Natural Background Determination and Impact Quantification in Trace Metal-Contaminated River Sediments

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Historic and current mining activities have contaminated stream sediments around the world with toxic heavy metals. A general lack of premining baseline data makes it difficult to quantify the extent of contamination and to set realistic remediation goals. These problems can be solved by modeling the downstream dispersion of metal anomalies based on dilution mixing of anomalous and tributary sediments. The model allows calculation of the dispersion curves of metals in stream sediments both before and after mining and also allows the quantification of any anthropogenic exaggeration of an anomaly. Mining activities were found to amplify naturally occurring metal anomalies up to 3 orders of magnitude, extending downstream dispersion trains from a natural limit of around 20 km to as much as 500 km. The dilution mixing model provides a useful tool for calculating premining dispersion trains and quantifying the effects of mining on a river basin. Such information is relevant to the understanding, litigation, and remediation of contaminated rivers around the world.

Introduction

Mining activities around the world have left countless streams and rivers contaminated with toxic heavy metals (1-4). Some of the most contaminated regions have a mining history spanning over a millennium. In many historic mining districts, metals released from mining wastes have completely obscured the natural contribution of metals to stream sediments. The natural component of the metal load may be overwhelmed by metals released from finely ground mill tailings, which were historically discharged directly into a local stream. The discharge of metal-rich tailings often overwhelmed the sediment-transport capacity of a stream, resulting in aggradation of the streambed and flood plain (5-8). Long after mining has ceased or mining practices have been altered, metals stored on the flood plain

may continue to enter the stream via cut-bank erosion and groundwater inputs (9). Metals from waste rock dumps and tailings ponds may also enter the stream through physical erosion and geochemical inputs. A lack of sediment baseline data in historic mining districts makes it difficult to quantify the increased metal load and set realistic remediation goals. In the absence of any baseline data, remediation goals may be subject to protracted legal debate as some argue that arbitrarily set cleanup goals are too stringent, while others argue they are not stringent enough. There is a need for an accepted method to determine premining conditions in stream sediments in order to set realistic remediation goals and quantify the increased metal load presently observed in the stream sediments.

Recent work has addressed the problem of determining the natural background geochemistry of water in mined areas (10) but not that of sediment. Water geochemistry is of particular interest in areas subject to acid-mine drainage, where high concentrations of metals are transported away from the site in the solute phase (11, 12). At non-acid-producing mine sites, the downstream transport of metals is primarily in the sediment load due to the low solubility of metals in water at neutral or higher pH (13, 14). Even in streams receiving acid-mine drainage, the solute metal load is rapidly precipitated or adsorbed onto sediment as the pH rises to neutral, usually within a few kilometers of the source (15, 16). From this point on, the problem primarily becomes one of sediment transport rather than aqueous geochemistry. However, the sedimentbound metal load receives much less attention even though it is generally responsible for the majority of downstream transport and can have long-lasting effects on the aquatic biota (9, 17-20).

It is important to establish the nature of the downstream dispersion of metal anomalies prior to mining in order to help quantify the impact of mining and set realistic remediation goals. This can be accomplished by modeling the downstream dispersion of natural metal anomalies by dilution mixing with un-enriched tributary sediments. Modeling allows the calculation of downstream dilution curves commonly referred to as dispersion trains. This paper presents a method to model the dispersion trains of metal anomalies both before and after mining. This information can then be used to quantify the increased metal load to stream sediments and help set realistic remediation goals in contaminated river basins.

Model Development

The conceptual basis for modeling the dispersion trains of natural and anthropogenic metal anomalies requires an understanding of the processes governing the downstream dispersion of metals. Prior to mining, an ore deposit weathers and erodes naturally, contributing metal-rich sediment into the local drainage. Metal-rich sediment is quickly diluted by un-enriched tributary sediments, attenuating the anomaly a short distance downstream. Even the largest ore deposits rarely have dispersion trains detectable more than $10-20~\rm km$ downstream, a fact well documented in the exploration geochemistry literature (21–

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25). Exploration geochemists first realized that the downstream dispersion of naturally occurring metal anomalies was primarily governed by dilution mixing with tributary sediments.

