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Date: April 28, 1995

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

by

Steven O. Helgen

B.A. Carleton College, 1990

presented in partial fulfillment of the requirements

for the degree of

Master of Science

The University of Montana

1995

Approved by:

Chair

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Natural Background Determination and Impact Quantification in Trace Metal Contaminated River Sediments (89 pp.)

Chair: Johnnie N. Moore

A handwritten signature in black ink, appearing to read "J. N. Moore". The signature is fluid and cursive, with the first letters of the first and last names being capitalized and prominent.

Historic and current mining activities have contaminated stream sediments around the world with toxic heavy metals. A historic lack of pre-mining baseline data makes it difficult to quantify the extent of contamination and 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. The model also allows the quantification of the anthropogenic exaggeration of an anomaly. Mining activities were found to amplify naturally occurring metal anomalies up to three orders of magnitude, extending downstream dispersion trains from a natural limit around 20 kilometers to as much as 500 kilometers. The dilution mixing model provides a useful tool for calculating pre-mining dispersion trains and helping to quantify the effects of mining on a river basin. These pieces of information are important to the understanding, litigation, and remediation of contaminated rivers around the world.

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Introduction

Mining activities have left countless streams and rivers contaminated with toxic heavy metals (Davies and Lewis, 1974; Horowitz et al., 1988; Moore and Luoma, 1990; James, 1991). 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 floodplain (Bradley and Cox, 1986; James, 1989; Moore et al., 1989; Nimick, 1990). Long after mining has ceased, or mining practices have been altered, metals stored on the floodplain may continue to enter the stream via cut-bank erosion and groundwater inputs (Axtmann et al., 1990). Metals from waste rock dumps and tailings ponds may also enter the stream through physical erosion and geochemical inputs as well. A lack of sediment baseline data in historic mining districts makes it difficult to quantify the increase in the metal load and set realistic remediation goals. In the absence of any baseline data arbitrarily set remediation goals may be subject to protracted legal debate as some argue that the cleanup goals are too stringent, while others argue they are not stringent enough. There is a need for an accepted method of determining pre-mining conditions in stream sediments in order to set realistic remediation goals and quantify the increased metal load to stream sediments.

Recent work has addressed the problem of determining the natural background geochemistry of water in mined areas (Runnels et al., 1992), but not 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 (Filipek et al., 1987; Eychaner, 1991). At non-acid producing 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 (Benjamin and Leckie, 1981; Forstner, 1982). 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 (Davis and Leckie, 1978; Pagenkopf and Cameron, 1979). From this point on, the problem primarily becomes one of sediment transport, rather than aqueous geochemistry. However, the sediment-bound 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 (Gibbs, 1973; Jenne and Luoma, 1977; Feltz, 1980; Giddings, 1983; Axtmann et al., 1990).

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 both natural and anthropogenic metal anomalies by dilution mixing with un-enriched tributary sediments. This type of modeling allows the calculation the downstream dilution curves, commonly referred to as dispersion trains, observed in stream sediments. 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 kilometers downstream, a fact well documented in the exploration geochemistry literature (Bradshaw, 1975; Bogoch and Brenner, 1977; Lovering and McCarthy, 1978; McLaurin, 1978; Bussey et al., 1993). Exploration geochemists studying dispersion trains first realized that the downstream dispersion of naturally occurring metal anomalies was primarily governed by dilution mixing with tributary sediments.

Exploration geochemists developed an equation to predict the size of an undiscovered anomaly based on an anomalous stream sediment sample. The equation calculates the product of the area and grade of the anomaly based on the concentration of an anomalous sediment sample collected downstream from the anomaly. This equation can easily be reversed and used to calculate the 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 concentration of 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: 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 (Hawkes, 1976; Marcus, 1987):

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

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 of the ore deposit, and C_o is the concentration of the surface anomaly of the ore deposit. This equation and its assumptions have been found to represent the natural dispersion trains of elements such as lead and copper in climates ranging from arid to tropical. This equation has also been used to aid in the interpretation of data from stream sediment surveys conducted for exploration (Meyer et al., 1979).

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. This exaggerated input 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. A new term, referred to as the exaggerated area (A_X), is used to account for the increased quantity of metal-rich sediment entering a stream. The increased sediment input often contains a higher concentration of metal than the natural input because the ore brought to the surface during mining is usually of a higher grade than the overlying surface material (Coolbaugh, 1979; Fleming and Neale, 1979). A second term, referred to as the exaggerated concentration (C_X), is required to account for any increase in metal concentration of the anomalous sediment due to mining. Each of the new terms is distinctive and representative of actual field parameters. When the exaggerated area and exaggerated concentration are considered, equation 1 can be modified as follows to account for metal inputs from mining/milling:

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

Where the new terms A_X and C_X represent the exaggerated area and exaggerated concentration, respectively, of the metal anomaly 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_o , 2) A_X was substituted for A_o in the numerator of 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 in order to account for the increased input of sediment. Mining activities result in an increased sediment load that cannot be explained by uniform erosion of the anomaly and basin. A_X is used to

account for the increased sediment load; A_X represents the area required to generate the increased quantity of anomalous sediment at the erosion rate assumed to apply in the basin. When A_X and C_X are set equal to A_O and C_O , equation 2 reverts to equation 1. With the addition of the terms A_X and C_X , equation 2 can now account for varying amounts of anthropogenic input 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 increasing A_X over three orders of magnitude. As A_X increases the curvature of the dispersion train decreases, but the origin is not altered. On the other hand, as C_X increases the origin moves upward but the lower end of the curve is not altered as dramatically (Figure 3). Holding the product of $A_X C_X$ constant but altering the individual values also results in an alteration of the shape of the mixing curve, a result that may not be immediately apparent from casual observation of equation 2. The downstream portion of the curve remains undisturbed, but the origin rises and falls with C_X (Figure 4). As a result, there will be a unique solution of A_X and C_X that provides the closest approximation of the model to an actual dispersion train.

Figure 1. Visual definition of terms used in equations 1 and 2.

Figure 2. Effects on the dispersion curve of increasing A_x three orders of magnitude.

Figure 3. Effects on the dispersion curve of increasing C_X three orders of magnitude.

Figure 4. Effects on the dispersion curve of holding the product of A_X and C_X constant at 20,000 while varying the individual values.

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 fraction (Chao and Theobald, 1976; Horowitz and Elrick, 1987). Sediment samples were wet sieved in situ through a 63 μm mesh using ambient stream water. Samples were stored on ice and dried immediately upon returning 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) and modeling was performed in a spreadsheet.

The first step in modeling a dispersion train 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_P) can be measured accurately from maps, or an equation can be used to generate area for any desired river kilometer. There is an established relationship between river kilometer and basin area (Figure 5) that has been shown to apply to all drainages, regardless of geologic control (Hack, 1957). The area equation was used to allow greater model flexibility. The area of mineralization (A_O) 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_O and C_X . It may also be possible to measure C_X directly by sampling

tailings deposits or contaminated tributaries within the source. Once the measurable parameters are set, a non-linear least squares routine can be employed to provide the best-fit value for A_X .

Figure 5. Area vs. river kilometer data from the Clark Fork River basin in western Montana, and two small basins in the New World mining district outside Cooke City, Montana. Relationship shown is almost identical to that found to hold true for all types of drainages, regardless of geologic control (Hack, 1957).

Model Application

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 6). Similar results were reported in other studies (Hawkes, 1976; Meyer et al., 1979; Marcus, 1987).

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 7 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 that the model is capable of approximating the dispersion trains of highly disturbed anomalies. After the various model parameters have been determined, the pre-mining dispersion train can be calculated and the exaggeration of the anomaly quantified.

An idealized pre-mining dispersion train can be calculated by setting A_X equal to A_O and C_X equal to C_O . The resulting curve should closely approximate the natural dispersion train of the deposit prior to mining, as shown previously in the model fits to unmined ore deposits. Idealized pre-mining dispersion trains are shown for four contaminated Montana streams and rivers in Figure 8. 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 kilometers downstream, even for the largest ore deposits (Bradshaw, 1975; Bogoch and Brenner, 1977; Lovering and McCarthy, 1978; McLaurin, 1978; Bussey et al., 1993). 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 8A). When the parameters of an anomaly are known both before and after mining it is possible to actually quantify the exaggeration of the anomaly.

There are various ways to conceptualize and quantify the exaggeration of an anomaly, the most obvious being the ratio of the exaggerated anomaly to the natural anomaly. This ratio is referred to as the enrichment factor (E_f) where E_f is defined as follows:

$$E_f = A_x C_x / A_o C_o \quad (3)$$

The enrichment factor is a dimensionless term expressing how many times the natural anomaly the exaggerated anomaly represents. The enrichment factor provides a relative measure of the increase in the metal load to stream sediments. Enrichment factors ranged from 70-1400 for the exaggerated anomalies examined. The exaggeration of copper and zinc anomalies was found to be as much as two orders 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 grade-tonnage term used to describe ore reserves, only two dimensional. The areal

grade (G_O) and exaggerated areal grade (G_X) are defined as the product of the area and concentration of the anomaly before and after mining, respectively. G_O represents the areal grade of an anomaly prior to mining:

$$G_O = A_O C_O \quad (4)$$

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

$$G_X = A_X C_X \quad (5)$$

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 9 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 300-1,500,000 km^2ppm for the disturbed anomalies examined. In contrast, the areal grades for a number of naturally occurring anomalies ranged from only 0.5-11,000 km^2ppm . In three out of the four cases examined, the exaggerated anomalies exceeded the range of naturally occurring anomalies by as much as two orders of magnitude. The areal grades and enrichment factor provide two ways to quantify the impact of mining on stream sediments.

