.g., Cu and Cd). Liming is greatest during periods of high discharge and continues through the summer until pH values reach greater than 9, at which point the lime additions cease. Particulate arsenic also increases during periods of high flow but can be remobilized at pH values >9, releasing high concentrations of dissolved arsenic (Gammons et al. 2007). Although we could not determine the exact cause of the threefold increase in arsenic bioaccumulation, it is possible that increased lime dosage within the ponds created favorable biogeochemical conditions suited for arsenic mobilization. While liming inhibits the release of cations such as Cu and Cd, anions such as arsenic could be easily mobilized, especially in a high pH environment.

Hydrologic effects on metal bioaccumulation

Discharge had no statistically detectable effect on metal bioaccumulation in the most contaminated reach (Reach A), perhaps due to irregular localized input of metals from highly contaminated banks and floodplains. However, the relationship between discharge and bioaccumulation was strong in Reaches B and C (Fig. 5). The magnitude of change in Cu and Cd bioaccumulation is higher at 85 km and 130 km (4–5 fold), as opposed to 190 km where concentrations increase by only 2–3 fold. The statistical difference in slope from the linear regression in Fig. 5 at the most downstream station may be due to both its distance from the contaminant sources as well as dilution from an adjacent tributary (Fig. 1).

Although dissolved concentrations also increase during high-flow events, laboratory exposure experiments indicate that *Hydropsyche* accumulate <10% of their Cu body burden and ~30% of their Cd body burden through the dissolved phase (Hornberger 2006). If dissolved concentration accounts for only a fraction of metal bioaccumulation in *Hydropsyche*, then dietary exposure is an important contributor to total metal body burden. This finding is consistent with other studies (Munger and Hare 1997, Meyer et al. 2005, Croteau and Luoma 2008) and illustrates the importance of reducing the presence of contaminated particulates (which influence food concentrations) in the watershed.

The one-year lag relationship between discharge and bioaccumulation suggests that earlier hydrologic events are also important in a contaminated lotic system. In mine-impacted rivers such as the CFR, discharge does not dilute the metal but instead redistributes and deposits contaminants throughout the system. Because *Hydropsyche* is univoltine (one-year life cycle) and new generations of *Hydropsyche* are sampled each year, the relationship with lagged discharge is not biological and is likely due to exposures from the cumulative transport and deposition of contaminated material in previous years.

Discharge must be considered when evaluating metal bioavailability in contaminated rivers. Biomonitors such as *Hydropsyche* will respond to the increase (or decrease) of metal exposures as remediation activities and natural climatic factors such as flooding redistribute stored material within the banks and floodplains. However, in order to measure the success of remediation, it is critical to monitor during years of both high and low discharge. Evaluating ecosystem recovery only during years of low (or high) flow would have yielded misleading results in the CFR.

Effect of upstream remediation on downstream stations—connectivity

The CFR study provides a rare opportunity to assess the impact of site-specific remediation at large spatial scales. The success of remediation in most mine-impacted rivers is dependent on the assumption that improvements upstream will transfer to the lower reach, although that assumption is rarely tested. Numerous studies have demonstrated that contaminants usually follow a longitudinal gradient in a lotic system (Moore and Luoma 1990, Axtmann and Luoma 1991, Axtmann et al. 1997, Clements et al. 2000). However, we found no previous study that quantified the site-specific influence of contamination from upstream sources to downstream reaches.

Localized spatial linkages indicate that metal concentrations in the CFR are strongly correlated between most adjacent stations, suggesting that upstream activities almost always influence the adjacent downstream station (Table 2). However, the strength of that association may be influenced by local factors. For example, Cu and Cd connectivity are lower at the 29 and 45 km station pair than at other Reach A station pairs, suggesting that some physical or chemical (e.g., groundwater influence) process is important here. Water-quality data show no large chemical differences in this reach of the river (e.g., temperature, pH, water hardness, conductivity; Dodge et al. 2006). However, a seasonally used weir upstream from the 29 km site could influence the natural depositional environment, disrupting the downstream transport of sediment. Although small in scale, the weir created a serial discontinuity, acting as an impoundment that restricts the transport of material from upstream sources (Ward and Stanford 1983). Changing the depositional nature of the river could increase variability at these two sites, obscuring the detection of trends related to remediation.

