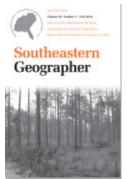# Legacy Hg-Cu Contamination of Active Stream Sediments in the Gold Hill Mining District, North Carolina

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Legacy Hg-Cu Contamination of Active Stream Sediments in the Gold Hill Mining District, North Carolina

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The purpose of this study is to evaluate the longitudinal trends of mercury (Hg) and copper (Cu) in active channel sediments downstream from the Gold Hill mining district in the Piedmont of North Carolina. Mining for gold (Au) and Cu from 1844 to 1915 released both Hg (associated with Au processing) and Cu in a 254 km² watershed. Multiple linear regression is used to quantify spatial and geochemical trends in 93 active channel samples collected from contaminated main stem and background tributary sites. Simple two-parameter regression models combining the effects of both watershed-scale dispersal processes (distance downstream) and reach-scale sediment transport (percent sand) explain 85 percent of the variance in Hg and 90 percent of the variance in Cu in active channel sediments. Contamination trends in two different sediment media, low bar and higher elevation bench deposits, were effectively similar when local grain size influence was accounted for in the two-parameter models. Background geochemistry models explain 84 percent of the variance of Hg and Cu in uncontaminated tributary

samples using parameters related to grain-size, secondary geochemical substrates, and mineral weathering sources. More than 45 percent of the variance of Hg and 20 percent of Cu in contaminated sediment can be explained by background parameters. Geochemical signatures differ between Hg and Cu in active channel sediments due to variations in mining inputs, background geochemistry, and present-day pollution sources.

El propósito de este estudio es evaluar la evolución longitudinal de mercurio (Hg) y cobre (Cu) en sedimentos de canales activos en la parte baja del distrito minero de Gold Hill, en el Piedmont de Carolina del Norte. La minería de oro (Au) y Cu desde 1844 a 1915 produjo Hg (asociados con el procesamiento de Au) y Cu en una cuenca de 254 km². Regresión lineal múltiple se utiliza para cuantificar las tendencias espaciales y geoquímicas en 93 muestras de canales activos, recolectadas en cauces principales contaminados y en localidades en tributarios secundarios. Modelos de regresión simple de dos parámetros combinando los efectos de ambos

procesos de dispersión a escala de las cuencas hidro-gráficas (distancia río abajo) y a escala del alcance del transporte de sedimentos (arena por ciento) ex-plican el 85 por ciento de la variación de Hg y 90 por ciento de la variación de Cu en los sedimentos de canales activos. Las tendencias de contaminación en dos diferentes medios de sedimentos, barra baja y bancos de depósitos de mayor elevación, fueron efec-tivamente similares cuando la influencia del tam-año del grano local se contabilizó en los modelos de dos parámetros. Modelos geoquímicos de antece-dentes explican el 84 por ciento de la variación de Hg y Cu en muestras no contaminadas de tributar-ios utilizando parámetros relacionados al tamaño de grano, sustratos geoquímicos secundarios, y fuentes de meteorización de minerales. Más del 45 por ciento de la variación de Hg y 20 por ciento de Cu en sedimentos contaminados puede ser expli-cada a través de parámetros de antecedentes. Firmas geoquímicas difieren entre Hg y Cu en los sedimentos de canales activos debido a variaciones en insumos mineros, trasfondo geoquímico, y las fuentes de contaminación actual.

INTRODUCTION

Mined watersheds provide an opportunity to investigate relationships between contaminated sediment patterns and the fluvial processes involved such as channel sediment transport and floodplain storage (Davies and Lewin 1974; Lewin et al. 1977; Knighton 1989; Graf 1985; Macklin 1985; Knox 1987; James 1989; Lecce and Pavlowsky 1997, 2001, 2004). Historical mining operations commonly introduced large volumes of mine wastes and associ-ated metal contaminants to river systems the world over (Down and Stocks 1977). After release to the river system, contami-nated mining sediment can be used as a geochemical tracer to identify input loca-tions, monitor transport and storage, and date alluvial deposits (Bradley 1989; Graf 1996; Miller and Orbock-Miller 2007). The geochemical contrast between undis-turbed river sediment and tailings inputs is typically high, so the mining signal can be detectable for relatively long distances below the source (Horowitz et al. 1988; Moore and Luoma 1990; Miller et al. 1998). Mining-contaminated sediment may also be stored in channel and floodplain de-posits for periods ranging from months to centuries or longer depending on the tim-ing for remobilization by mass-wasting, erosion, and/or weathering (Bradley 1989). Thus, mining sediment tracers are potentially useful to investigate fluvial pro-cesses across a range of watershed sizes and timescales (Ongley 1987).