Figure 6. 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, Montana. (B) Model fit to sediment data from a stream draining the Rosemont copper porphyry deposit, Arizona (Hawkes, 1976). (C) Model fit to sediment data from a stream draining the Gamsberg stratiform zinc deposit, South Africa (McLaurin, 1978). (D) Model fit to sediment data from Ivanhoe Creek, draining a small lead prospect in the Anaconda-Pintlar Wilderness, Montana.

Figure 7. 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, Montana with a 125 year mining history (Meyer et al., 1968). Silver Bow Creek, above tailings ponds, $E_f=156$, $G_X=1,556,000 \text{ km}^2\text{ppm Pb}$; Clark Fork River, below tailings ponds, $E_f=70$, $G_X=700,000 \text{ km}^2\text{ppm Pb}$. Values obtained using an estimated A_0 of 33 km^2 and C_0 of 300 ppm Pb . (B) Model fit to the Blackfoot River, Montana, headwaters contain the Heddleston mining district where Ag-Pb-Zn veins were mined in the early 1900s (McClernan, 1983; Moore et al., 1991). $E_f=750$, $G_X=27,600 \text{ km}^2\text{ppm Cu}$. Values obtained using an estimated A_0 of 0.004 km^2 and C_0 of $10,000 \text{ ppm Cu}$. (C) Model fit to Dunkleberg Creek, Montana, draining a limestone hosted Ag-Pb-Zn vein mined from 1884-mid 1900s (Pardee, 1917; Johnson, 1994), $E_f=500$, $G_X=256 \text{ km}^2\text{ppm Pb}$. Values obtained using an estimated A_0 of 0.00003 km^2 and C_0 of $20,000 \text{ ppm Pb}$. (D) Model fit to Flint Creek, Montana. The Phillipsburg mining district, site of extensive Mn vein mining in the early to mid 1900s, lies midway down the drainage (Goddard, 1940; Mohsen, 1969), $E_f=325$, $G_X=233,000 \text{ km}^2\text{ppm Pb}$. Values obtained using an estimated A_0 of 0.026 km^2 and C_0 of $28,000 \text{ ppm Pb}$.

Figure 8. Calculated pre-mining 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, Montana. (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.

Figure 9. Pre-mining areal grades of the surface anomalies of a number of ore deposits showing the range and distribution of natural anomalies (Bradshaw, 1975; Hawkes, 1976; Lovering and McCarthy, 1978; McLaurin, 1978; Coolbaugh, 1979). 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 two orders of magnitude.

Discussion

Estimation of the pre-mining dispersion train and quantification of the exaggerated anomaly are important pieces of information relative to the understanding, litigation, and remediation of contaminated rivers around the world. An idealized pre-mining dispersion train allows realistic remediation goals to be set. Without this type of data there is a risk that unrealistic remediation goals may be implemented. It would be virtually impossible to attain metal concentrations below those of the estimated pre-mining dispersion train. The pre-mining dispersion train also allows the quantification of the exaggerated anomaly resulting from mining. The exaggeration of an anomaly can be quantified using the enrichment factor and the areal grades. Some small deposits may be found to be exaggerated several hundred times but still be well within the range of naturally occurring anomalies, while some large deposits with a long history of mining may be found to far exceed the range of naturally occurring anomalies. This type of information is useful for assigning cleanup priorities and categorizing impacted sites based on the extent of contamination.

The accuracy of the calculated pre-mining 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_t , A_o , and C_b can be measured accurately, but C_o , C_x , and A_x may have varying degrees of uncertainty associated with them. The concentration of the exaggerated anomaly (C_x) can be limited to the range between the highest observed sediment concentration and the grade of the processed ore. Values for C_x may also be found in mining reports that include the grade of tailings, or it may be possible to collect samples directly from tailings deposits. Any chance to

directly sample C_O has usually been obliterated by mining, so an estimation must be relied upon.

The original concentration of the surface anomaly (C_O) 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_O from data that is available. Some published case histories provide the results of stream sediment surveys, soil and rock surveys, and core drilling for individual deposits (Leggo, 1977; Coolbaugh, 1979; Fleming and Neale, 1979; Ribeiro et al., 1979; Friedrich et al., 1984; Learned et al., 1985). 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 (Mosser and Zeegers, 1988). 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 C_O without fully investigating all available data on a deposit. Regardless of the geologic setting, the range of concentrations available for C_O 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 C_0 do not dramatically effect the shape of the calculated dispersion train.

Another factor affecting the accuracy of a model fit is the validity of the model assumptions in a particular drainage. One such assumption is that the metal chosen for modeling remains conservative within the sediment. The reactivity of a metal under surface geochemical conditions determines the validity of this assumption for a particular metal. Less reactive elements such as lead are thought to primarily enter stream sediments through physical erosion, while more mobile elements such as 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 (Blowes and Jambor, 1990; Callender et al., 1991). Once precipitated or adsorbed onto stream sediments many metals, such as lead, copper and zinc, generally behave conservatively under surface water conditions (Gibbs, 1973; Meyer et al., 1979; Forstner, 1982; Horowitz and Elrick, 1987). Both lead and copper appeared to remain conservative in the stream sediments modeled, while 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 of conservation 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 (Davis et al., 1991). 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 10A). The model does not allow fractionation between the solute and sediment loads and is not representative 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 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 (Nordstrom, 1991; Smith et al., 1991). 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 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 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.

Another assumption affecting the accuracy of the model fit 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 floodplain downstream from the mineralized zone. However, tailings stored on the floodplain 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 floodplain 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 (Hermann and Neumann-Mahlkau, 1985; Axtmann et al., 1990), mimicking an upstream point source. Eventually tailings stored on a floodplain 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 metal 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 floodplain (Axtmann et al., 1990), a rough estimation is that it would take several thousand years to completely exhaust the metal supply stored on the floodplain at the current rate of sediment transport (Lambing, 1991). The metal supply stored on the floodplain is capable of maintaining the currently observed dispersion train the entire time.

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 10B). 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 (Yim, 1981; Fletcher et al., 1987). 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 (Meyer et al., 1979; Horowitz and Elrick, 1987).

Figure 10. (A) Model fit to Fisher Creek in the New World district outside Cooke City, Montana. Historic mining of sulfide ore in the headwaters of Fisher Creek (Eyrich, 1969) was observed to be causing acid drainage. Stream water pH as low as three was measured in the headwaters of Fisher Creek. Significant solute transport of metals occurs in the acidic reach causing a deviation of the field data from the model prediction. (B) Model fit to a small stream draining a stratabound Cu deposit in the Cabinet Mountain Wilderness (Cazes, 1981). Multiple outcrops of the deposit cause secondary anomalies resulting in deviations from the calculated mixing curve.

Conclusion

The main goal of the dilution mixing model presented here is the accurate approximation of 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 with no obvious violations of the assumptions were quite acceptable, and even in some of the drainages exhibiting 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 and the model is an important tool for determining pre-mining dispersion trains and quantifying the impact of mining.

Modeling the dispersion trains of metal anomalies before and after mining provides useful information relevant to the understanding, litigation, and remediation of contaminated rivers. The model allows the calculation of an idealized pre-mining dispersion curve, as well as relative and absolute quantification of the exaggerated anomaly resulting from mining activities. This information 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 a greater understanding of the processes affecting the downstream dispersion of metals in stream sediments. This increased understanding along with the pre-mining dispersion curve and quantification of the exaggerated anomaly can be use to prioritize contaminated sites and establish realistic remediation goals. The information provided by the model is relevant to the understanding, litigation, remediation, and regulation of metal contaminated rivers around the world.

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Appendix I. Field Area Descriptions and Maps

A. Senate Mine-Ivanhoe Lake Area

The Senate Mine and Ivanhoe Lake drainages are adjacent tributaries of the Middle Fork of Rock Creek on the border on the Anaconda-Pintlar Wilderness, Montana (Map 1). An overview of the area is given by Elliott and Close (1984). The area is located in the Anaconda Range, which is made up of sedimentary rocks of Proterozoic and Paleozoic age and plutonic igneous rocks of Cretaceous to Tertiary age. Mineral surveys indicate probable resource potential for Ag, Cu, Mo, Pb, W, Sn, Au, and Zn in the region. Surveys were conducted in 1978-80 by the U.S. Bureau of Mines, and in 1980-82 by the U.S. Geological Survey (Welsh et al., 1983; Siems et al., 1982). The Senate Mine area was noted as containing the strongest resource potential. In the Senate Mine area a structurally controlled zone of shearing, quartz veins, and replacement minerals is present. There is sparse sulfide mineralization including chalcopyrite, pyrite, and galena in veins and disseminated in the wall rocks. The mineralization is present in a zone of highly fractured belt rocks that promoted secondary permeability and allowed in ore-bearing fluids.