In order to predict the size of an undiscovered metal anomaly, an equation was developed to calculate the product of the area and grade of an anomaly based on the concentration of an anomalous sediment sample and the background concentration and area of the basin (26, 27). This equation can easily be reversed and used to calculate the metal concentration of a particular sediment sample based on the area and grade of an upstream anomaly. The equation is based on the concept that the sediment concentration of a metal at a particular point in a stream represents steady-state mixing of sediments of anomalous and background concentrations eroded in the upstream basin. If a few simplifying assumptions are made, the metal concentration of a sediment sample can be related mathematically to the sum of the relative portions of basin area at background and anomalous concentrations. The assumptions are as follows: (1) there is a uniform average erosion rate over the entire basin, (2) there is a single source of anomalous sediment in the basin, (3) the metal behaves conservatively in the river sediment, and (4) the sediment sample represents steady-state mixing of tributary sediments. These assumptions allow the units of mass and time (erosion rate) to be removed from the equation, leaving only units of area and concentration, where area conceptually represents a quantity of sediment. The resulting formula relates the metal concentration of a sediment sample to the sum of the relative portions of background and anomalous area:

$$[Me]_{km} = C_b \frac{A_t - A_o}{A_t} + C_o \frac{A_o}{A_t}$$
 (1)

where $[Me]_{km}$ is the sediment metal concentration at a particular river kilometer, C_b is the average background concentration of the basin, A_t is the total area of the basin upstream from the sample location, A_o is the area of the surface anomaly for a particular metal, and C_o is the concentration of that metal in the surface anomaly of the ore deposit. The basic assumptions of this equation have been shown to apply in climates ranging from arid to tropical (28).

Equation 1 can closely approximate the dispersion trains of undisturbed ore deposits but cannot account for the additional input of metals resulting from mining activities. Large-scale metal extraction generates large quantities of waste rock and finely ground tailings. Metals may be released from these wastes by physical or geochemical processes, resulting in an exaggerated input of metal-rich sediment to a stream. Two new terms, referred to as the exaggerated area (A_x) , and the exaggerated concentration (C_x) , are used to account for the increased input of a particular metal into the stream sediment. The exaggerated input of metal can be thought of as an amplification of the natural erosion rate of the ore deposit, or since the model assumes a uniform erosion rate, the additional metal input can be represented as an increase in the area of the anomaly. The exaggerated area conceptually accounts for the increased quantity of metal-rich sediment entering a stream. The exaggerated sediment input often contains a higher concentration of metal than the natural input because ore brought to the surface during mining is usually of a higher

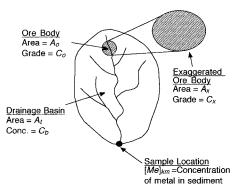


FIGURE 1. Basin diagram showing visual definitions of terms used in eqs 1 and 2.

grade than the overlying surface material (29, 30). The exaggerated concentration (C_x) accounts for any increase in the metal concentration of the anomalous sediment due to mining. Each term is distinctive and representative of actual field parameters. When the exaggerated area and exaggerated concentration are considered, eq 1 can be modified as follows to account for metal inputs from mining/milling:

$$[Me]_{km} = C_b \frac{A_t - A_o}{A_t + (A_x - A_o)} + C_x \frac{A_x}{A_t + (A_x - A_o)}$$
(2)

where the new terms A_x and C_x represent the exaggerated area and exaggerated concentration, respectively, of a specific metal due to mining activities (Figure 1). These parameters represent an amplified anomaly that includes the anthropogenic increases in quantity and concentration of anomalous sediment. Equation 2 contains the following modifications: (1) C_x was substituted for C_0 , (2) A_x was substituted for A_0 in the numerator on the right-hand portion of the equation, and (3) the exaggerated area not already included in A_t was added to the denominators of both portions of the equation. The total area had to be increased due to the use of area to conceptually account for the increased input of sediment in the equation. When A_x and C_x are set equal to A_0 and C_0 , eq 2 reverts to eq 1. With the addition of the terms A_x and C_x , eq 2 can now account for anthropogenic inputs resulting from mining activities.

Increasing either A_x or C_x alters the shape of the dispersion curve in different ways. Figure 2 shows the effects of (a) increasing A_x 3 orders of magnitude, (b) increasing C_x 3 orders of magnitude, and (c) holding the product of A_xC_x constant while altering the individual values. The resulting alterations of the shape of the dispersion curve may not be immediately apparent from casual observation of eq 2. Figure 2 shows that there are unique solutions of A_x and C_x that provide the closest approximation of the model to an actual dispersion train.

Model Application

Methods. The model was applied to several data sets from streams with both mined and unmined ore deposits in their headwaters to see how accurately the model approximates actual dispersion trains. Data sets from several Montana streams and rivers were used along with data sets from the exploration literature. Fine-grained sediment samples were chosen for field sampling in order to minimize grain size effects on metal concentration caused by the tendency of trace metals to partition into the fine-grained sediment

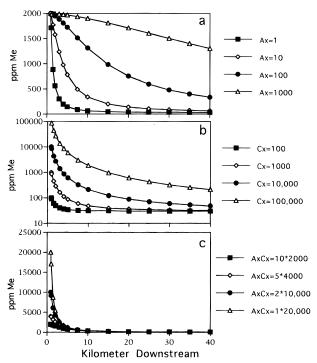


FIGURE 2. (a) Effects on the dispersion curve of increasing $A_{\rm x}$ 3 orders of magnitude. (b) Effects on the dispersion curve of increasing $C_{\rm x}$ 3 orders of magnitude. (c) Effects on the dispersion curve of holding the product of $A_{\rm x}$ and $C_{\rm x}$ constant at 20 000 while varying the individual values.