Geochemical monitoring of active chan-nel sediment is often used to evaluate present-day risks posed by the reintroduc-tion of contaminated legacy mining sedi-ment back into the channel network in mined watersheds (Wolfenden and Lewin 1978; Bradley and Cox 1990; Graf 1996). Active channel deposits are composed of recently eroded and transported materi-als, reflect the influence of the present flood regime, and have the potential to be remobilized by frequent flood events oc-curring several times annually (Wolf-enden and Lewin 1978; Marcus 1987). Channel sediments can become contami-nated from three mining-related sources which are differentiated according to mine history and input process: (i) direct discharge of tailings and effluents during mining operations; (ii) medium-term ero-sion and leaching of in-transit mining sedi-ment as well as abandoned tailings piles;

and (iii) long-term erosion and weathering of previously contaminated alluvial deposits or legacy sediment (Moore and Luoma 1990). Where mining operations have been closed for several decades, on-site sources of contaminated tailings and mining sediment have usually been controlled or depleted. Hence, contemporary contamination trends are primarily controlled by the rates of contaminant remobilization by weathering and erosion from channel and floodplain storages (Bradley 1989; James 1989; Moore and Luoma 1990).

Longitudinal variations in metal concentrations in channel sediments affected by mining inputs are strongly influenced by watershed factors such as upland erosion rates, sedimentary mixing/dilution, and bedrock type in rivers affected by mineralization and/or mining inputs (Rose et al. 1970; Hawkes 1976). Contamination levels generally decrease exponentially downstream from mine waste sources (Wolfenden and Lewin 1978; Ongley 1987; Lecce and Pavlowsky 1997, 2001). Logarithmic regression equations of metal concentration versus distance (or drainage area) are commonly applied to field data to quantify longitudinal contamination trends (Marcus 1987). The results of these decay models represent the cumulative influence of several transport processes operating in the river and have been referred to as "composite" curves (Lewin et al. 1977). In most rivers, the primary processes accounting for the downstream decrease in sediment-metal concentrations below a mining source at the watershed-scale are tributary dilution and mixing (Marcus 1987) and sedimentary deposition and storage (Bradley 1989).

Empirical longitudinal decay models

can yield errors of one-half an order of magnitude or more depending on the variable influence of local factors such as bed-form type, sediment sorting, and mineralogy of sediment inputs. It is well known that silt and clay particles (i.e., <63 μm fraction) tend to contain higher concentrations of metals compared to coarser sediments in both undisturbed and contaminated river systems (Hakanson 1984; Horowitz 1991). Compared to coarse grains, fine particles have larger surface areas per unit mass and contain higher percentages of secondary geochemical substrates that can bind metals in relatively high concentrations (Horowitz 1991; Miller and Orbock-Miller 2007). However, the coarse fraction can be a more important sink for metal contaminants where ore-processing mills produce large amounts of metalliferous sand- and gravel-sized materials (Bradley and Cox 1986; Brook and Moore 1988; Leenaers et al. 1988). Tailings materials may also contain heavily contaminated high density particles in the form of sulfide mineral grains or metal flakes that can become concentrated locally in areas of flow separation in the channel (Best and Brayshaw 1985; Macklin and Dowsett 1989).

The mineralogy and geochemical behavior of the undisturbed fine-grained sediment supply to the channel is usually much different than that found in tailings materials and other mine wastes. Given that most fluvial deposits in a river contaminated by mining activities will contain a mixture of mine tailings and uncontaminated sediment, background sediment properties can also affect geochemical variations in contaminated active channel sediments (Horowitz 1991). These background source effects refer to the metal
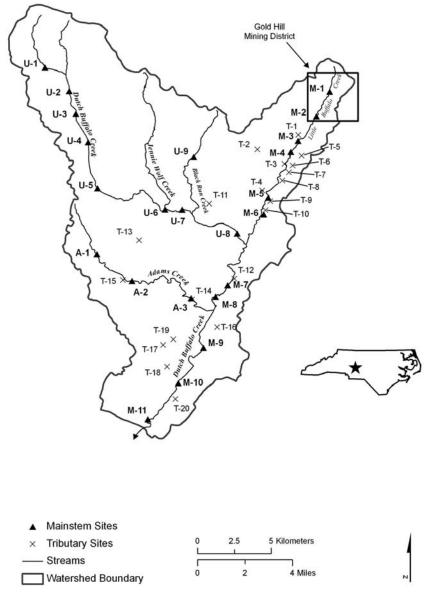
Figure 1. Study area map with sampling site locations where "M" refers to main stem contaminated sites and "T" refers to background tributary sites. Sites with "A" and "U" were also visited but the results are not included in this study.

content and sediment geochemistry in uncontaminated sediment loads or deposits, assuming no mining influence. If particle size of the sediment is held constant, the variability of metal concentrations in undisturbed channel sediments can generally be related to the influence of three geochemical controls: (i) bedrock mineralogy as indicated by aluminum (Al) and calcium (Ca); (ii) secondary iron (Fe) and/or manganese (Mn) oxide coatings; and (iii) organic matter or carbon (C) (Horowitz et al. 1989).