The Senate Mine produced a small quantity of copper ore from two visible adits. The lower adit is collapsed, but the upper adit is an open narrow tunnel, now flooded. Mine drainage was neutral, and malachite was observed submerged in the pool at the entrance to the adit. Visible copper minerals such as azurite and malachite were common on the surface around the mine, and copper values as high as 20,000 ppm have been reported in the vicinity. Lead values as high as 20,000 ppm have been reported in the adjacent Ivanhoe Lake drainage (Welsh et al., 1983). Senate Mine Creek was sampled August 12-13, 1993.

B. New World Mining District

The New World mining district is located outside of Cooke City, Montana between Yellowstone National Park and the Absaroka-Beartooth Wilderness. Overviews of the district are given by Lovering (1929) and Eyrich (1969). Prospecting and small-scale mining began in the 1870's with sporadic attempts at mining and smelting continuing until 1934, when the McLaren Gold Mines Company started continuous production from 1934 to 1953. The district produced approximately 370,000 tons of ore, principally gold and copper, worth a total of \$4,000,000. The bulk of production was processed at the McLaren mill at Cooke City. Plans for further large-scale gold and copper mining continue today. Natural and anthropogenic acid drainage and erosion of enriched sediments form strong metal anomalies in the Miller Creek, Fisher Creek, and Little Daisy Creek drainages (Maps 2-6). Iron oxidation from the weathering of the deposit is visible in the red coloring of Fisher Mountain.

Of these three drainages, the headwaters of Miller Creek were observed as being the least disturbed, but the drainage did contain a small remediated tailings pile on the outskirts of Cooke City (Maps 2,3). Above town, the Miller Creek drainage showed very little evidence of mining impact, and the pH of the stream was above 7. A few natural looking acidic iron-stained seeps were noted on the banks in the mineralized zone. In the town of Cooke City, the stream has been re-routed around a tailings pile from one of the old mills. The tailings pile had received recent remedial work, and did not seem to be providing additional sediment into the stream. Iron oxide coatings on stream cobbles below the tailings site suggested a possible groundwater input of metal to the creek. Field data revealed no increase in metal levels below the tailings pile, and it is thought to currently have little impact on the drainage.

The headwaters of Fisher Creek were observed to contain tailings piles and an abandoned pit mine (Maps 4,5). Fisher Creek was observed originating from a tailings pile at a pH of three. A large deep red platform of iron oxy-hydroxides had formed where the acidic water emanated from the tailings and bright orange to red coatings covered all the cobbles for the first few kilometers of the stream. Remedial activities were observed in the headwaters of Fisher Creek during the sampling period of September 20-21, 1993. Some of the Fisher Creek drainage showed scars from the Yellowstone forest fires of 1988. Fisher and Miller Creeks were sampled September 20-21, 1993.

The headwaters of Little Daisy Creek were also impacted by historic mining activities (Map 6). The very top of the drainage showed little sign of disruption, but just a few hundred meters downstream a tributary draining a large disturbed slope entered. On the day Little Daisy Creek was sampled (Sept. 20, 1993) the slope was undergoing remedial work by bulldozer, and a light snow melt was causing Little Daisy Creek to run a milky orange. The pH of the Creek below the orange input was near three, and it took two miles to reach neutral. Cobbles in Little Daisy Creek were also covered with orange coatings, and the coatings were still present, but not as thick, two miles downstream. Little Daisy Creek was sampled September 20, 1993.

New World District, Miller Creek Field Map 2

Cooke City, Montana-Wyoming Quadrangle
 7.5 minute series (topographic)
 U.S. Geological Survey
 Sampled Sept. 20-21, 1993

New World District, Miller Creek Field Map 3

New World District, Fisher Creek Field Map 4

Cooke City, Montana-Wyoming Quadrangle
7.5 minute series (topographic)
U.S. Geological Survey
Sampled Sept. 20-21, 1993

New World District, Fisher Creek Field Map 5

Absaroka-Beartooth Wilderness Custer,
Gallatin, and Shoshone National Forests
Montana and Wyoming Principal
and Sixth Principal Meridians
U.S. Forest Service, 1988
Sampled Sept. 20-21, 1993

New World District, Little Daisy Creek Field Map 6

1 km

North

Cooke City, Montana-Wyoming Quadrangle
7.5 minute series (topographic)
U.S. Geological Survey
Sampled Sept. 20, 1993

C. Flint Creek-Phillipsburg Mining District

The Phillipsburg Mining District is located on the west slope of the Flint Creek Range, Montana. Descriptions of the mining district are provided by Goddard (1940) and Mohsen (1969). The district covers 20 square kilometers containing silver and manganese vein deposits. The limestone-hosted manganese deposits are limited to a 5 square kilometer area east of the town of Phillipsburg. A low arch of Paleozoic limestone was truncated and deformed on the east and south edge by the Phillipsburg Batholith. Hydrothermal alteration along vein fissures produced irregular and tabular bodies of manganese ore in the limestone bordering the steeply dipping silver and zinc veins to the north. Silver mining began in the district in 1864, but manganese was not mined extensively until World War I. As of 1940, 477,000 tons of high grade ore had been produced. The manganese ore contained from 30-43% Mn which was refined in the mills at Phillipsburg to 70% MnO_2 prior to shipping. Two mills were operating at near capacity in Phillipsburg in 1939. Over 40 mines have been reported in the district, and tailings in the basin were reported to average 20% Mn. Tailings stored on the floodplain continue to supply Flint Creek with a substantial quantity of trace metals, far in excess of its natural load.

Flint Creek was sampled October 3, 1993 from upstream of Phillipsburg to the confluence with the Clark Fork River (Map 7). The number of sample locations was limited by accessibility. Outwardly, Flint Creek did not seem particularly impacted by mining. The floodplain was noted to be covered with vegetation, and aside from some placer tailings in some of the tributaries, no obvious sources of metals were observed.

Flint Creek Field Map 7

10 km

North

Butte, Montana 1:250,000 NL 12-4
 Western United States
 U.S. Geological Survey, 1977
 Sampled Oct. 3, 1993

Appendix II. Models of Unmined Deposits

A. Ivanhoe Lake Model

The Ivanhoe lake drainage contains a prospect with reported values of 20,000 ppm Pb. Sediment samples were collected from the outflow of the lake to the confluence with the Middle Fork of Rock Creek, and a few miles downstream. The lead concentration increased down the Ivanhoe lake drainage to a maximum at the edge of a claim on the Wilderness Area boundary (Map 1). The high-gradient drainage contained virtually no fine-grained sediment, and samples were collected in the anomalous reach by squeezing sediment out of moss growing in the stream. Lead levels were so high (>5%) as to make modeling the anomaly impossible using the standard assumptions. In order to match the high concentration of lead in the anomalous sediment sample, the entire basin upstream would have to contain >5% lead. If such numbers are entered into the model, the resulting anomaly is so large that the rapid dilution rate observed can not be matched. It is suspected that the anomaly is of hydromorphic origin and is not the result of sediment erosion and mixing as assumed in the model.

There is still a well defined dispersion train downstream from the anomaly that can be modeled if it is assumed that there is no dilution of the anomaly due to the area of drainage upstream of the anomaly, which may be a reasonable assumption given the sediment-starved nature of the drainage (Model 1). If the actual area above the anomaly is included, the amount of dilution makes it impossible to reach the high concentration of lead found in the anomalous sediment midway down the small drainage. A model fit including upstream dilution was also included (Model 2).

Model 1

Anaconda-Pintlars Ivanhoe lake Pb Model, no dilution above anomaly

kilometer	Sed Pb	Sed Mn	km	At	Model Pb
0.05	65	1130	0.6	0.00	58149
0.05	81	1005	0.90	0.17	235
0.10	171	3639	1.10	0.39	128
0.22	1684	3288	1.90	1.86	62
0.60	58000	9916	3.00	5.13	51
0.90	207	1249	5.10	14.57	47
1.10	97	753			
1.90	79	390			
3.00	81	862			
5.10	47	565	Ao	Co	Cb
5.10	46	451	0.000425	75000	45

Model 2

Anaconda-Pintlars Ivanhoe lake Pb Model, dilution from above anomaly

kilometer	Sed Pb	Sed Mn	km	At	Model Pb
0.05	65	1130	0.6	0.50	108
0.05	81	1005	0.90	0.99	77
0.10	171	3639	1.10	1.39	68
0.22	1684	3288	1.90	3.45	54
0.60	58000	9916	3.00	7.38	49
0.90	207	1249	5.10	17.89	47
1.10	97	753			
1.90	79	390			
3.00	81	862			
5.10	47	565	Ao	Co	Cb
5.10	46	451	0.000425	75000	45

B. Miller Creek Model

The copper and lead stream sediment anomalies in Miller creek were modeled successfully; no exaggeration of the anomaly was necessary to match the field sediment data (Models 3,4). The area above the starting model point was used for the area of mineralization, and the concentration of the peak sediment sample used for the anomaly grade. Tributary samples established a range of values for basin background, and good model fits were achieved using values from within the range. The small tailings pile at Cooke City seemed to push the start of the dispersion train downstream a kilometer, but otherwise had no noticeable effect on the dispersion train.