While small-scale disturbances (e.g., weir) may impede detection of trends at some stations, this does not appear to impact trends at large spatial scales. Copper connectivity is high along the length of the study site, while Cd connectivity is strongest in the upper 85 km (Table 2). Large-scale regional patterns also elucidate site-specific sources which control spatial metal trends along the entire study reach. The high connectivity values at 5, 11, and 18 km (Fig. 7) suggest that a large source of contaminants in the CFR come from this reach of the river. Stream banks are highly contaminated (Axtmann and Luoma 1991, Hochella et al. 2005), and remain an important source of particulate Cu and Cd (Lambing 1998). Further remediation at these stations is likely to positively influence stations in the unremediated reaches. Connectivity is weaker at 29 and 45 km ($r = 0.55$, $r = 0.47$, respectively). Bank deposits here are also highly contaminated, but local factors may increase temporal variability in this reach of the river. Remediation at these sites should also have a positive impact on downstream stations, but temporal trends related to large-scale connectivity are weaker than those observed upstream (Fig. 7).

The low connectivity strength at −2 km (Fig. 7) suggests that this station has very little influence on any downstream station. A major demonstration project in 1993 removed nearly all the adjacent bank and floodplain material and created a new bypass stream channel for the river. Concentrations in all indicators were reduced by as much as 50% within 2 years (Figs. 3 and 4). This station could be defined as "completely remediated" because it is no longer a source of material for the rest of the river. However, the low connectivity strength suggests that there is not enough clean material transported from this station to dilute the high metal concentrations downstream.

Although upstream activities influenced downstream sediment concentrations of metals, trends in *Hydropsyche* bioaccumulation were more complex. Trends over time are apparent at only the most upstream stations and suggest that the proximity of remediation is important in controlling metal bioaccumulation patterns. The disconnect between large-scale improvements in sediment and metal bioavailability may be a lagged response to decreasing metal exposures. *Hydropsyche* are not directly responding to sediment concentrations but rather to a portion of bioavailable metal associated with particulates in the water column. Reductions in sediment contamination will ultimately result in reduced bioavailable metal in the system, but such an effect may only be detectable with increased remediation efforts.

Conclusions

Spatiotemporal analysis of a 19-year data set allowed us to measure the effect of remediation in a mine-impacted river. Few studies have the long-term data necessary to adequately address the objectives presented here. We demonstrated that remediation in the Clark Fork River in western Montana, USA positively influenced stations that are in close proximity to remediation activities. Multiple indicators all declined through time. An unintended consequence however, at least in some years, was the increase of bioavailable arsenic. Remediation efforts which target cations such as Cu and Cd may increase the bioavailability of anions such as arsenic.

By testing spatial connectivity, we demonstrated the validity of the assumption that remediation of the most contaminated sites will ultimately affect stations in the downstream reaches. Strong temporal correlations between most adjacent sites indicate that upstream events almost always impact the next downstream station. However, the strength of these associations is variable. Understanding mechanisms controlling the strength in spatial connectivity could help identify site-specific areas in need of focused attention or activities that might enhance or impede objectives. Large-scale regional connectivity identified reach-specific areas that are largely influential in controlling metal patterns downstream. Targeted effort in these areas will positively impact the unremediated stations.

The detection of remediation on metal bioavailability in the lower reaches was confounded by a relationship between metal bioaccumulation and hydrologic conditions within a year as well as conditions from the previous year. In this system, metals are not flushed out of the river during periods of high flow but instead are redistributed with each high flow event. Until the bulk of contaminated material is removed, this will likely continue. Ongoing monitoring during years of both high and low discharge will help determine when the source material has dissipated.

Long-term, large-scale monitoring is critical in systems heavily influenced by contaminants, especially in lotic systems where the redistribution of material is often dependent on hydrologic conditions. Such monitoring is rare; it is even more rare to evaluate both sediment and bioavailable metal. Because of the large financial investment, remediation should be balanced by sufficient feedback so that the success (or failure) of those efforts can be continuously evaluated.

Acknowledgments

Long-term time series studies such as this could not have been done without the assistance of numerous individuals. We gratefully acknowledge the field and laboratory contributions of Dan Cain, Ellen Axtmann, Robin Bouse, Cynthia Brown, Stacey Andrews, Jessica Dyke, Allison Lorenzi, Carlos Primo David, and Irene Lavigne. John Lambing of the U.S. Geological Survey Montana Water Science Center provided technical guidance and logistical support throughout the project. The thorough and thoughtful colleague reviews by Dan Cain, Marty Gurtz, and two anonymous reviewers greatly improved an earlier draft of this manuscript. Funding was provided by the U.S. EPA and the U.S. Geological Survey National Research Program.

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