Reach-scale variations in mining sediment composition and contaminant geochemistry can limit the precision and effectiveness of larger-scale longitudinal models of metal-sediment contamination in river systems (Lewin et al. 1977; Horowitz et al. 1989). However, few studies have tried to reconcile spatial-scale problems in metal-sediment models. The purpose of this study is to use both watershed- and reach-scale parameters to quantify the longitudinal trends of mercury (Hg) and copper (Cu) concentrations in active channel sediments in the Little Buffalo Creek–Dutch Buffalo Creek river system located in the Piedmont Province of North Carolina (Figure 1). The main goal will be to improve both precision and application of sediment-contaminant decay models by combining multiple-scale effects in modeling results using a relatively simple regression approach. The specific objectives are to (i) quantify the spatial and geochemical variability of contaminated active channel sediments, (ii) quantify the geochemical variability of uncontaminated source contributions as distinct from mining influence, and (iii) compare contamination trends between different active in-channel deposits sampled at low bar and bench channel locations.

The presence of gold mining-related Hg in alluvial sediments in the southern Piedmont gold belt has been previously reported in North Carolina (Callahan et al. 1994) and Georgia (Leigh 1994, 1997). A pilot project in the study area by the authors in 2006 found high concentrations of Hg and Cu in channel and floodplain sediments along the entire main stem of the Little Buffalo Creek–Dutch Buffalo Creek system below Gold Hill (about 20–25 km) (Lecce et al. 2008). The present study utilizes a more intensive sampling approach to distinguish the influence of both watershed-scale trends (i.e., dilution and sediment storage) from more localized reach-scale variations (i.e., particle size, geochemical substrates, background influence) to better understand the spatial distribution and fluvial mobility of sediment Hg and Cu.

STUDY AREA

The Gold Hill mining district is located in the headwaters of Little Buffalo Creek (39 km²) in southern Rowan and northern Cabarrus counties about 50 km northeast of Charlotte, North Carolina. Little Buffalo Creek is a tributary of Dutch Buffalo Creek (254 km²) which flows south into the much larger Rocky River system (Figure 1). The Gold Hill mining district was a major Au producer that operated in the northern headwaters of the watershed from 1842 to 1915, with peak production for Au in 1856 and Cu in 1906. Mineralization occurred along a north-south fault zone forming the boundary between the igneous intrusive rocks of the Charlotte

Belt on the west and metavolcanic and metasedimentary rocks of the Carolina Slate belt to the east. Most of the gold-bearing deposits were in a chlorite-sericite phyllite to the east of the fault line (Carpenter 1976). Hg was used industrially to amalgamate and extract Au from crushed rock and then released to the environment via wash water discharges and as a residual during dump erosion. In contrast, Cu was the target of mining itself and was enriched in mineralized zones composed of the primary sulfides bornite, chalcopyrite, and chalcocite (Carpenter 1976). Secondary Cu releases occurred early during the mining period when metalliferous soil enriched by geologic weathering was excavated and mobilized during Au mining. Later during the Cu mining period, contaminated mill wastes were released to nearby streams during mineral processing. Milling operations produced contaminated mining sediment that was typically sand-sized and smaller (<2 mm), so it was easily transported downstream. See Lecce et al. (2008) for a more complete description of the geological setting and mining history of the study area.

METHODS

Field sampling for this project occurred during the summer of 2007. Active channel sediment samples were collected from two distinct areas: (i) contaminated sections below Gold Hill along the main stems of Little Buffalo Creek and lower Dutch Buffalo Creek, and (ii) tributaries not affected by mining including small second and third order streams and the upper Dutch Buffalo Creek (above the confluence with Little Buffalo Creek) (Figure 1). Sediment sampling in mining-affected river segments occurred at locations where historical mining inputs were found to have contaminated overbank floodplain deposits with Hg and Cu (Lecce et al. 2008). Uncontaminated sediment samples were collected in watersheds not reported to contain historical Au or Cu mines (Pardee and Park 1948; Knapp and Glass 1999). Samples collected from unmined areas were used to determine the background geochemistry of active sediments.

Fine-grained (typically <2 mm in diameter) sediment samples were collected from the surfaces of two different in-channel deposits at places where recent deposition was observed: (i) low subaerial bar deposits within an elevation of 5 cm from the baseflow water line commonly at the tail end of bars and riffles, and (ii) low bench features typically formed as a narrow step about 0.5–1 m above the bank toe. Grab samples of active channel deposits were collected at a depth of 0–3 cm using a non-contaminating shovel and placed in labeled quart-size plastic freezer bags. A total of 93 active channel sediment samples were collected and were fairly evenly distributed among the different sedimentary deposits (Table 1).

It was assumed that low bar deposits would be frequently remobilized by floods of all magnitudes. To better understand flood frequency conditions present at bench sampling sites, channel capacity and bench stage were evaluated at three sites: (i) M4 on upper Little Buffalo Creek below Gold Hill, drainage area of 17.4 km²; (ii) M6 on lower Little Buffalo Creek, 39.4 km²; and (iii) M11 on lower Dutch Buffalo Creek above confluence with Rocky River, 253.1 km² (Figure 1). The channel sections evaluated have relatively narrow meander

Table 1. Sediment Properties and Geochemistry of Active Channel Sediments.