Model 3 New World District Miller Creek Cu

Sample Name	Cu	Pb	Mile	Mile	At	Model Cu
NWSB1	47	46		3.00	4.00	1100
NWCC1	38	44		3.02	4.50	982
NWPC1	33	26		3.35	5.98	748
NWSC1	40	25		3.50	6.43	697
NWM2	262	252	0.80	4.00	8.04	565
NWM3	265	249	1.00	4.00	8.04	565
NWM4	380	257	1.20	6.00	15.86	304
NWM1	921	252	1.43	10.00	37.31	149
NWM5	834	260	1.78	15.00	73.57	93
NWM5D	816	255	1.78	20.00	119.11	71
NWM6	1084	268	2.38	25.00	173.07	60
NWM7	821	264	3.03			
NWSB2	752	203	3.53			
NWSB3	61	38	6.03			
NWSB4	69	44	8.23			
NWSB5	67	40	14.53	Ao	Co	Cb
NWSB6	63	33	22.08	4.00	1100.00	35

Model 4 New World District Miller Creek Pb

Sample Name	Cu	Pb	Mile	Mile	At	Model Cu
NWSB1	47	46		3.00	4.00	265
NWCC1	38	44		3.02	4.50	238
NWPC1	33	26		3.35	5.98	186
NWSC1	40	25		3.50	6.43	174
NWM2	262	252	0.80	4.00	8.04	144
NWM3	265	249	1.00	4.00	8.04	144
NWM4	380	257	1.20	6.00	15.86	86
NWM1	921	252	1.43	10.00	37.31	51
NWM5	834	260	1.78	15.00	73.57	38
NWM5D	816	255	1.78	20.00	119.11	33
NWM6	1084	268	2.38	25.00	173.07	31
NWM7	821	264	3.03			
NWSB2	752	203	3.53			
NWSB3	61	38	6.03			
NWSB4	69	44	8.23			
NWSB5	67	40	14.53	Ao	Co	Cb
NWSB6	63	33	22.08	4.00	265	25

C. Models of Literature Data

Data sets for several un-mined ore deposits were located in the exploration literature (Hawkes, 1976; McLaurin, 1978). The Gamsberg deposit, South Africa (Models 5,6), the Rosemont deposit, Arizona (Model 7), the Cerro Colorado deposit, Panama (Model 8), and the Casino deposit, Yukon (Model 9) were all modeled using the values for area and grade provided in the literature. Acceptable fits were obtained for the Gamsberg, Rosemont, and Cerro Colorado deposits, and a marginal fit obtained for the Casino deposit. The Casino data set consisted of only four points, of which the first and last were matched; it is unknown if a better fit would be achieved using a more complete data set, or if there is an unknown violation of one of the model assumptions altering the shape of the dispersion train. The close fits of the model to stream sediment data sets from un-mined deposits provides convincing evidence of the validity of the calculated pre-mining dispersion trains for contaminated river systems. The limitation of the accuracy of the predictions relates primarily to the accurate quantification of the area and grade of the deposit prior to mining.

Model 5 Gamsberg, South Africa Pb (McLaurin, 1978)

km	Mile	Sed. Zn	Sed. Pb	Area	Mile	Model Pb
4	2.50	1150	160	9	3.75	145
5	3.13	760	110	10	4.00	133
8	5.00	1025	140	15	5.00	99
8.6	5.38	560	120	20	6.00	79
9.6	6.00	195	70	32	8.00	58
10.8	6.75	215	50	46	10.00	48
11.8	7.38	205	60	63	12.00	41
13	8.13	145	60	81	14.00	37
15.5	9.69	270	60	102	16.00	35
18	11.25	130	40	124	18.00	33
19.7	12.31	155	40	147	20.00	31
33	20.63	75	30	173	22.00	30

Ao **Co** **Cb**
 0.22 5000 24

Model 6 Gamsberg, South Africa Zn (McLaurin, 1978)

km	Mile	Sed. Zn	Sed. Pb	Area	Mile	Model Zn
4	2.50	1150	160	9	3.75	1057
5	3.13	760	110	10	4.00	952
8	5.00	1025	140	15	5.00	664
8.6	5.38	560	120	20	6.00	497
9.6	6.00	195	70	32	8.00	317
10.8	6.75	215	50	46	10.00	226
11.8	7.38	205	60	63	12.00	174
13	8.13	145	60	81	14.00	140
15.5	9.69	270	60	102	16.00	117
18	11.25	130	40	124	18.00	101
19.7	12.31	155	40	147	20.00	88
33	20.63	75	30	173	22.00	79

Ao Co Cb
 0.22 42500 25

Model 7 Rosemont Deposit, Arizona (Hawkes, 1976)
Rosemont $A_o=1$, $Co=2200$, $Cb=17$

km	area	Cu		km	area	Model Cu
26	140	35	A_o	26	140	33
23	136	30	1	23	136	33
22	124	30	Co	22	124	35
16	109	35	2200	16	109	37
15	105	40	Cb	15	105	38
12	83	45	17	12	83	43
10	63	55		10	63	52
7	36	100		7	36	78
6	28	100		6	28	95
3.5	15	95		3.5	15	163
1.5	5.3	450		1.5	5.3	429

Model 8 Cerro Colorado, Panama (Hawkes, 1976)
Cerro Ao=1.5, Co=7500, Cb=115

km	area	Cu		km	area	Model Cu
47	300	160	Ao	47	300	152
6	48	195	1.5	6	48	346
4	45	350	Co	4	45	361
2.5	16.5	650	7500	2.5	16.5	786
1	10.6	1308	Cb	1	10.6	1160
			115

Model 9 Casino, Yukon (Hawkes, 1976)

Casino $A_o=.35$, $C_o=2000$, $C_b=54$

km	area	Sed. Cu
13	80.5	122
10	39.4	306
5	20.2	780
1.6	2.34	1000

	km	area	Model Cu
A_o	13	80.5	81
0.4	10	39.4	109
C_o	5	20.2	162
5500	1.6	2.34	985
C_b			
54

Appendix III. Models of Mined Deposits

A. Silver Bow Creek-Clark Fork River Model

Silver Bow Creek originates in Butte, Montana, home of one of the world's largest copper deposits. The ore deposit at Butte consists of a central zone of copper mineralization surrounded by a much larger zone of silver-lead-zinc veins. Mining began in the late 1800's and continues today. In the early days tailings were discharged directly into Silver Bow Creek, causing aggradation of the floodplain. Improved mining practices have eliminated the direct input of metals, but tailings stored on the floodplain continue to provide a tremendous input of metals to the Clark Fork River.

Silver Bow Creek and the Clark Fork River were modeled in separate sections because the tailings ponds at their confluence alters the slope of the dispersion train. As a result, different values for exaggerated area and concentration were required to fit the dispersion train above and below the tailings ponds. The exaggerated copper, lead and zinc anomalies in the Clark Fork basin were successfully modeled (Models 10-12). The pre-mining metal anomalies were found to be amplified 150 times for lead, 530 times for copper, and 1400 times for zinc. The relative amplification of the various metals seems to relate to the chemical mobility of the metal. Geochemically mobile metals would have been more depleted in the pre-mining anomaly than more stable elements like lead, and would be readily liberated from the tailings stored on the floodplain after mining. It is possible that the exaggerated anomaly required to match the lead anomaly reflects only the physical erosion of floodplain-stored tailings, while the exaggerated anomalies required to represent the copper and zinc anomalies represent a substantial geochemical component in addition to the physical component.

Model 10 Clark Fork River Cu

Mile	Sed. Cu	Pb	Zn	mile	Area	Model Cu			
23.25	8583	1699	8343	18.00	124	11414			
25.35	8638	2170	6630	26.00	228	8322			
27.05	10240	2140	7458	32.00	323	6690			
29.35	10506	1663	8882	35.00	374	6038			
30.05	11502	1792	9556	40.00	468	5140			
30.85	11595	1789	9567	60.00	920	1812			
31.65	11495	1531	10084	80.00	1485	1211			
32.35	8529	1290	9121	100.00	2154	873			
34.35	9396	1255	10612	120.00	2919	665			
34.85	10276	1258	11554	140.00	3775	527			
36.75	7404	1301	8519	160.00	4716	431			
37.75	7308	1165	8575	200.00	6840	309			
40.35	3767	537	5507	250.00	9921	222			
45.95	928	128	1198	300.00	13444	171			
46.69	2298	235	3561						
46.95	1190	183	1667				Ao	Co	Cb
47.45	1067	150	1757				3	2000	25
50.75	1650	196	1839	SBC			Ax	Cx	
51.31	1558	156	2062				160	20000	
52.15	1782	231	1773	CFR			Ax	Cx	
54.05	1462	195	1619				200	10000

Model 11 Clark Fork River Pb

Mile	Cu	Sed. Pb	Zn	mile	Area	Model Pb			
23.25	8583	1699	8343		18	124			2290
25.35	8638	2170	6630		26	228			1651
27.05	10240	2140	7458		32	323			1320
29.35	10506	1663	8882		35	374			1190
30.05	11502	1792	9556		40	468			1011
30.85	11595	1789	9567		60	920			214
31.65	11495	1531	10084		80	1485			157
32.35	8529	1290	9121		100	2154			122
34.35	9396	1255	10612		120	2919			99
34.85	10276	1258	11554		140	3775			83
36.75	7404	1301	8519		160	4716			71
37.75	7308	1165	8575		200	6840			56
40.35	3767	537	5507		250	9921			45
45.95	928	128	1198		300	13444			39
46.69	2298	235	3561						
46.95	1190	183	1667			Ao		Co	
47.45	1067	150	1757			13		300	
50.75	1650	196	1839	SBC		Ax		Cx	
51.31	1558	156	2062			156		3900	
52.15	1782	231	1773	CFR		Ax		Cx	
54.05	1462	195	1619			455		600

