# Distinguishing natural from man-caused trace element contamination using causal inferential methods for Ecoepidemiologists

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## ABSTRACT

*Although a number of studies have attempted to separate natural from man-caused loading, there is no reliable technique to clearly distinguish these two sources of trace element contamination in soil, water and sediments. In the absence of empirical methods to partition metal loading between background and mining sources, inferential methods for epidemiologists can be used to test whether the relationship between mining and environmental contamination is causal. The objective of this study was to characterise the biogeochemistry of water and sediments in the Methow River valley on the eastern slopes of the north Cascade Mountains in Washington State (U.S.A) and test the hypothesis that a causal relationship exists between trace element contamination and the presence of mining activities using causal epidemiological criteria. Ore deposits in the area were mined for gold silver copper and zinc until the early 1950's. A variety of mineralogical and analytical methods were used including scanning electron microscopy coupled to an energy dispersive system, microprobe analysis, sequential chemical extraction and the spectrophotometric measurement of trace element concentrations. The epidemiological criteria used to establish a cause-effect relationship were (1) coherence [i.e., the cause-effect hypothesis should not conflict with generally known facts and theory], (2) strength of association [i.e., what was degree or size of an effect when exposed to a cause], (3) time order [i.e., did cause precede effect in time], (4) specificity [i.e., does cause lead to only one effect or is effect caused only by one cause], and (5) consistency on replication [i.e., has the association been repeatedly observed by different persons, in different places, circumstances, and times]. Epidemiological criteria support the hypothesis that contamination of sediments in the Methow River by Cd, Cu, Mn and Pb is caused by the release and dispersion of acid rock drainage from the abandoned Alder Mine, Red Shirt Mill and Alder Mill.*

**KEY WORDS:** mine waste contamination; cause-and-effect; inferential methods; epidemiology

## INTRODUCTION

Abandoned hardrock mines have the potential to cause considerable environmental damage due to acid rock drainage (ARD) discharged from mine adits, mine waste and mill tailings piles, long after the cessation of mining activities. While individual mines are typically in operation for only 5 to 15 years, contamination can occur for hundreds or even thousands of years following the cessation of mining (Carpenter 1924, Davis et al. 2000, Palanques et al. 1995).

Near the Methow River in Washington State (U.S.A.) the contamination of a domestic drinking water well by arsenic was reported by Spencer (1986). It was later revealed that there are carcinogenic risks exceeding 1-in-77 associated with the exposure of residents, living near the abandoned Alder Mine, Red Shirt Mill and Alder Mill, to As in drinking water (Peplow 2003). Additional non-carcinogenic risks of toxicity were also associated with exposure to As, Pb, and Se. Other potential targets related to groundwater exposure pathways were documented and a potentially affected population, estimated to be between 1000 and 1287 residents, was identified within a 6.5 km (4 mi) radius of the mill.

There is also concern that aquatic invertebrates and endangered fish in the Methow River could be influenced by contamination from the abandoned Alder Mine, Red Shirt Mill and Alder Mill. High levels of metals, however, can also occur naturally in groundwater, streamwater and sediments and a number of studies have attempted to separate natural from man-caused loading (Nimick and von Guerard 1998). Isotopes and tracers have been used to try to identify natural sources and loading caused by leaching from unmined ore bodies. However, to date there has been no reliable technique developed to clearly separate them (Dissmeyer 2000).

In epidemiology, inferential methods are used to make comparisons within a geographic area and identify a causal effect by its coincidence, when it occurs beyond the bounds of chance (Susser 1986, Somers 1987). The routine application of inferential methods to ecologic studies in epidemiology suggests similar methods could be used to determine whether mines near the Methow River cause trace metal contamination. Susser (1986) and Fox (1991) suggested five epidemiological criteria be used to establish a cause-effect relationship: (1) coherence [i.e., the cause-effect hypothesis should not conflict with generally known facts and theory], (2) strength of association [i.e., what was degree or size of an effect when exposed to a cause], (3) time order [i.e., did cause precede effect in time], (4) specificity [i.e., does cause lead to only one effect or is effect caused only by one cause], and (5) consistency on replication [i.e., has the association been repeatedly observed by different persons, in different places, circumstances, and times]. The objective of this study was to apply epidemiological criteria to biogeochemical results and test the hypothesis that a causal relationship exists between the presence of abandoned mines and trace element contamination in the Methow River.

## METHODS

## SITE DESCRIPTION

## LOCATION

Study sites were located in the Methow River basin near the town of Twisp in Okanogan County, Washington (Fig. 1). The Methow River basin is located in north central Washington east of the Cascade mountains and is bordered by Canada on the north. Draining nearly 4,662 $km^2$ , the Methow River flows southward through western Okanogan County and empties into the Columbia River at km 843 near the town of Pateros (Andonaegui 2000). Three abandoned mine and mill sites are located south of Twisp near the Methow River: Alder Mill, Alder Mine, and Red Shirt Mine (Fig. 1).