fraction (31, 32). Sediment samples were wet sieved in situ through a 63-µm mesh using ambient streamwater. Samples were stored on ice and dried immediately when we returned to the lab. The dried sediment was powdered and digested using a microwave aqua-regia technique. Multi-element analysis was performed by inductively coupled argon plasma spectroscopy (ICP); recoveries for Cu, Pb, and Zn were >95%. Modeling was performed in a spreadsheet.

The first step in modeling a dispersion train for a particular metal is the determination of the measurable model parameters. All of the parameters except A_x can be measured with some degree of accuracy. Basin area (A_t) can be measured accurately from maps, or an equation can be used to generate approximate area for any desired river kilometer (33). The area of mineralization (A_0) can be measured accurately from geologic maps of the ore deposit. Tributary sediment samples can provide an average value for the background concentration in the basin (C_b), and mining reports can provide information on C_0 and C_x . C_x can also be directly sampled from tailings deposits or contaminated tributaries within the source. Once the measurable parameters are set, a visually-fit value for A_x can be entered as a starting point into a nonlinear least squares routine to provide a statistically best-fit value for

Results. The model was first applied to data sets from streams draining unmined ore deposits in order to show that it can accurately approximate the dispersion trains of undisturbed anomalies. The various parameters of the anomalies were determined and entered into the model. The resulting curves were found to closely approximate the dispersion trains observed in sediment data from four undisturbed deposits (Figure 3). Similar results were

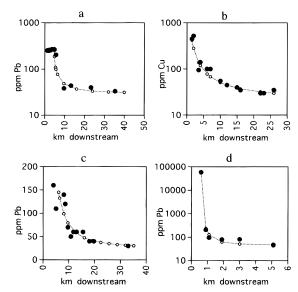


FIGURE 3. Model fits to relatively undisturbed ore deposits shown by open circles with dashed lines; field sediment data shown by solid circles. (a) Model fit to sediment data from Miller Creek, draining a large sulfide deposit at Cooke City, MT. (b) Model fit to data from a stream draining the Rosemont copper porphyry deposit, Arizona (26). (c) Model fit to data from a stream draining the Gamsberg stratiform zinc deposit, South Africa (24). (d) Model fit to sediment data from Ivanhoe Creek, draining a small lead prospect in the Anaconda—Pintlar Wilderness, Montana.

reported in other studies using the same basic concepts (26-28).

The model was then applied to streams and rivers with disturbed ore deposits in their drainages to see if it could accurately represent exaggerated anomalies. In each of the drainages, tailings from historic mining act as a continuing source of metals, providing strong exaggerated anomalies. Figure 4 shows model fits to four contaminated rivers. In each case, an acceptable fit to the sediment data was achieved using the measured parameters and a best-fit A_x , showing the model capable of approximating the dispersion trains of highly disturbed anomalies. Once the various model parameters have been determined, the premining dispersion train can be calculated and the exaggeration of the anomaly quantified.

An idealized premining dispersion train can be calculated by setting A_x equal to A_0 and C_x equal to C_0 . The resulting curve should closely approximate the natural dispersion train of the deposit prior to mining, as shown by the previous model fits to unmined ore deposits. Idealized premining dispersion trains are shown for four contaminated Montana streams and rivers in Figure 5. The lengths of the calculated dispersion trains are within the range of reported dispersion trains for undisturbed ore deposits. Prior to mining, metal levels greater than twice the regional background rarely extend more than 20 km downstream, even for the largest ore deposits (21-25). By contrast, metal levels of twice the regional background were found to extend 500 km downstream in one of the contaminated river systems examined (Figure 5a). Once the parameters of an anomaly are known both before and after mining, it is also possible to quantify the impact of mining.