Model 12 Clark Fork River Zn

Mile	Cu	Pb	Sed. Zn	mile	Area	Model Zn			
23.25	8583	1699	8343	18.00	124	10992			
25.35	8638	2170	6630	26.00	228	8787			
27.05	10240	2140	7458	32.00	323	7446			
29.35	10506	1663	8882	35.00	374	6871			
30.05	11502	1792	9556	40.00	468	6037			
30.85	11595	1789	9567	60.00	920	2522			
31.65	11495	1531	10084	75.00	1334	2012			
32.35	8529	1290	9121	100.00	2154	1452			
34.35	9396	1255	10612	125.00	3125	1108			
34.85	10276	1258	11554	150.00	4235	883			
36.75	7404	1301	8519	175.00	5475	728			
37.75	7308	1165	8575	200.00	6840	618			
40.35	3767	537	5507	250.00	9921	474			
45.95	928	128	1198	300.00	13444	386			
46.69	2298	235	3561						
46.95	1190	183	1667				Ao	Co	Cb
47.45	1067	150	1757				13	240	125
50.75	1650	196	1839	SBC	Ax			Cx	
51.31	1558	156	2062				300	15000	
52.15	1782	231	1773	CFR	Ax			Cx	
54.05	1462	195	1619				625	6000

B. Blackfoot River Model

The Blackfoot River originates in the Heddleston Mining District, western Montana . The Heddleston District hosted several mines, but the bulk of the production in the area is credited to the Mike Horse Mine. Reserves of the Mike Horse Mine were reported to contained 7.14 percent lead and 5.88 percent zinc (McClernan 1983). Substantial metal anomalies extend downstream from the abandoned mine workings (Moore and Luoma, 1991). Of the various metal dispersion trains, copper, lead, and zinc were chosen for modeling. Excellent model fits were obtained for all three metals (Models 13-15). Pre-mining anomalies were found to be amplified 700 times for copper and zinc, but only 60 times for lead. As in the Clark Fork River, it is suspected that the relative difference in input relates to the chemical mobility of the metals. The headwaters of the Blackfoot receive acid drainage from the abandoned mines (Moore and Luoma, 1991), apparently contributing far more copper and zinc to the river sediments than lead. It is suspected that the lead anomaly reflects physical erosion of mine wastes, while the copper and zinc anomalies reflect substantial geochemical inputs as well.

Model 13 Blackfoot River Cu

Mile	Cu	Pb	Zn	Mile	Area	Mod Cu	Ao	Co	Cb
121.5	29	19	93	125	2122	30	0.0014	10000	25
88.625	29	24	84	90	1552	31	Ax	Cx	
49.5625	35	27	93	50	804	37	1.00	10000	
39.3125	41	20	119	40	606	41			
32.3125	42	29	123	30	410	49			
29.8125	45	29	134	20	224	69			
18.5	42	25	277	15	141	95			
17.8125	86	38	628	10	70	166			
17.375	74	42	1022	8	46	237			
16.375	92	48	918	6	26	391			
14.375	88	49	1520	5	18	546			
12.25	103	55	706	4	11	833			
11.3125	140	132	1771	3	6	1446			
9.8125	137	111	2314	2.5	4	2032			
8.0625	275	214	4398	2	2	3008			
7.8125	322	162	1703	1.75	2	3726			
7	524	684	2881	1.5	1	4650			
5.5625	1405	161	3100	1.45	1	4862			
4.1875	2287	1475	10555						
4	2224	1540	13296						
3.875	1888	2969	8581						
3.5625	428	1156	1677						
3.5	1797	3378	14446						
3.25	2385	3837	10846						
3.125	2811	4406	21159						
2.875	3033	4809	13470						
2.75	4051	4301	31793						
2.0625	5081	3699	51950						
0.75	11570	3095	149448

Model 14 Blackfoot River Pb

Mile	Cu	Pb	Zn	Mile	Area	Mod Pb	Ao	Co	Cb
121.5	29	19	93	125	2122	21	0.0014	71400	18
88.625	29	24	84	90	1552	22	Ax	Cx	
49.5625	35	27	93	50	804	25	0.08	71400	
39.3125	41	20	119	40	606	27			
32.3125	42	29	123	30	410	32			
29.8125	45	29	134	20	224	43			
18.5	42	25	277	15	141	58			
17.8125	86	38	628	10	70	100			
17.375	74	42	1022	8	46	142			
16.375	92	48	918	6	26	235			
14.375	88	49	1520	5	18	331			
12.25	103	55	706	4	11	518			
11.3125	140	132	1771	3	6	954			
9.8125	137	111	2314	2.5	4	1428			
8.0625	275	214	4398	2	2	2374			
7.8125	322	162	1703	1.75	2	3235			
7	524	684	2881	1.5	1	4635			
5.5625	1405	161	3100	1.45	1	5017			
4.1875	2287	1475	10555						
4	2224	1540	13296						
3.875	1888	2969	8581						
3.5625	428	1156	1677						
3.5	1797	3378	14446						
3.25	2385	3837	10846						
3.125	2811	4406	21159						
2.875	3033	4809	13470						
2.75	4051	4301	31793						
2.0625	5081	3699	51950						
0.75	11570	3095	149448

Model 15 Blackfoot River Zn

Mile	Cu	Pb	Zn	Mile	Area	Mod Zn
121.5	29	19	93	125	2122	98
88.625	29	24	84	90	1552	109
49.5625	35	27	93	50	804	145
39.3125	41	20	119	40	606	169
32.3125	42	29	123	30	410	216
29.8125	45	29	134	20	224	337
18.5	42	25	277	15	141	495
17.8125	86	38	628	10	70	928
17.375	74	42	1022	8	46	1365
16.375	92	48	918	6	26	2326
14.375	88	49	1520	5	18	3321
12.25	103	55	706	4	11	5223
11.3125	140	132	1771	3	6	9557
9.8125	137	111	2314	2.5	4	14119
8.0625	275	214	4398	2	2	22755
7.8125	322	162	1703	1.75	2	30129
7	524	684	2881	1.5	1	41240
5.5625	1405	161	3100	1.45	1	44096
4.1875	2287	1475	10555			
4	2224	1540	13296			
3.875	1888	2969	8581			
3.5625	428	1156	1677			
3.5	1797	3378	14446			
3.25	2385	3837	10846			
3.125	2811	4406	21159			
2.875	3033	4809	13470			
2.75	4051	4301	31793			
2.0625	5081	3699	51950			
0.75	11570	3095	149448			

Ao	Co	Cb
0.0014	58800	70
Ax	Cx	
0.30	200000

C. Flint Creek Model

The large lead and zinc anomalies in the sediments of Flint Creek were successfully modeled using enrichment factors of 325 and 400 respectively (Models 16,17). Manganese was found to be too reactive in the sediments to model reliably. The history of mining in many of the tributary drainages originating in the Flint Creek Range required manual calculation of basin background values for lead as various enriched tributaries enter Flint Creek. Background was calculated at each model point by assigning tributary sediment values to the area of the tributary drainage and updating the total average background as each additional tributary entered. This technique provided a better fit than assuming a uniform single background concentration, which is not the case in the Flint Creek Valley. Another observed feature of the model fits is that the peak of the dispersion train in Flint Creek appears to have been rounded off since mining operations ceased. This is attributed to slight exhaustion of the source material since mining operations ceased.

Model 16 Flint Creek Pb

Mile	As	Mn	Sed. Pb	Zn	Cb Pb	Mile	Area	Mod Pb
3.50	25	1644	57	187	110	20	147	712
12.00	307	1299	161	352	100	23	179	597
14.00	456	2499	339	931	95	24	204	533
16.00	408	5119	441	1091	88	28	251	445
17.00	443	4527	518	1291	85	33	331	356
20.00	428	4978	512	1303	70	36	392	299
22.50	508	5336	571	1547				
24.30	531	5136	485	1490				
27.50	462	5416	462	1320				
32.50	367	3612	378	1092				
36.00	224	2562	270	780				
bgd	47	798	280	530		Ao	Co	Cb
bgd	bd	394	23	240		0.01	28000	70
bgd	bd	460	27	67		Ax	Cx	
						3.25	28000

Model 17 Flint Creek Zn

Mile	As	Mn	Pb	Sed. Zn	Cb	Pb	Mile	Area	Model Zn
3.50	25	1644	57	187		50	20.00	147	1913
12.00	307	1299	161	352		87	22.50	179	1614
14.00	456	2499	339	931		87	24.30	204	1447
16.00	408	5119	441	1091		150	27.50	251	1218
17.00	443	4527	518	1291		125	32.50	331	974
20.00	428	4978	512	1303		110	36.00	392	854
22.50	508	5336	571	1547		100			
24.30	531	5136	485	1490		95			
27.50	462	5416	462	1320		88			
32.50	367	3612	378	1092		85			
36.00	224	2562	270	780		70			
bgd	47	798	280	530			Ao	Co	Cb
bgd	bd	394	23	240			0.01	65000	200
bgd	bd	460	27	67			Ax	Cx	
							4	65000

D. Dunkleberg and Douglas Creek Models

The Dunkleberg Creek drainage contains the abandoned workings of the Forest Rose Mine, located in the shale and limestone of the Dunkleberg anticline. About 31,000 cubic yards of waste rock and tailings are present on the site, left over from abandoned silver, lead, and zinc mining in the district. Dunkleberg Creek had been allowed to flow through the tailings, but has recently been re-routed following a breach of tailings containment. Anomalous values for several metals have been reported in the sediments of Dunkleberg Creek (Johnson, 1994); lead was chosen for modeling. In order to successfully model the lead anomaly in Dunkleberg Creek, a high local background value of 625 ppm lead was required in order to explain the two mile level portion of the dispersion train at 625 ppm (Model 18). This is a plausible assumption if the district is host to more lead-zinc veins than the Forest Rose mine exploited. If the high background in the drainage is natural, then the impact from the Forest Rose mine is minimal. If, on the other hand, the level portion of the dispersion train is the result of unknown anthropogenic causes, then the contamination of the basin is more severe.