Deposit Type	n	Al (%)	Ca (%)	Fe (%)	Mn (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Total C (%)	Sand (% wet)
Geometric Mean									
Contaminated Bar	21	1.45	0.25	3.75	895	78	0.18	0.91	65
Contaminated Bench	24	1.79	0.31	3.46	1366	86	0.30	1.99	48
Background Bar	31	1.30	0.26	3.80	1134	24	0.02	0.96	69
Background Bench	17	1.37	0.30	3.49	958	27	0.03	1.70	63
Maximum Value									
Contaminated Bar	21	4.11	0.89	8.25	1585	1300	1.33	6.28	98
Contaminated Bench	24	2.50	0.42	5.27	2590	350	1.34	4.29	92
Background Bar	31	3.45	0.46	9.55	4930	65	0.08	5.96	98
Background Bench	17	2.71	0.61	8.73	3610	69	0.12	6.57	97

belts with almost no active floodplain area. The maximum flood capacity of the full channel at valley floor stage decreases downstream as follows: 3.4-yr flood at M4, 2.1-yr flood at M6, and 1.8-yr flood at M11 (Pope et al. 2001). The height of the low bench stage relative to bankfull stage (around 1.4-yr flood) also decreases downstream as follows: 71 percent of mean bankfull depth at M4; 52 percent at M6; and 33 percent at M11 (Harman et al. 1999). The bench surfaces sampled for this study are probably inundated several times a year and reflect channel sedimentation controls rather than channel levee or overbank floodplain processes. Compared to low bar deposits, however, bench surfaces are believed to be better preserved and more stable under flood conditions.

Bed sediment trends in contaminated river segments were evaluated using pebble count procedures according to recommendations in Bunte and Abt (2001). Pebble counts were completed at 9 sites along the main stem (sites M3 to M11 in Fig-

ure 1). At each reach, blind sampling occurred at uniform grid points spaced at 1 or 2 m across the active channel along 10 to 20 transects at one channel width intervals. The presence of bedrock, saprolite, fines, and sand were recorded, but bedrock and saprolite samples were not included in size distribution statistics. A ruler was used to determine the B-axis diameter of each potentially mobile pebble. The number of counted pebbles at each reach typically ranged from 100 to 220.

Sample preparation and physical analysis was carried out at the Water and Soil Laboratory of the Ozarks Environmental and Water Resources Institute at Missouri State University following standard methods and operation procedures (http://oewri.missouristate.edu/). The samples were oven-dried in the laboratory at low heat, disaggregated, and sieved through a 2 mm sieve. Sand content (63 μm to 2 mm) was determined by wet sieving. Total carbon was determined using an Elementar Vario EL CNHS Analyzer. Separate tests showed that there was very little car-

bonate present in the weathered soils and fluvial sediments in the region and that total carbon was a good indicator of organic carbon in the sample. Geochemical analyses for all metals were completed on the <2 mm sediment fraction by a commercial laboratory (ALS Chemex, Sparks, NV) using a hot 3:1 nitric-hydrochloric acid extraction (Mudroch et al. 1997). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to analyze Al, Ca, Fe, Mn, and Cu, while cold vapor atomic absorption spectroscopy (AA) was used to analyze Hg. Duplicate analyses typically yielded relative difference values of <10 percent for all metals.

Linear least squares regression analysis was used to quantify the relationship between sediment-metal contamination and spatial/geochemical predictors (Draper and Smith 1981). Two spatial variables were considered for use in the regression models: drainage area at the sampling site and distance of the sampling site below the source point at Gold Hill (Marcus 1987). These variables represent the watershed-scale influence of progressive dilution/mixing with uncontaminated sediment downstream and the removal of contaminant metal from the channel by sedimentation and longer-term storage. Variables tested to describe the reach-scale variability of sediment geochemistry included sand content, total carbon content, Al, Ca, Fe, and Mn. Spatial variables (drainage area and distance) were not included in regression testing for uncontaminated tributary sediments because there is no specific source point associated with the origin of the geochemical background signal. Different combinations of arithmetic and logged values were used to determine the best regression equation. Final model selections and regression model errors were evaluated using Pearson correlation analysis with two-tailed significance testing and standard regression statistics such as coefficient of determination (R^2), standard error of the Y-estimate (SE), and F-ratio (Fr).

RESULTS

*Composition of Bar and
Bench Deposits*

Depositional environment and the degree of mining contamination generally explain the textural and geochemical composition of the active channel deposits (Table 1). Overall, laboratory results for bench surface samples reflect conditions associated with a lower energy fluvial environment. Bench samples tend to contain more organic matter (i.e., total carbon) and are slightly finer in texture (i.e., less sand) compared to lower elevation bar areas (Table 1). Coarser substrates would be expected to occur in low bar areas given the greater importance of hydraulic scour and bed load transport near the bed. In contrast, sedimentation on bench surfaces probably involves a greater contribution from the suspended load. The higher concentrations of Al, Ca, Cu, Hg, and C measured in bench deposits are expected since they typically bind to finer particles and are associated with organic matter. While bench surfaces may accrete laterally and vertically over time, bench occurrence in itself indicates a more stable feature that is not reworked as often as sandy bar deposits. Moreover, insipient A-horizon development and vegetation growth would be expected to occur on bench surfaces and increase the organic matter content over

Table 2. Correlation Matrix for Mainstem Channel Sites[a].