There are various ways to conceptualize and quantify the impact of mining, the most obvious one being the ratio of the exaggerated anomaly to the natural anomaly. This

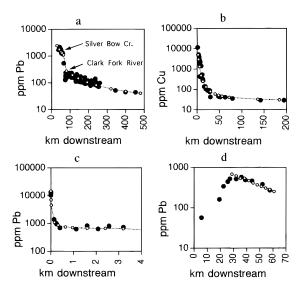


FIGURE 4. Model fits to contaminated rivers shown by open circles with dashed lines; field data shown by solid circles. (a) Model fit to Silver Bow Creek—Clark Fork River; headwaters host a very large Cu porphyry deposit at Butte, MT, with a 125-year mining history (48). Silver Bow Creek, above tailings ponds, $E_f = 156$, $G_x = 1556000$ km² ppm Pb; Clark Fork River, below tailings ponds, $E_f = 70$, $G_x =$ 700 000 km² ppm Pb. Values obtained using an estimated A_0 of 33 km² and C_0 of 300 ppm Pb. (b) Model fit to the Blackfoot River, MT, headwaters contain the Heddleston mining district where Ag-Pb-Zn veins were mined in the early 1900s (49, 50). $E_f = 750$, $G_x = 27600$ km² ppm Cu. Values obtained using an estimated A₀ of 0.004 km² and a Co of 10 000 ppm Cu. (c) Model fit to Dunkleberg Creek, MT, draining a limestone hosted Ag-Pb-Zn vein mined from 1884 to mid-1900s (51, 52), $E_f = 500$, $G_x = 256$ km² ppm Pb. Values obtained using an estimated A_o of 0.00003 km² and a C_o of 20 000 ppm Pb. (d) Model fit to Flint Creek, MT. The Phillipsburg mining district, site of extensive Mn vein mining in the early to mid-1900s, lies midway down the drainage (53, 54), $E_{\rm f} = 325$, $G_{\rm x} = 233\,000\,{\rm km^2}\,{\rm ppm}\,{\rm Pb}$. Values obtained using an estimated A_0 of 0.026 km² and C_0 of 28,000 ppm Pb.

ratio is referred to as the enrichment factor (E_f) where E_f is defined as follows:

$$E_{\rm f} = A_{\rm x} C_{\rm x} / A_{\rm o} C_{\rm o} \tag{3}$$

The enrichment factor is a dimensionless term expressing the extent of exaggeration of the natural anomaly. The enrichment factor provides a relative measure of how disturbed a deposit is. Enrichment factors ranged from 70 to 1400 for the exaggerated anomalies examined. The exaggeration of copper and zinc anomalies was found to be as much as an order of magnitude greater than the exaggeration of the lead anomaly for the same deposit, a result attributed to the greater geochemical mobility of copper and zinc out of the source material. The enrichment factor quantifies relative enrichment but does not quantify the magnitude of the exaggerated anomaly. Another term is required in order to quantify the magnitude of the exaggerated anomaly.

A quantitative value representing the magnitude of an anomaly can be calculated by taking the product of the area and concentration of the anomaly. This quantity is referred to as the areal grade, a term similar to the gradetonnage term used to describe ore reserves, only two dimensional. The areal grade (G_0) and exaggerated areal grade (G_x) are defined as the product of the area and concentration of the anomaly before and after mining,

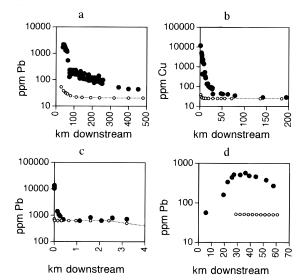


FIGURE 5. Calculated premining dispersion curves shown by open circles with dashed lines, field data shown by solid circles. (a) Silver Bow Creek/Clark Fork River; metal levels of twice background calculated to have originally extended only 15 km downstream from the ore deposit at Butte, MT. (b) Blackfoot River; metal levels greater than twice background calculated to have occurred only in the immediate vicinity of the vein deposits with no significant dispersion train present. (c) Dunkleberg Creek; mined vein calculated to have been insignificant by itself, but high regional background in the mineralized zone dominated the downstream trend. (d) Flint Creek; due to significant area of drainage upstream from the deposit, calculated metal levels in Flint Creek barely influenced at all by the veins at Phillipsburg.

respectively. G_0 represents the areal grade of an anomaly prior to mining:

$$G_0 = A_0 C_0 \tag{4}$$

 G_x represents the exaggerated areal grade of the anomaly after mining:

$$G_{\mathbf{x}} = A_{\mathbf{x}} C_{\mathbf{x}} \tag{5}$$

The areal grades conceptually represent sediment metal loads, all that is needed to convert them into actual metal loads is the average erosion rate of the basin. Figure 6 shows the areal grades for a number of undisturbed ore deposits as well as the exaggerated areal grades for four of the disturbed anomalies examined. Exaggerated areal grades ranged from 300 to 1 500 000 km² ppm for the disturbed anomalies examined. In contrast, the areal grades for a number of naturally occurring anomalies ranged from only 0.5 to 11 000 km² ppm. In three out of the four cases examined, the exaggerated anomalies exceeded the range of naturally occurring anomalies by as much as 2 orders of magnitude. The areal grades and enrichment factor provide two ways to quantify the impact of mining on stream sediments.