The Douglas Creek drainage is just over a pass from the Dunkleberg drainage in similar geologic terrain. The ruins of the Wasa Mine mark the very headwaters of Douglas Creek. The creek originates from one of the old adits, then disappears under a small pile of waste rock, re-emerging at the lower end. Anomalous dispersion trains were reported for several metals in the sediments of Douglas creek (Nagorski and Sjostrom, 1994). Copper, lead, and zinc were chosen for modeling (Models 19-21). The zinc and copper anomalies were found to be amplified 4000 and 6000 times, respectively, in contrast to an amplification of the lead anomaly of only 20 times. This marked difference is once again attributed to the chemical mobility of the elements.

Model 18 Dunkleberg Creek-Forest Rose Mine Pb (Johnson,1994)

Mile	Sed. Pb	Mile	Area	Model Pb	Cb Pb
0.01	10361	0.001	0.002	14484	625
0.01	10852	0.005	0.01	7088	625
0.01	11426	0.01	0.02	4502	625
0.10	1403	0.1	0.2	1098	625
0.14	1053	0.2	0.4	864	625
0.17	936	0.4	0.8	745	625
0.26	694	0.6	1.2	705	625
0.71	626	1	2	673	625
1.01	834	2	4	649	625
1.31	631	3	6	516	500
1.61	784	4	8	312	300
1.61	814	5	10	170	160
2.01	726	5.6	11.2	99	90
4.21	254				
3.11	504				
5.21	137				
0.01	12253	Ao	Co	Ax	Cx
0.01	13495	0.00001	20000	0.005	20000
		Cb			
		625

Model 19 Douglas Creek Cu (Nagorski and Sjoström, 1994)

Sed. Cu	Sed. Pb	Sed. Zn	Mile	Mile	Area	Model Cu	Ao
1830	368	14755	0.00	0	0.10	1877	0.0001
1818	246	12762	0.01	0.01	0.11	1836	Co
3461	222	27013	0.03	0.03	0.12	1757	900
1424	190	13946	0.05	0.05	0.13	1681	Ax
987	153	9911	0.06	0.06	0.14	1644	0.2
2076	187	23589	0.08	0.08	0.16	1573	Cx
1795	206	23155	0.11	0.11	0.18	1473	2800
1513	166	22963	0.16	0.16	0.23	1322	Cb
223	77	2335	0.21	0.21	0.27	1190	15
506	95	6844	0.51	0.51	0.63	684	
287	75	3303	0.81	0.81	1.10	443	
293	66	4809	1.31	1.31	2.10	257	
203	53	4128	2.41	2.41	5.11	120	
132	48	2769	2.51	2.51	5.43	114	
85	51	1420	3.21	3.21	7.92	84	
85	48	1570	3.70	3.7	9.87	70	
28	29	384	7.42	7.42	29.83	34

Model 20 Douglas Creek Pb (Nagorski and Sjostrom, 1994)

Sed. Cu	Sed. Pb	Sed. Zn	Mile	Mile	Area	Model Pb	Ao
1830	368	14755	0.00	0	0.10	341	0.0001
1818	246	12762	0.01	0.01	0.11	322	Co
3461	222	27013	0.03	0.03	0.12	291	15000
1424	190	13946	0.05	0.05	0.13	264	Ax
987	153	9911	0.06	0.06	0.14	253	0.002
2076	187	23589	0.08	0.08	0.16	233	Cx
1795	206	23155	0.11	0.11	0.18	207	15000
1513	166	22963	0.16	0.16	0.23	176	Cb
223	77	2335	0.21	0.21	0.27	153	45
506	95	6844	0.51	0.51	0.63	92	
287	75	3303	0.81	0.81	1.10	72	
293	66	4809	1.31	1.31	2.10	59	
203	53	4128	2.41	2.41	5.11	51	
132	48	2769	2.51	2.51	5.43	51	
85	51	1420	3.21	3.21	7.92	49	
85	48	1570	3.70	3.7	9.87	48	Cb
28	29	384	7.42	7.42	29.83	31	30

Model 21 Douglas Creek Zn (Nagorski and Sjostrom, 1994)

Sed. Cu	Sed. Pb	Sed. Zn	Mile	Mile	Area	Model Zn	Ao
1830	368	14755	0.00	0	0.10	19254	0.0001
1818	246	12762	0.01	0.01	0.11	19000	Co
3461	222	27013	0.03	0.03	0.12	18494	22300
1424	190	13946	0.05	0.05	0.13	17991	Ax
987	153	9911	0.06	0.06	0.14	17742	0.4
2076	187	23589	0.08	0.08	0.16	17248	Cx
1795	206	23155	0.11	0.11	0.18	16524	24000
1513	166	22963	0.16	0.16	0.23	15367	Cb
223	77	2335	0.21	0.21	0.27	14284	100
506	95	6844	0.51	0.51	0.63	9356	
287	75	3303	0.81	0.81	1.10	6465	
293	66	4809	1.31	1.31	2.10	3927	
203	53	4128	2.41	2.41	5.11	1836	
132	48	2769	2.51	2.51	5.43	1740	
85	51	1420	3.21	3.21	7.92	1250	
85	48	1570	3.70	3.7	9.87	1031	
28	29	384	7.42	7.42	29.83	416

E. Fisher and Little Daisy Creek Models

The acid drainage in the headwaters of Fisher Creek displaces the anomaly downstream. Metals are carried in solution until the pH nears neutral, causing the precipitation and adsorption of the metals onto the stream sediments. The copper and lead anomalies in Fisher Creek were modeled, but required some exaggeration of the estimated anomaly in order to match the downstream portion of the stream sediment data (Models 22, 23). The model was not able to account for the observed sediment metal concentrations within the acidic reach due to downstream displacement of the anomaly by the acid drainage.

Little Daisy Creek was too acidic in the reach sampled to be successfully modeled, but provides an interesting look at the effects of pH on sediment metal concentrations. An attempt was made to model the copper and lead anomalies in the drainage with little success. The acidity of the sampled stream reach made it impossible to accurately model the copper dispersion train (Model 24). Better results were achieved by modeling the downstream portion of the lead anomaly, which partitions into the sediment at a lower pH than copper. An acceptable fit was achieved to the sample points where the pH was >4.9 (Model 25). The Little Daisy drainage illustrates the problems resulting from the violation of the assumption of conservation caused by acidic stream water.

Model 22 New World District Fisher Creek Cu

sample	mile	Sed. Cu	pb	pH	mile	Area	Model Cu
NWF1	0.65	355	155	3.46	1	1.00	4823
NWF2	0.85	336	148	3.42	1.5	1.97	3021
NWF3	1.15	402	159	3.74	2	3.17	2065
NWF4	1.55	981	166	5	2.5	4.61	1507
NWF5	2	2758	179	5.7	3	6.24	1155
NWF6	2.35	4705	178	6.35	4	10.08	752
NWF7	2.9	3815	167	6.57	6	19.81	410
NWF8	4.3	3726	159	7.1	10	46.42	198
NWCFY5	5.35	3662	157	>7	15	91.23	118
NWCFY4	6.45	677	83	>7	20	147.36	87
NWCFY3	11.65	146	28	>7			
NWCFY2	15.35	108	32	>7	Ao	Co	Cb
NWCFY1	23	81	26	>7	0.5	2000	35
					Ax	Cx	
					1.1	7000

Model 23 New World District Fisher Creek Pb

sample	mile	Cu	Sed. Pb	pH	mile	Area	Model Pb
NWF1	0.65	355	155	3.46	1	1.00	204
NWF2	0.85	336	148	3.42	1.5	1.97	154
NWF3	1.15	402	159	3.74	2	3.17	120
NWF4	1.55	981	166	5	2.5	4.61	97
NWF5	2	2758	179	5.7	3	6.24	81
NWF6	2.35	4705	178	6.35	4	10.08	61
NWF7	2.9	3815	167	6.57	6	19.81	43
NWF8	4.3	3726	159	7.1	10	46.42	32
NWCFY5	5.35	3662	157	>7	17	112.40	26
NWCFY4	6.45	677	83	>7	25	213.75	24
NWCFY3	11.65	146	28	>7			
NWCFY2	15.35	108	32	>7	Ao	Co	Cb
NWCFY1	23	81	26	>7	0.5	250	22
					Ax	Cx	
					2	250