	A_d	Dist	Al	Ca	Fe	Mn	Cu	Hg	C_t	Sand
Low Bar (n=20)										
A_d	1.00									
Dist	0.97**	1.00								
Al	−0.39	−0.36	1.00							
Ca	−0.26	−0.23	0.81**	1.00						
Fe	−0.37	−0.39	0.68**	0.71**	1.00					
Mn	0.24	0.23	0.46*	0.60**	0.30	1.00				
Cu	−0.52*	−0.56**	0.12	0.03	0.04	−0.05	1.00			
Hg	−0.68**	−0.71**	0.49*	0.19	0.31	0.02	0.76**	1.00		
C_t	−0.44	−0.44*	0.18	0.07	−0.02	0.16	0.81**	0.61**	1.00	
Sand	0.13	0.06	−0.63**	−0.20	−0.07	−0.25	−0.15	−0.48*	−0.33	1.00
Low Bench (n=25)										
A_d	1.00									
Dist	0.97**	1.00								
Al	0.31	0.46*	1.00							
Ca	0.29	0.41*	0.71**	1.00						
Fe	−0.22	−0.18	0.11	−0.12	1.00					
Mn	0.41*	0.50**	0.87**	0.47**	0.14	1.00				
Cu	−0.79**	−0.76**	−0.25	−0.39*	0.27	−0.24	1.00			
Hg	−0.73**	−0.62**	0.19	0.17	0.20	0.10	0.67**	1.00		
C_t	−0.07	0.08	0.66**	0.63**	−0.08	0.48*	0.04	0.54**	1.00	
Sand	−0.33	−0.47**	−0.90**	−0.72**	0.18	−0.77**	0.26	−0.23	−0.78**	1.00

[a]A_d = drainage area, Dist = distance from mining source, and C_t = total carbon.

** significant at $p = 0.01$.

* significant at $p = 0.05$.

time. Vegetation growth might also aid in trapping silty sediment on bench surfaces.

Higher Fe concentrations are found in the active low bar deposits examined in this study, possibly due to favorable redox conditions for the formation of secondary oxide coatings on silt and sand grains during periodic saturation cycles (Evans and Davies 1994). Secondary Fe-Mn oxides have the capacity to bind and co-precipitate mining-related metals to relatively high concentrations (Horowitz 1991). Fe and Mn concentrations are poorly correlated in contaminated bar and bench deposits (Table 2), but are significantly correlated in uncontaminated channel sediments (Table 3). These contrasting relationships may be explained either by tributary sediments having a different Mn geochemistry than main stem segments or that mining sediment geochemistry masks the background Fe-Mn geochemistry in contaminated bar and bench deposits.

Contaminated active channel deposits

Table 3. Correlation Matrix for Unmined Tributary Sites[a].

	Al	Ca	Fe	Mn	Cu	Hg	C_t	Sand
Bar (n=31)								
Al	1.00							
Ca	0.26	1.00						
Fe	0.72**	0.20	1.00					
Mn	0.68**	−0.13	0.59**	1.00				
Cu	0.73**	0.54**	0.77**	0.38*	1.00			
Hg	0.64**	0.19	0.23	0.45**	0.42*	1.00		
C_t	0.53**	0.29	0.15	0.25	0.36	0.68**	1.00	
Sand	−0.59**	−0.10	0.02	−0.28	−0.18	−0.71**	−0.77**	1.00
Low Bench (n=17)								
Al	1.00							
Ca	0.45	1.00						
Fe	0.79**	0.15	1.00					
Mn	0.64**	0.18	0.53*	1.00				
Cu	0.76**	0.66**	0.63**	0.30	1.00			
Hg	0.67**	0.54	0.29	0.59**	0.57*	1.00		
C_t	0.81**	0.25	0.52*	0.84**	0.43	0.71**	1.00	
Sand	−0.79**	−0.41	−0.39	−0.46	−0.58**	−0.87**	−0.77**	1.00

[a]C_t = total carbon.

** significant at p = 0.01.

* significant at p = 0.05.

contain higher concentrations of Al, Cu, and Hg and lower concentrations of Fe and Mn compared to uncontaminated samples (Table 1). Levels of Hg contamination are 9 to 11 (up to 17) times those found in uncontaminated sediments (Table 1). Cu concentrations in contaminated samples are 3 to 5 (up to 20) times those found in uncontaminated tributaries. Potentially toxic levels of sediment contamination were measured below Gold Hill in main stem segments of both Little Buffalo Creek and Dutch Buffalo Creek. For Hg, 9 percent of active channel samples had concentrations above the "probable effect concentration" (PEC) of 1.06 mg/kg and only 47 percent of the samples were below the "threshold effect concentration" (TEC) of 0.18 mg/kg (MacDonald et al. 2000). The PEC is the expected concentration above which harmful effects are likely to be observed and the TEC is the expected concentration below which harmful effect are not likely to be observed. For Cu, 30 percent of active channel samples had concentrations above the PEC of 149 mg/kg and only 12 percent of the samples were below the TEC of 31.6 mg/kg (MacDonald et al. 2000). These aquatic sediment quality criteria do not take into account varia-

tions in sediment grain-size and geochemistry and represent general values for fine-grained sediments from low-energy, depositional environments with low sand content.