Discussion

The accuracy of the calculated premining dispersion train and the quantification of the amplification of an anomaly are primarily limited by the accuracy of the various model parameters and the validity of the model assumptions in a particular drainage. The parameters $A_{\rm t}$, $A_{\rm o}$, and $C_{\rm b}$ can be measured accurately, but $C_{\rm o}$, $C_{\rm x}$, and $A_{\rm x}$ may have varying degrees of uncertainty associated with them. The concentration of the exaggerated anomaly $(C_{\rm x})$ can be limited

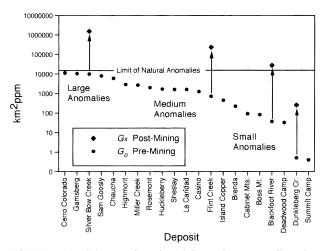


FIGURE 6. Premining areal grades of the surface anomalies of a number of ore deposits showing the range and distribution of natural anomalies (21, 22, 24, 26, 29). Arrows show the amplification of the natural anomalies due to mining activities for the four contaminated streams and rivers examined. Three of the river basins presently contain metal anomalies that exceed the range of naturally occurring anomalies by as much as 2 orders of magnitude.

to the range between the highest observed sediment concentration and the grade of the processed ore. Mining reports sometime include the grade of tailings, and it may also be possible to collect samples directly from tailings deposits. Any chance to directly sample C_0 has usually been obliterated by mining, so an estimation must be relied upon.

The original concentration of the surface anomaly (C_0) is the most difficult parameter to determine. A mined ore deposit generally has detailed records of the grade and tonnage of ore mined, but the surface material is rarely described in detail. It may then be necessary to estimate a likely concentration for C_0 from data that are available. Some published case histories provide the results of stream sediment surveys, soil and rock surveys, and core drilling for individual deposits (29, 30, 34-37). Such case studies provide insight into the probable surface conditions at similar deposits in similar geologic terrain. The concentration of a residual soil anomaly depends on the geochemical traits of the metal in question as well as local soil and climate characteristics. Fast erosion rates usually result in higher concentrations near the surface than slower rates. Strong residual soil anomalies are often present over deposits in tropical climates, even for more mobile elements such as copper, despite the deep weathering encountered (38). The weakest surface anomalies often occur where erosion rates are low and meteoric water infiltrates the ground carrying metals down to a supergene enrichment zone above the main ore stock. Despite these general trends observed in the case studies, each deposit is unique, and care must be taken not to generalize too greatly about probable values for Co without fully investigating all available data on a deposit. Regardless of the geologic setting, the range of concentrations available for C_0 is limited by the ore grade at the high end and the regional background at the low end. Within these bounds, a reasonable estimation or range of estimations must be determined. Fortunately, small variations in Co do not dramatically effect the calculated dispersion train.

Another factor affecting the accuracy of a model fit is the validity of the simplifying assumptions in a particular drainage. One such assumption is that there is a single

source of metal-rich sediment in the drainage. This assumption may not seem representative in some contaminated rivers where the primary source of metals is dispersed tailings deposited on the flood plain downstream from the mineralized zone. However, tailings stored on the flood plain of a river can mimic an upstream point source several decades after mining practices have been altered or mining has ceased. The concentrations of metals stored on the flood plain during periods of aggradation reflect the downstream trend in metals at the time of deposition, since the same principles of downstream dilution applied when tailings were being actively discharged into the river. Cut-bank erosion and groundwater inputs can act as continuing sources of these metals (9, 39), mimicking an upstream point source. Eventually tailings stored on a flood plain are expected to exhaust themselves, but the time scale may be much greater than anticipated. For example, little or no overall change is seen in input over a period of several years in the Clark Fork River, despite it having been several decades since the construction of tailings ponds designed to prevent the downstream transport of metals. Given the quantity of tailings estimated to be stored on the Clark Fork River flood plain (9), a rough estimation is that it would take several thousand years to completely exhaust the metal supply stored on the flood plain at the current rate of sediment transport (40). The metal supply stored on the flood plain is capable of maintaining the currently observed dispersion train the entire time.

Another assumption affecting the accuracy of the model fits is the assumption that the metal chosen for modeling remains conservative within the sediment. Some elements may be geochemically mobile in subsurface environments, but behave conservatively under the geochemical conditions common in surface waters. Conservative elements such as lead are thought to primarily enter stream sediments through physical erosion, while more mobile elements such and copper and zinc usually have a substantial geochemical input as well. Tailings and waste rock deposits often contain geochemical conditions favorable to the release and groundwater transport of more reactive metals, resulting in the precipitation and adsorption of metals onto stream sediments at the groundwater-surface water interface (41, 42). Once precipitated or adsorbed onto stream sediments, many metals, such as lead, copper and zinc, generally behave conservatively under surface water conditions (14, 18, 28, 31). Both lead and copper appeared to remain conservative in the stream sediments modeled. Zinc was noted to be somewhat reactive under surface conditions, but still conservative enough for modeling. Manganese was found to be too reactive for modeling.