Model 24 New World Little Daisy Cu

sample	mile	Sed. Cu	Pb	pH	Mile	At	Model Cu
NWLD1	0.1	600	682	7.37	0.5	0.31	5912
NWLD2	0.12		334	3.26	0.75	0.62	4557
NWLD3	0.2	1360	369	3.43	1	1.00	3544
NWLD4	0.36	1610	354	3.58	1.5	1.97	2273
NWLD5	0.73	1588	349	3.5	2	3.17	1574
NWLD6	1.18	598	681	4.89	2.5	4.61	1159
NWLD8	1.78	5752	314	5.31			
NWLD9	2.18	4245	296	7.62			
					Ao	Co	Cb
					0.3	2000	35
					Ax	Cx	
					1	6000

Model 25 New World Little Daisy Pb

sample	mile	Cu	Sed. Pb	pH	Mile	At	Model Pb
NWLD1	0.1	600	682	7.37	1.2	1.36	702
NWLD2	0.12		334	3.26	1.3	1.55	618
NWLD3	0.2	1360	369	3.43	1.5	1.97	494
NWLD4	0.36	1610	354	3.58	1.75	2.54	389
NWLD5	0.73	1588	349	3.5	2	3.17	317
NWLD6	1.18	598	681	4.89	2.25	3.86	266
NWLD8	1.78	5752	314	5.31			
NWLD9	2.18	4245	296	7.62			
					Ao	Co	Cb
					1.36	300	30
					Ax	Cx	
					1.36	700

F. Senate Mine Model

The copper anomaly in the Senate mine drainage was chosen for modeling. The copper dispersion train from the old adit proved to be insignificant, despite a disturbed area of approximately 2500 square meters present on the hillside above the mine. The impact from the old mine seems to be limited to the immediate vicinity of the mine, but an apparently natural copper anomaly was found extending further down the drainage. The extent of mineralization in the drainage is apparently much greater than that exploited by the Senate mine, which would explain the signs of recent exploration activity observed in the drainage.

Modeling was started at the downstream edge of the anomaly, and a good fit to the stream sediment data was achieved (Model 26). No exaggeration of the anomaly was required to match the field data. The anomaly present in the Senate mine drainage was found to have little influence downstream; background values were reached almost immediately below the confluence with the Middle Fork of Rock Creek.

Model 26 Anaconda-Pintlars Senate Mine Cu
Senate Mine

kilometer	Sed. Cu	Sed. Zn
0.30	23	60
0.30	25	56
0.55	21666	422
0.60	173	76
0.62	273	74
0.64	324	76
0.67	139	96
0.73	163	104
0.90	242	115
1.25	289	127
2.15	215	135
2.15	213	114
2.30	56	99
3.40	50	96
5.50	32	65
5.50	33	67

Model Data

Mod km	Area	Model Cu
2.1	1.13	225
2.2	10.82	50
2.5	12.28	48
3	14.88	45
4	20.65	41
5	27.16	38
5.6	31.40	37
Ao	Co	Cb
1	250	30

Appendix IV. Complete Methods

A. Field Methods-Sediment Collection

Samples of fine-grained active channel sediments were used for modeling. The samples were collected from the top 1-2 centimeters of recently deposited sediment using a plastic scoop. Small scoops of sediment were collected from as many locations as could be found along a 25-50 meter reach of a river. In smaller streams the sampling density was much higher and samples were collected from as many locations as could be found in a 10-20 meter reach. In smaller, high-gradient streams it was often difficult to locate fine-grained sediment, and samples may have been collected from deposits found in eddies, under rocks, amongst the roots of aquatic vegetation, or wherever fine-grained sediment in contact with stream water could be located. The sediment was wet-sieved through a 63 μm synthetic sieve mounted in a large plastic funnel housing. The sediment from various points in a stream reach was homogenized and stirred until enough sediment and stream water had passed through the sieve to fill a 250 ml widemouth HDPE bottle (Nalgene®). The bottles were then placed on ice in a cooler as soon as practical after collection. The samples were returned to the lab and centrifuged at 1800-2000 rpm for 15 minutes. The excess liquid was decanted and the bottles placed in a drying oven set at 70 degrees C. After the samples were dried, they were ground in the original sample bottle using an acid-washed glass rod. The ground sediment was then transferred into a polystyrene vial for storage using a sheet of weighing paper. Samples were stored in a desiccator until they could be digested.

B. Lab Methods-Sediment Digestion

- 1) Dried, ground sediment samples were weighed into tared, serially numbered, 120 ml Teflon digestion vessels (Savillex Corp. #578) in batches of seven. Large chunks of clay (>1mm) not powdered during grinding were avoided. Target sample weight was 0.5 grams; actual weight was recorded to ten-thousandths of a gram.
- 2) After seven samples had been weighed, 0.5 ml of Milli-q water was added to each sample. Samples selected for spiking received 0.1 ml of spike, and 0.4 ml Milli-q water. Vessels were swirled and tapped to evenly wet the sediment. All samples were then allowed to sit loosely covered for a period of 30 minutes.
- 3) 3.75 ml of trace metal grade hydrochloric acid and 1.25 ml of trace metal grade nitric acid were then added to each digestion vessel. Vessels were swirled and tapped to break up any lumps that formed after addition of the acids. Caps were threaded on, but not tightened.
- 4) After a one hour pre-digestion period, vessel caps on the first batch of seven were tightened using the plastic wrenches supplied by the manufacturer. Pressure relief tops were then carefully tightened. Pressure tops were tightened about 1/4 turn after initial contact was made. The pressure tops were tightened by hand, care being taken not to over or under-tighten them. If the pressure top felt like it was seating smoothly on the cap base, it was tightened snugly. Interference from the ribs on the vessel cap was remedied by trimming the tops off the ribs with a razor blade. If the pressure top did seat properly, sample venting could occur during digestion.

5) A batch of seven vessels was then placed in a plastic cake keeper. Vent tubes for each vessel were inserted into the pressure caps and the free ends immersed in vials containing a weak indicator solution (5 drops 0.5M NaOH in 250 ml H₂O with several drops phenolphthalein added). The vials were placed in a beaker half full on water in the center of the cake keeper. The indicator vials were used to detect sample venting from the individual digestion vessels. Samples also vented through the threads of the vessel cap, causing all the indicator solutions to lighten, but not turn clear completely. Duplicate samples were used to determine what level of sample venting was acceptable.

6) The sealed cake-keeper with vessels and indicator vials inside was placed on a microwave turntable carefully centered in the microwave oven. Four 250 ml plastic bottles filled with cold tap water were placed in the four corners of the microwave. The turntable was started and the samples were microwaved on high power (~570 watts) for a period of six minutes.

7) Venting during microwave digestion resulted in a chlorine smell in the vicinity of the oven. During severe venting fumes could get quite strong and care was taken to limit exposure. When the oven cycle was complete, the cake keeper was taken directly to a fume hood. Ideally, the oven should have been operated in a fume hood. The cake keeper was never opened outside a fume hood. After removing the top of the cake keeper, indicator vials were examined to determine which samples, if any vented. Notes were made immediately because all solutions could turn clear in a few moments if one of the vessels had vented severely. Sealed vessels were allowed to cool for a period of at least 15 minutes.

8) Pressure tops on the cooled vessels were carefully opened IN A FUME HOOD with the pressure release opening pointed INTO the hood. Vessels that had vented did not display a sudden release of pressure. Vessel caps were then loosened with the wrenches and the contents transferred to numbered, pre-weighed (minus cap) 50 ml centrifuge tubes. Quantitative transfer was achieved by at least three rinses of the vessel and cap with Milli-q water. Care was taken not to use too much water in the earlier rinses in order to prevent overfilling the centrifuge tube.

9) Centrifuge tubes were then brought to a target solution weight of 50 grams using Milli-q water. Centrifuge tubes were supported on the balance in a tared Styrofoam block. Actual weights were recorded on a data sheet next to the empty vial weights to allow later calculation of digest weight.

10) Centrifuge tubes were tightly capped and centrifuged for 5 minutes at 2500 rpm to clarify the digest.

11) Clarified digests were transferred into 60 ml polyethylene storage bottles marked with the complete original sample name for later analysis.

C. Modeling Methods

Modeling was performed on a Apple Macintosh computer using Microsoft Excel version 4.0. Spreadsheets were prepared that contained field data broken down by river kilometer and sediment metal concentration. Desired river kilometers for modeling were entered in a column, then the equation used to calculate total basin area was pasted down alongside. Equation 2 was then pasted in to calculate the metal concentration for each particular river kilometer. Single cells containing the values for original anomaly area and concentration, exaggerated area and concentration, and basin background were hard-linked into equation 2. A plot of model points and field data vs. river kilometer was hot-linked to the spreadsheet and sized to allow alteration of the variables and instantaneous visual feedback of the results on one screen. This arrangement allowed easy visual calibration of the exaggerated area to the field data. Once the model parameters were visually calibrated, A best-fit A_x was obtained using a non-linear least squares fit in the program Mathcad®.