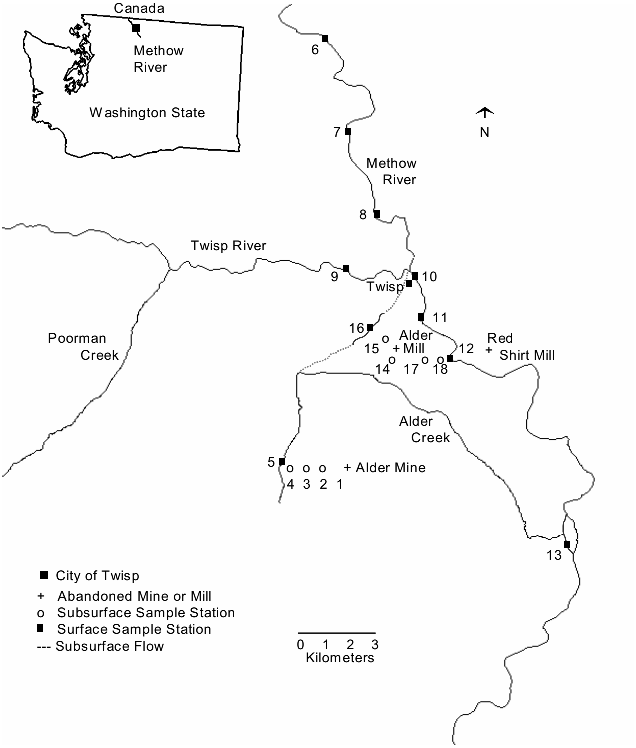

*Figure 1. Map showing study area, abandoned mine and mill sites, and sample stations.*

## ALDER MILL

The Alder Mill (48°.21’.13.5”N, 120°.07’.31.6”W, elev. 575 m) is located approximately 1.6 km south of Twisp (Fig. 1) and approximately 500 m west of the Methow River at river mile (RM) 39.5 (63.4 km from the confluence of the Methow and Columbia rivers). The Mill consists of several buildings and two tailings impoundments. The impoundments contain approximately 55,845 $m^3$ of material. Inputs and springs supplied by Alder Creek feed the upper impoundment creating a contaminated wetlands environment. Private residences with groundwater wells are located adjacent to the site (Figure 3). The pH of the groundwater in the tailings impoundment was <3.0 + 0.4.

## ALDER MINE

The Alder Mine (48°.19’.24.1”N, 120°.09’.38.4”W, elev. 1043 m) is an inactive mine located approximately 4.8 km southwest of Twisp (Fig. 1). The site consists of an open adit on the north, an adit retention pond, an open pit, and waste rock dumps. The site is on the north slope of a north-trending ridge. Slopes at the site range from 50-80%. Estimates from aerial photographs indicate that waste rock covers approximately 3.2 ha. The flow rate of drainage from the Alder Mine adit ranges from 5-15 L min$^{-1}$. The pH of ARD discharged at station 1 was 2.9 ± 0.2.

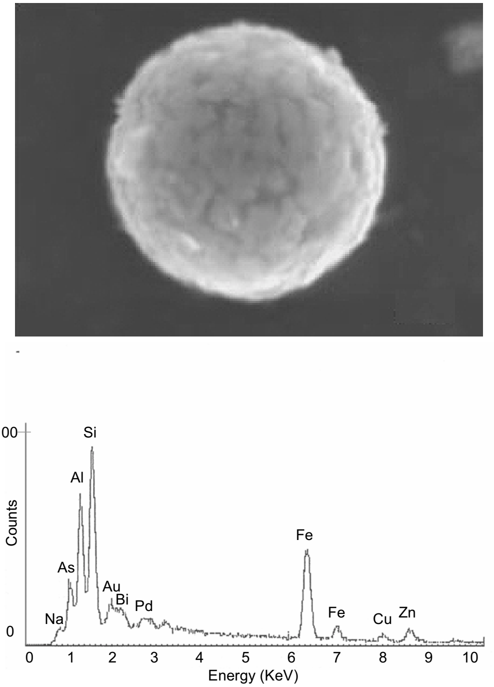

*Figure 2. Scanning electron micrograph and EDS spectrum showing results of X-ray analysis of sample of tailings from Alder Mill. The framboidal sphere is approximately 10 µm in diameter, was frrom a sample of tailings from the Alder Mill and is composed of Fe-oxides, and contains Zn, As, and Cu.*

## RED SHIRT MILL

The Red Shirt Mill (48°.21’.05.0”N, 120°.06’.08.1”W, elev. 487 m) is located approximately 1.6 km southeast of Twisp (Fig. 1) and east of the Methow River at RM 39.5 (63.4 km from the confluence of the Methow and Columbia rivers). The mill consists of a single building and a tailings pile. The tailings pile is estimated to cover approximately 4,650 $m^2$ of surface area and contains less than 30,600 $m^3$ of material. Approximately 4 $m^3$ of tailings are recruited annually by the Methow River. The site is located adjacent to the Twisp city limits and residences, with private groundwater wells, are located on and adjacent to the site.