The most commonly encountered violation of the assumption that a metal is conservative occurs in streams with acid drainage in their headwaters. In streams with acidic headwaters, significant transport of metals occurs in the solute fraction until the pH is neutralized sufficiently to allow precipitation and adsorption of metals onto the sediment load (43). This usually takes place within the first few kilometers from the source, but the model cannot accurately account for the sediment metal concentrations within the acidic reach (Figure 7a). The model does not allow fractionation between the solute and sediment loads and can break down when there is active feedback between the two, as is the case during neutralization of an acidic stream. The model could be expanded to include pH-based

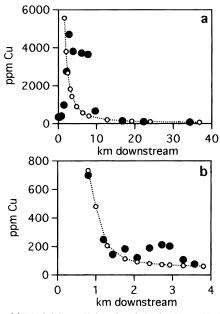


FIGURE 7. (a) Model fit to Fisher Creek in the New World district outside Cooke City, MT. Acid drainage from historic mining was observed in the headwaters of Fisher Creek (55). Streamwater pH as low as 3 was causing significant solute transport of metals resulting in a deviation of the field data from the model calculation. (b) Model fit to a small stream draining a stratabound Cu deposit in the Cabinet Mountain Wilderness, MT (56). Multiple outcrops of the deposit cause secondary anomalies resulting in deviations from the calculated mixing curve.

partitioning of metals between the solute and sediment loads, but the effect of pH on metals partitioning would be specific to each metal as well as to the geochemical environment of the river (44, 45). Accurate quantification of the new variables required would involve detailed investigation of the geochemical processes affecting each metal of interest and would add great complexity in exchange for an increase in accuracy only in acidic reaches.

A less significant violation of the assumption of conservation may occur if river sediments stagnate for several months, allowing the gradual transfer of metals from the sediment to the solute load. The assumption that a metal behaves conservatively is most representative when sediment is actively moving in the main channel and its tributaries. If sampling is carried out after an extended period of low water with little or no sediment transport, the observed dispersion train may be at a lower metal concentration than when sediment is being actively transported. To avoid this type of problem, active channel sediments should be sampled only during or soon after periods of sediment transport.

The opposite effect can result from the formation of hydromorphic anomalies caused by the direct precipitation and adsorption of metals onto stream sediment by enriched groundwater input. This type of anomaly may form in certain stream reaches in mineralized or contaminated areas. If a hydromorphic anomaly forms in active stream sediments, the model will still be applicable, but when hydromorphic anomalies form in stagnant stream sediments with no active mixing or transport, the model may be unable to account for the magnitude of the anomaly. Interference from hydromorphic anomalies can also be minimized by sampling only during or shortly after periods of active sediment transport.

The assumptions of uniform erosion or uniform background can also affect the accuracy of a model fit, but the effects are scale-dependent. In large-scale basins, spatial variability of the erosion rate or background concentration has little influence on the observed concentration of metals in stream sediments because the variations are averaged over a large area. However, in small-scale drainages, spatial variability in the erosion rate and background value may influence the observed concentration of metals in sediments if the scale of observation is such that the spatial variations are significant. Variations in background can be corrected for in the model, but large variations in the erosion rate have the potential to cause deviations from the calculated dispersion train in small-scale drainages.

The assumption of a single source of anomalous sediment may occasionally be violated by secondary anomalies. Secondary anomalies may alter the shape of the dispersion train, especially within the mineralized zone (Figure 7b). Some deposits, particularly stratabound or vein-type deposits, may be made up of several smaller anomalies rather than one large anomaly common in porphyry-type deposits. Multiple anomalies can be modeled starting at the downstream edge of the entire mineralized zone, or if desired, the additional sources can be incorporated into the model as additional terms using the same relative area principles the rest of the model works on. If the secondary source is of much lower magnitude than the primary source, it can often be ignored.

A less commonly encountered physical process capable of causing deviations from the calculated dispersion train may result from attempting to model metals transported in a dense mineral phase. Metals primarily transported in a dense mineral phase, such as tin in the mineral cassiterite, are subject to hydraulic effects that concentrate the mineral in certain stream reaches. Natural sluicing action in high gradient reaches has been shown to concentrate cassiterite to surprisingly high levels far downstream from the source (46, 47). Accordingly, it is important to be aware of the phase a metal is transported in prior to modeling. Modeling difficulties may arise if metals are transported in a dense mineral or elemental phase, such as tin or gold. The best results will be achieved with metals that partition into the fine-grained sediment load, which is commonly the case (28, 31).