Appendix V. Field Data

Quality Control/Quality Assurance on analytical technique

Table 1. Standard recovery

	Al	As	Cd	Cu	Fe	Mg	Mn	Ni	Pb	Zn
USGS SED2:	5530	159	8.09	1188	22000	4370	1573	10.30	154	1626
	5630	160	8.39	1225	20300	4410	1584	10.20	161	1656
	5880	139	7.80	1196	19900	4520	1530	9.10	154	1517
	5940	137	8.60	1165	21600	4650	1530	9.90	158	1591
	6080	150	8.51	1214	22000	4830	1596	10.70	163	1627
	6040	150	8.58	1210	22100	4810	1600	10.50	164	1631
	6105	161	10	1283	21178	4613	1548	11	170	1688
Mean:	5886	151	8.61	1212	21297	4600	1566	10.22	161	1619
StDev:	225	10	0.81	37	884	180	30	0.59	6	54
USGS reported:	8800	144	8.3	1100	22800	5200	1500	10.8	149	1500
Std recovery:	67%	105%	104%	110%	93%	88%	104%	95%	108%	108%

Table 2. Duplicate sediment samples

	Al	As	Cd	Cu	Fe	Mg	Mn	Ni	Pb	Zn
Dupe recovery:	103%		87%	97%	117%	97%	113%	123%	111%	112%
	88%	108%	83%	86%	93%	92%	91%	102%	86%	88%
	92%	95%	98%	96%	92%	94%	96%	89%	96%	96%
	111%	105%	136%	103%	111%	104%	106%	122%	110%	105%
	117%	112%	104%	105%	111%	111%	105%	109%	106%	103%
	101%		112%	104%	104%	112%	104%	110%	104%	105%
	95%		98%	102%	105%	102%	103%	96%	102%	103%
	100%	102%	101%	99%	99%	100%	101%	105%	101%	102%
	111%	93%	98%	102%	112%	107%	100%	101%	103%	101%
	95%	101%	86%	98%	101%	99%	100%	101%		100%
	103%		121%	100%	102%	103%	101%	98%	103%	101%
	92%	107%	97%	97%	90%	94%	99%	101%	98%	98%
	120%	122%	97%	105%	116%	112%	104%	114%	105%	102%
Mean:	102%	105%	101%	100%	104%	102%	102%	106%	102%	101%
St Dev:	10%	9%	15%	5%	9%	7%	5%	10%	7%	5%

Table 3. Spike recovery from contaminated sediments*

	As	Cd	Cu	Pb	Zn
Spike Rec.:	90%	96%	98%	100%	80%
	113%	114%	103%	110%	159%
	90%	113%	57%	102%	78%
	116%	136%	36%	144%	365%
	15%	113%	34%	106%	68%
Mean:	85%	111%	73%	110%	143%
St Dev:	41%	14%	33%	18%	126%

*-Low spike recoveries due to spiked amount being less than 10% of sample concentration.

Table 4. Spike recovery from background sediments

	105%	103%	85%	111%	113%
		93%	110%	103%	110%
Mean:	105%	98%	97%	107%	111%

Field data from the Senate Mine-Ivanhoe Lake Area

Table 5A. Senate Mine

Sample Name	kilometer	Al	Cd	Cu	Fe	Mn	Ni	Pb	Zn
APSM1X	0.30	5836	0.42	23	19720	1185	7	34	60
APSM1Y	0.30	4481	0.59	25	19461	1377	6	41	56
APSM2	0.55	4195	1.16	21666	79896	6595	48	226	422
APSM3X	0.60	12648	0.80	173	17266	1288	9	58	76
APSM3Y	0.62	6836	0.65	273	14192	822	9	47	74
APSM4	0.64	4913	0.82	324	12432	692	9	46	76
APSM5	0.67	8717	0.67	139	13964	612	10	58	96
APSM6	0.73	8065	0.80	163	17110	1137	10	71	104
APSM7	0.90	7382	1.06	242	16161	1516	15	71	115
APSM8	1.25	7250	1.05	289	14041	1836	12	67	127
APSM9X	2.15	8497	0.84	215	16893	1885	14	61	135
APSM9Y	2.15	8660	0.73	213	16902	2718	13	57	114
APMFR1	2.30	17379	0.29	56	28865	390	17	79	99
APMFR2	3.40	10475	0.48	50	22247	862	15	81	96
APMFR3X	5.50	11180	0.38	32	18067	565	12	47	65
APMFR3Y	5.50	12339	0.44	33	16979	451	12	46	67

Table 5B. Ivanhoe Lake

Sample Name	kilometer	Al	Cd	Cu	Fe	Mn	Ni	Pb	Zn
APIL1X	0.05	8160	0.69	77	20850	1130	6	65	45
APIL1Y	0.05	9201	0.86	81	16320	1005	9	81	60
APIL2X	0.10	10367	1.81	142	21730	3639	18	171	129
APIL3X	0.22	7196	1.20	102	21648	3288	19	1684	109
APIL4X	0.60	5250	0.69	308	75952	9916	26	58000	189
APIL6	0.90	7442	0.88	270	17235	1249	17	207	119
APIL7	1.10	11931	0.53	43	21255	753	15	97	105
APMFR1	1.90	17379	0.29	56	28865	390	17	79	99
APMFR2	3.00	10475	0.48	50	22247	862	15	81	96
APMFR3X	5.10	11180	0.38	32	18067	565	12	47	65
APMFR3Y	5.10	12339	0.44	33	16979	451	12	46	67
APIL5	upstream	12224	0.68	47	20641	911	15	64	98

Table 6. New World Mining District Field Data

Sample Name	Al	Cd	Cu	Fe	Mg	Mn	Ni	Pb	Zn
NWCC1	19496	1.80	38	32591	4539	2589	26	44	81
NWCFY1	10304	0.51	81	33413	24410	723	78	26	87
NWCFY1Spike	10882	2.34	135	35022	24634	741	80	76	140
NWCFY2	12974	0.56	108	44112	28443	859	100	32	104
NWCFY3	11463	0.51	146	38576	29107	870	101	28	107
NWCFY4	15179	1.43	677	39404	13671	1799	64	83	224
NWCFY5	16229	2.44	3662	59006	2444	1561	58	157	656
NWF1	5864	0.05	355	92522	1313	201	7	155	78
NWF2	4484	0.19	336	94837	731	185	5	148	68
NWF3	7129	0.23	402	102549	1762	244	9	159	89
NWF4	13516	0.42	981	80602	1213	268	7	166	88
NWF5	16617	0.60	2758	83884	1552	306	10	179	141
NWF6	20842	0.86	4705	79860	1653	436	16	178	252
NWF7	18411	1.11	3815	71843	3552	508	29	167	313
NWF8	14897	1.95	3726	66287	2240	1301	43	159	552
NWLD1	8816	2.28	600	67928	2816	1675	33	682	528
NWLD2	9258				2871	199	7	334	
NWLD3	8773	0.75	1360	170863	2868	181	9	369	194
NWLD4	9877	1.07	1610	161991	3536	257	10	354	227
NWLD5	10605	1.11	1588	144697	3756	318	12	349	239
NWLD5Dupe	10609	1.00	1545	141113	3393	308	11	337	229
NWLD6	8982	2.28	598	64555	2947	1665	34	681	528
NWLD7	6558	0.72	203	33739	2615	733	23	126	202
NWLD8	21582	3.46	5752	109415	4527	893	35	314	638
NWLD9	19338	2.35	4245	96291	5762	523	25	296	547
NWM1	8935	1.49	921	40162	3897	930	36	252	365
NWM2	10083	1.35	262	42308	4587	999	27	252	396
NWM3	10458	1.33	265	41431	4897	1008	29	249	397
NWM4	11010	1.39	380	43344	5068	1078	33	257	408
NWM5	11774	1.61	834	46997	5697	1029	41	260	431
NWM5Dupe	12336	1.63	816	44667	5561	996	42	255	417
NWM6	12442	1.96	1084	51375	6733	1068	51	268	526
NWM7	12460	1.58	821	57416	7456	963	38	264	381
NWPC1	12310	0.27	33	29023	23119	517	77	26	58
NWSB1	12025	0.54	47	40250	25243	764	70	46	114
NWSB2	9270	3.42	752	143000	6280	2776	52	203	537
NWSB3	17565	0.57	61	42715	39920	974	131	38	91
NWSB4	12232	0.54	69	39081	26054	781	88	44	111
NWSB5	10745	0.63	67	36453	26009	714	77	40	101
NWSB6	10553	0.27	63	32964	20402	667	63	33	82
NWSC1	14724	0.38	40	36759	35356	682	148	25	64

Table 7. Flint Creek sediment data (collected 10/3&29/94)

Sample Name	Al	As	Cd	Cu	Fe	Mg	Mn	Ni	Pb	Zn
FC1 10/3/93	8223	25	1	52	16722	5872	1644	11	57	187
FC10 10/29	8318	443	2	134	14115	4910	4527	7	518	1291
FC11 10/29	8318	428	2	136	14418	5243	4978	7	512	1303
FC2	7794	307	bd	41	12495	3620	1299	7	161	352
FC3	7093	456	1	85	12086	4230	2499	6	339	931
FC4	7752	508	2	147	14086	5544	5336	8	571	1547
FC5	5680	531	2	170	12037	5651	5136	6	485	1490
FC6	6043	462	2	117	12266	5228	5416	6	462	1320
FC6DUP	5401	438	1	112	11002	5011	5089	5	417	1252
FC7	7344	367	2	101	13278	5209	3612	8	378	1092
FC8	7025	224	2	81	12043	4988	2562	8	270	780
FC910/29	8435	408	2	116	14076	4715	5119	7	441	1091
FCB1	7606	47	3	180	19457	17394	798	13	280	530
FCBLANK	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
FCD1	7639	bd	3	20	11966	3919	394	13	23	240
FCG1	8049	bd	1	14	11957	5114	460	10	27	67