Spatial Modeling using
Distance Downstream

The spatial variable selected for inclusion in all contaminated sediment regression models was the $\log_{10}$ value of the distance below the mine source at Gold Hill. This decision was made based on the following reasons: (i) there is a very strong correlation between site distance and drainage area so that there is almost no statistical difference between them (r = 0.97; Table 2); (ii) log-distance usually resulted in the regression equation with the least error; and (iii) distance values are easier to conceptualize and apply to management problems than drainage area.

Spatial regression modeling shows that a one-parameter model with distance from the mine explains only 38–49 percent of the downstream variance in Hg concentrations (Table 4). However, the same one-parameter model explains over 78–83 percent for Cu. The high Cu correlation is caused to some extent by the heavy weighting of one high concentration sample near the mine site at distance 3.01 km (Figure 3). However, if this extreme value (1,300 mg/kg Cu) is omitted from the regression analysis, the explained variance only decreases by 7 percent (0.82 to 0.75) for low bar and 3 percent (0.78 to 0.75) for combined active sediment one-parameter models. Future monitoring should test this area immediately below Gold Hill again to determine whether or not these high levels are typical. In addition, four samples from one site at 1.3 km were omitted from the

modeling procedure because the site appeared to be above the main source of mine waste inputs and not affected by the geochemical decay processes of concern in this study. This highlights the importance of accurately identifying source areas and their linkages to the channel network for contamination assessments in mined watersheds.

Error differences between distance-concentration models for Hg and Cu are related to the overall scatter of the sample concentrations downstream and the degree to which low bar and bench sample populations overlap. The relationship for Hg has the most scatter as indicated by a relatively low R^2 value (Figure 2). It is visually obvious that the Cu trend is less affected by data scatter (Figure 3). The larger scatter associated with Hg is probably due to its wider range in concentrations between background and contaminated sediment populations and the stronger association of Cu with sediment inputs in the form of mill tailings sources. Bar and bench samples tend to overlap in their distribution along the regression trend line (Figures 2 and 3). This condition is most obvious for Cu and less so for Hg. The increased sample size used for regression analysis of the combined bar and bench data set improves the significance of both models (i.e., larger F-ratio for Hg and Cu equation), but the amount of variance explained by the equation decreases by 5 to 10 percent (Table 4). This finding suggests that there are real reach-scale variations in geochemical composition not explained by the distance decay process alone and that bar and bench deposit sampling methods used are sensitive to these variations.

While there are some differences between bar and bench deposits, the overlap
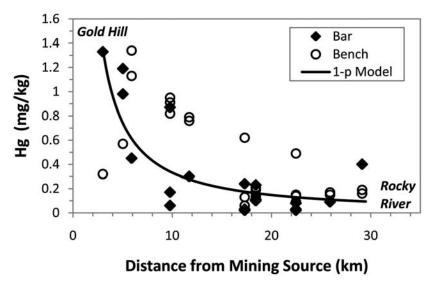
Figure 2. Longitudinal trends in contamination of sediments by Hg. The one-parameter spatial regression model for all-combined samples is shown as the curve for Log Hg over Log distance (Table 4).
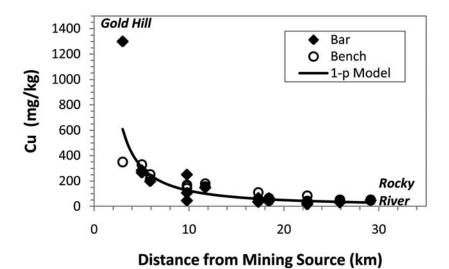

Figure 3. Longitudinal trends in contamination of sediments by Cu. The one-parameter spatial regression model for all-combined samples is shown as the curve for Log Cu over Log distance (Table 4).

Table 4. Spatial Models for Contaminated Sediments[a,b].

Dependent Variable	n	R^2	SE	Fr	b_0	b_1	b_2
Low Bar Deposits							
Log Hg	19	0.486	0.438	16	0.862	−1.481 (Log Dist)	
Log Hg	19	0.860	0.236	49	1.816	−1.354 (Log Dist)	−0.016 (Sd)
Log Cu	19	0.824	0.210	80	3.633	−1.579 (Log Dist)	
Log Cu	19	0.901	0.162	73	3.987	−1.532 (Log Dist)	−0.006 (Sd)
Low Bench Surface							
Log Hg	24	0.420	0.312	16	0.613	−0.983 (Log Dist)	
Log Hg	24	0.838	0.168	54	1.971	−1.471 (Log Dist)	−0.015 (Sd)
Log Cu	24	0.826	0.141	105	3.252	−1.137 (Log Dist)	
Log Cu	24	0.931	0.091	141	3.813	−1.339 (Log Dist)	−0.006 (Sd)
Active Sediments (combined)							
Log Hg	43	0.383	0.402	25	0.687	−1.166 (Log Dist)	
Log Hg	43	0.860	0.194	123	1.908	−1.416 (Log Dist)	−0.016 (Sd)
Log Cu	43	0.782	0.190	147	3.417	−1.325 (Log Dist)	
Log Cu	43	0.908	0.125	197	3.916	−1.427 (Log Dist)	−0.006 (Sd)