Conclusion

The main goal of the dilution mixing model presented here is to accurately approximate natural and exaggerated dispersion trains while maintaining simplicity and global applicability. Testing of the model showed it capable of providing reasonable approximations of natural and exaggerated dispersion trains in a variety of drainages. Model fits in drainages exhibiting no obvious violations of the assumptions were quite acceptable, and even in drainages exhibiting minor violations of the assumptions, model fits were still within reason. The model could be expanded to accommodate more commonly encountered violations of the assumptions, but the resulting model would be complicated and site-specific, which has been avoided in this paper. The model presented here is simple and widely applicable, yet still capable of accurately representing most natural and exaggerated dispersion trains. The ability of the model to provide acceptable fits in a variety of drainages emphasizes the dominance of dilution mixing and anomaly size as the primary variables governing the downstream

dispersion of metal anomalies. The basic concepts of the dilution mixing model are supported by data from a variety of climates (28), making the model an important tool for determining premining dispersion trains and quantifying the impact of mining.

Estimation of premining dispersion trains and quantification of exaggerated anomalies provides useful information relevant to the understanding, litigation, and remediation of contaminated rivers. An idealized premining dispersion train allows realistic remediation goals to be set. Without this type of data there is a risk that unrealistic goals may be implemented. This information also illustrates how mining activities can amplify metal anomalies well beyond their naturally occurring range, extending the environmental impact of increased trace metals far downstream. The model also provides insight into the processes governing the downstream dispersion of metals in stream sediments. This increased understanding of metals dispersion can be used to prioritize contaminated sites and establish realistic remediation goals. Such information is important to the understanding, litigation, remediation, and regulation of metal-contaminated rivers around the world.

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Literature Cited

- (1) Moore, J. N.; Luoma, S. N. Environ. Sci. Technol. 1990, 24, 1279-
- James, L. A. Geomorphology 1991, 4, 125-144.
- Davies, B. E.; Lewis, J. Environ. Pollut. 1974, 6, 49-57
- Horowitz, A. J.; Elrick, K. E.; Callender, E. Chem. Geol. 1988, 67,
- Nimick, D. A. In The Proceedings of the Clark Fork River Symposium; Watson, V., Ed.; University of Montana: Missoula, MT, 1990; pp 194-197.
- Moore, J. N.; Brook, E. J.; Johns, C. A. Environ. Geol. Water. Sci. **1989**, *14*, 107–115.
- Bradley, S. B.; Cox, J. J. Sci. Total Environ. 1986, 50, 103-128.
- James, L. A. Ann. Assoc. Am. Geograph. 1989, 79, 570-592.
- Axtmann, E. V.; Cain, D. J.; Luoma, S. N. In The Proceedings of the Clark Fork River Symposium; Watson, V., Ed.; University of Montana: Missoula, MT, 1990; pp 1–18.
- (10) Runnels, D. D.; Shepherd, T. A.; Angino, E. E. Environ. Sci. Technol. **1992**, 26, 2316-2323.
- (11) Filipek, L. H.; Nordstrom, D. K.; Ficklin, W. H. Environ. Sci. Technol. **1987**, 21, 388–396.
- Eychaner, J. H. U.S. Geological Survey Toxic Substances Hydrology Program; Proceedings of the Technical Meeting, Monterey, CA, 1991.
- (13) Benjamin, M. M.; Leckie, J. O. J. Colloid Interface Sci. 1981, 79,
- (14) Forstner, U. Hydrobiologia 1982, 91, 269-284.
- (15) Davis, J. A.; Leckie, J. O. Environ. Sci. Technol. 1978, 12, 1309-
- (16) Pagenkopf, G. K.; Cameron, D. Water, Air, Soil Pollut. 1979, 11, 429-435.
- (17) Feltz, H. R. In Contaminants and Sediments; Baker, R. A., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; pp 271-279.
- Gibbs, R. J. Science 1973, 180, 71-73.
- Jenne, E. A.; Luoma, S. N. Biological Implications of Metals in the Environment; CONF-750929; NTIS: Springfield, VA, 1977.
- Giddings, J. M. In Environment and Solid Waste, Characterization, Treatment, and Disposal; Francis, C. E., Auerbach, S. I., Eds.; Butterworths: Boston, 1983; pp 245-258.