[a]Regression equation form: $Y = b_0 + b_1X_1 + b_2X_2$

[b]Independent variables: Sd = percent sand; Dist = distance downstream (km)

of bar and bench sample populations suggests a similar contaminant supply and/or flood event delivery process for both depositional environments. Both bar and bench areas are inundated by seasonal floods with a recurrence interval of around one year or less. Field observations support these flood frequency estimates since high water marks and evidence for sediment deposition at bank elevations occur more than one meter above bench surfaces. Not surprisingly, the precision of combined

"active sediment" models improves measurably when percent sand is added as a second predictor variable. Model improvements help to explain reach-scale variations in geochemistry relating to the effects of vertical sorting and deposition of sediment mixtures within the channel as indicated by bar and bench samples (Table 4) (Hakanson 1984). These effects are further discussed below.

Spatial Modeling using Distance Downstream and Sand Content

The primary goal of this study was to develop an approach for combining watershed- and reach-scale variables in longitudinal models in order to improve model precision and basic understanding of the metal-sediment transport process. The watershed-scale predictor selected for use was distance from the mine source. In order to select the reach-scale predictor, three criteria were used: (i) predictor effect on metal-sediment concentration had to be understood and relatively simple to apply; (ii) spatial autocorrelation and co-linearity effects had to be minimized; and (iii) predictor must have a relationship to fluvial processes and channel sedimentation.

After analyzing the data set with the above criteria in mind, percent sand was selected as the reach-scale variable. In most cases, sand content is negatively related to metal concentration due to dilution and low binding capacity (Horowitz 1991). In this data set, sand percent is usually poorly or weakly correlated with both Hg and Cu and other related metals (Table 2). Furthermore, variations in texture of the active bed and sand content of the low bar and bench deposits are documented (Figure 4). While the dominant texture of the bed shifts from gravel to sand down-

stream, bar and bench deposits range widely in sand content from 30 to 90 percent in Little Buffalo Creek to 10 to 98 percent in Dutch Buffalo Creek (recall that higher sand content reflects a coarsening of the deposit). Sand content decreases significantly downstream in bench deposits ($r = -0.47$, $p = 0.01$) due to the leverage effects on the correlation from the high sand content upstream of river kilometer 5 and relatively low sand content at river kilometer 29 (Figure 4). However, there is no downstream trend shown for percent sand in low bar sediment samples ($r = 0.06$) (Table 2).

Results using the two-parameter model stress the importance of combining watershed- and local-scale parameters to improve the precision of spatial models. When percent sand was combined with distance downstream, the variance explained by the combined model increased from 38 to 86 percent for Hg and 78 to 92 percent for Cu (Table 4). This simple model approach has effectively linked watershed and reach processes to improve the spatial resolution of contaminated sediment assessments in this river system. Additional predictors were added to the regression models with a slight improvement of precision. However, the increased complexity of the model did not yield as great improvement overall as did percent sand. Moreover, the explanatory value of additional variables in the regression model did not improve since they only had an incremental effect on improving precision.

Background Geochemistry

Background geochemistry varies between Hg and Cu in the Little Buffalo Creek–Dutch Buffalo Creek watershed. Hg is released in trace amounts from rock
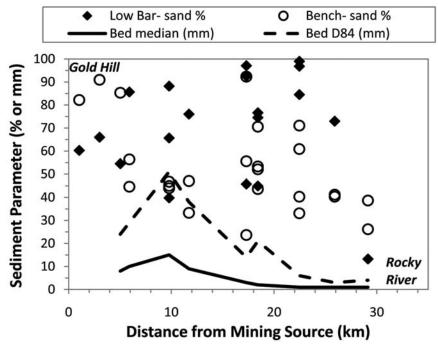
Figure 4. Downstream trends in sediment parameters.

weathering and there may be some atmospheric inputs from anthropogenic sources, but generally concentrations are low (0.1 mg/kg) and comparable with background levels reported elsewhere (Reimann and Caritat 1998; Xinmin et al. 2006). For Hg, the best three-parameter regression equation explains 84 percent of the variability in background Hg concentrations (Table 5). Hg concentrations are negatively related to sand content (grain size control) and positively related to organic matter and Fe (secondary geochemical substrates). Again, this result is consistent with the typical expectation that metal concentrations increase in sediments that have less sand (i.e., more silt/clay particles), more organic matter, and more geochemical substrates with high sorption capacity such as Fe/Mn oxides (Horowitz 1991).

Sources of background Cu relate to bedrock type and local sulfide mineralization. Cu is often associated with urban runoff or industrial effluents. However, watershed land use is mostly rural or suburban and urban inputs of Cu were not detected in this study. For Cu, the best three-parameter regression equation also explains 84 percent of the variability in background Cu concentrations (Table 5). Cu concentrations are positively related to Al, Ca, and sand content. The importance of Al and Ca may relate to the release of Cu from silicate minerals, Cu mineralization in the area, or the binding of Cu within clay residuum lattices (Horowitz et al. 1989). While sand content is included in the Cu background equation

Table 5. Geochemical Substrate Models for Background Tributary Sediments[a,b].

Dependent Variable	n	R^2	SE	Fr	b_0	b_1	b_2	b_3	Check R^{2c}
Log Hg	45	0.713	0.173	107	−0.660	−0.014 (Sd)			0.315
Log Hg	45	0.816	0.140	93	−1.058	−0.008 (Sd)	0.287 (Log C)		0.425
Log Hg	45	0.841	0.132	72	−1.120	−0.010 (Sd)	0.193 (Log C)	0.287 (Log Fe)	0.474
Log Cu	45	0.752	0.126	130	1.275	0.940 (Log Al)			0.098
Log Cu	45	0.805	0.113	87	1.533	0.822 (Log Al)	0.429 (Log Ca)		0.204
Log Cu	45	0.839	0.104	71	1.247	1.021 (Log Al)	0.365 (Log Ca)	0.003 (Sd)	0.218

[a]Regression equation form: $Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3$

[b]Independent variables: Sd = percent sand; C = Total carbon (%); Fe = iron (%); Al = Aluminum (%); Ca = calcium (%)

[c]Percent of the variance these same parameters explain using all contaminated samples (n = 43)

for the best three-parameter model, it only slightly improved the precision (by 3 percent) so should not be weighted too heavily for its explanatory value. But it may be possible that weathered bedrock units or overlying soils which supply the most sand to tributary streams contain naturally higher levels of Cu.

To evaluate the potential influence of background processes on contaminated sediment trends, the same predictors used in regression models developed for tributary sediments were applied for regression analysis in the contaminated data set. For Hg, regression analysis using percent sand, total carbon, and iron concentration explains 47 percent of the variance in contaminated sediments (see "check R^2 column in Table 5). For Cu, regression analysis using Al concentration, Ca concentration, and

sand percent explains 22 percent of the variance in contaminated sediments. Background predictors explain a little more than half of the variance explained by the contaminated sediment model for Hg and about one-quarter for Cu.

The ability of background predictors to explain contaminant variance suggests the possibility that the level of disturbance from mining has not completely masked the influence of regional background source contributions in the contaminated portions of the river system. The degree of overlap between background geochemistry in predicting contaminant concentrations is probably related to input source. Hg was introduced to the stream system as an industrial pollutant that is relatively mobile in the environment. Furthermore, there may be slight influence of atmo-

spheric Hg deposition on the geochemistry of soils and sediment of the region. Thus, Hg is associated with secondary geochemical substrates that bind mobile H under both contaminated and uncontaminated conditions. In contrast, Cu contamination is more associated with mineral forms in crushed rock particles (tailings inputs) that are less mobile and not as available for redistribution to secondary substrates.

MANAGEMENT IMPLICATIONS

A simple and effective approach to metal-sediment modeling has been presented. This approach has improved precision and reduced error in empirical concentration-distance models that can be used to monitor and track contamination in mined watersheds. The models discussed use well known predictors that are relatively easy to derive. In addition, this study provides a management framework for active channel sediment sampling and provides a procedure for combining geochemical information from different sampling targets including bar and bench landforms. Similar approaches can be applied to other river systems affected by mining contamination. More complex models can be developed that involve more predictors and watershed data, but the two-parameter models developed for this study explain >85 percent of the variance in Cu and Hg concentrations in active channel sediments.

CONCLUSIONS

Multiple linear regression has been shown to be useful for quantifying spatial and geochemical trends of sediment contamination in the Little Buffalo Creek–Dutch Buffalo Creek river system. Simple two-parameter models combining the effects of both watershed-scale dispersal processes (distance downstream) and reach-scale sediment transport (percent sand) explain 86 percent of the variance of Hg and 91 percent of the variance of Cu in active channel sediments. Background effects are controlled by grain-size, geochemical substrates, and mineral weathering sources, and three-parameter models explain 84 percent of the variance of Hg and Cu in uncontaminated tributary samples. Moreover, the imprint of regional background processes is evident even in mining contaminated sediments. More than 45 percent of the variance in contaminated Hg and 20 percent of the variance in contaminated Cu can be explained by background parameters. The potential differences in background influence probably are related to releases of Hg in a geochemically active form that is similar to some degree to background processes, while Cu contamination is more associated with less mobile mineral forms in tailings. An effort was made to compare the contamination trends between bar and bench samples. Even though the characteristics of the two deposits vary with flow energy and geochemical boundary conditions, the overall sediment supply and its composition appear to be similar and the effectiveness of combined reach- and watershed-scale modeling support this interpretation. This finding underscores the need for more research on understanding the effects of bed sorting, selective transport, and bar/bank sedimentation on legacy metal storage and cycling in mined watersheds.

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