- (21) Bradshaw, P. M. D. J. Geochem. Explor. 1975, 4, 1-213.
- (22) Lovering, T. G.; McCarthy, J. H. J. Geochem. Explor. 1978, 9, 113 - 276
- (23) Bogoch, R.; Brenner, I. B. J. Geochem. Explor. 1977, 8, 529-535.
- (24) McLaurin, A. N. J. Geochem. Explor. 1978, 10, 295-306.
- (25) Bussey, S. D.; Taufen, P. M.; Suchomel, B. J.; Ward, M. J. Geochem. Explor. 1993, 47, 217-234.
- (26) Hawkes, H. E. J. Geochem. Explor. 1976, 6, 345-358.
- (27) Marcus, W. A. Earth Surf. Proc. 1987, 12, 217–228.
 (28) Meyer, W. T.; Theobald, P. K.; Bloom, H. In Geophysics and Geochemistry in the Search for Metallic Ores; Hood, P. J., Ed.; Geological Survey of Canada: Ontario, 1979; pp 411-434.
- Coolbaugh, D. F. In Geophysics and Geochemistry in the Search for Metallic Ores; Hood, P. J., Ed.; Geological Survey of Canada: Ontario, 1979; pp 721-725.
- (30) Fleming, A. W.; Neale, T. I. J. Geochem. Explor. 1979, 11, 33-51.
- (31) Horowitz, A. J.; Elrick, K. A. Appl. Geochem. 1987, 2, 437–451.
 (32) Chao, T. T.; P K Theobald, J. Econ. Geol. 1976, 71, 1560–1569.
- (33) Hack, J. T. Studies of longitudinal stream profiles in Virginia and Maryland; U.S. Geol. Surv. Prof. Pap. 1957, No. 294-B.
- (34) Leggo, M. D. J. Geochem. Explor. 1977, 8, 431-456.
- (35) Ribeiro, M. J.; Santos, M. M. D.; Bressan, S. R. J. Geochem. Explor. **1979**, *12*, 9–19.
- (36) Friedrich, G.; Herzig, P.; Keyssner, S.; Maliotis, G. J. Geochem. Explor. 1984, 21, 167-174.
- (37) Learned, R. E.; Chao, T. T.; Sanzolone, R. F. J. Geochem. Explor. **1985**, 24, 175-195.
- (38) Mosser, C.; Zeegers, H. J. Geochem. Explor. 1988, 30, 145-166.
- (39) Hermann, R.; Neumann-Mahlkau, P. Sci. Total Environ. 1985,
- (40) Lambing, J. H. Water-quality and transport characteristics of suspended sediment and trace elements in streamflow of the Upper Clark Fork Basin from Galen to Missoula, Montana, 1985– 90. Water-Resour. Invest. (U.S. Geol. Surv.) 1991, No. 91-4139.
- (41) Blowes, D. W.; Jambor, J. L. Appl. Geochem. 1990, 5, 327-346.
- (42) Callender, E.; Kimball, B. A.; Axtmann, E. V. U.S. Geological Survey Toxic Substances Hydrology Program; Proceedings of the Technical Meeting, Monterey, CA, 1991.
- (43) Davis, A.; Olsen, R. L.; Walker, D. R. Appl. Geochem. 1991, 6,
- (44) Smith, K. S.; Ranville, J. F.; Macalady, D. L. U.S. Geological Survey Toxic Substances Hydrology Program; Proceedings of the Technical Meeting, Monterey, CA, 1991.
- (45) Nordstrom, D. K. U.S. Geological Survey Toxic Substance Hydrology Program, Proceedings of the Technical Meeting, Monterey, CA, 1991.
- (46) Yim, W. W. S. Environ. Geol. 1981, 3, 245-256.
- (47) Fletcher, W. K.; Dousset, P. E.; Ismail, Y. B. J. Geochem. Explor. **1987**, 28, 385-408.
- (48) Meyer, C.; Shea, E. P. Jr., In Ore Deposits of the United States, 1933-1967; Ridge, J. D., Ed.; American Institute of Mining, Metallurgical, and Petroleum Engineers: New York, 1968; pp
- (49) McClernan, H. G. Metallic mineral deposits of Lewis and Clark County, Montana; Montana Bureau of Mines and Geology Memoir 52; Bureau of Mines and Geology: Missoula, MT, 1983.
- (50) Moore, J. N.; Luoma, S. N.; Peters, D. Can. J. Fish. Aquat. Sci. 1991, 48, 222-232.
- (51) Pardee, J. T. The Dunkleberg Mining District, Granite County, Montana; U.S. Geol. Surv. Bull. 1917, No. 660-G.
- (52) Johnson, J. Senior Thesis, University of Montana, 1994.
- (53) Goddard, E. N. Manganese deposits at Phillipsburg Granite County, Montana; U.S. Geol. Surv. Bull. 1940, No. 922-G.
- (54) Mohsen, L. A. Doctoral Thesis, Boston University, 1969.
- (55) Eyrich, H. T. Doctoral Thesis, Washington State University, 1969.
- (56) Cazes, D. K. Geochemical analyses of stream sediments and heavy mineral concentrates collected near a stratabound Cu-Ag occurence in the Cabinet Mountains Wilderness, Montana; Open-File Rep. (U.S. Geol. Surv.) 1981, No. 81-665.

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