## TOPOGRAPHY, SOILS, CLIMATE, HYDROLOGY AND VEGETATION

Topography within the Methow River basin ranges from mountainous terrain along the Cascade Crest to a gently sloping, wide valley found along the middle reaches. Elevation ranges from 2600 m in the headwaters of the basin to approximately 240 m at the confluence of the Methow and Columbia Rivers (Andonaegui 2000). Soils in the valley consist of sandy loams that are underlain by alluvium and glacial outwash with very high permeability (Waitt 1972). The major groundwater aquifers of the Methow Valley exist in layers of unconsolidated sediments underlain by bedrock. Groundwater occurrence, movement and availability are primarily related to recharge sources and the configuration of depositional sediments.

The climate in the Methow Valley is within the Cascade Mountain rain shadow. Mean annual precipitation ranges from 25 to 38 cm and the mean annual temperature is below 10°C. Precipitation is seasonal with roughly two-thirds occurring between October and March. Summers are generally hot and are characterized by extended dry periods. Precipitation increases in the fall and generally peaks in the winter with most precipitation in the basin occurring as snow between December and February. Since most of the precipitation occurs as snow, the seasonal distribution of runoff is strongly affected by snow storage.

Flows in the Methow River exhibit a strong peak during spring and early summer with roughly 60 percent of the mean annual discharge occurring during May and June. Streamflow remains relatively high during July, but decreases substantially from August through October in response to a reduced snowpack, low precipitation, and decreased soil moisture. Streamflow in the Methow River at Pateros generally reaches an annual low during late September and early October, with some sections going subsurface during dry years. Winter flows typically remain low in response to low autumn precipitation and freezing winter temperatures. Runoff between years is also highly variable. Maximum and minimum flows for the Methow River at Twisp was 40,800 cfs (May 1948) and 134 cfs (September 1926), respectively.

Vegetation at the site is characterized by Douglas-fir (*Pseudotsuga menziesii*) and ponderosa pine (*Pinus ponderosa)*, which dominate the overstory. Pinegrass (*Calamagrostis rubescens*) dominates the understory to the extent that other species are inconspicuous. Shrubs are normally a minor component of the stand. Soil texture is sandy loam to sand and the parent material is granitic rock. Soils are spodosols. Slope position is mid to lower one-third at approximately 30% with a western aspect.

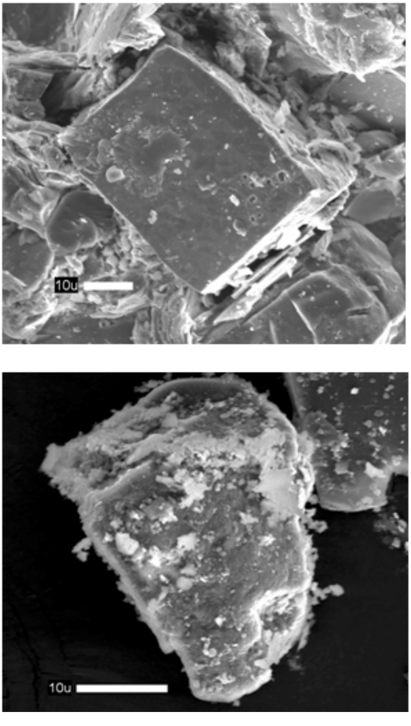

*Figure 3. Scanning electron micrographs of pyrite in quartz showing little evidence of weathering (above) and pyrite particle with rounded corners, pitting and amorphous iron oxide coatings in tailings from Alder Mill (below).*

## RESIDENT FISH IN THE METHOW RIVER

The stream and rivers in the area are utilized by resident trout and salmon for habitat and spawning. Endangered and threatened species of juvenile salmonids, including bull trout, steelhead, and chinook salmon, use the Methow River and Alder Creek as rearing habitat. Spring Chinook, Summer Chinook, Steelhead/Rainbow and Bull trout have been found to occur in the Methow River between stations 6 and 13 (Fig. 1) and at station 13 a survey conducted by direct underwater observation (snorkeling) identified native steelhead/rainbow trout and Chinook salmon (Peplow 1998).

## GEOLOGY OF ORE DEPOSITS AT ALDER MINE

The massive sulfide ore deposits at the Alder Mine are composed largely of chemically precipitated silica in a 4.6-22.9 m wide zone of Cretaceous-Jurassic plutonic (intrusive) igneous stock (granite) in the Newby Group of volcanic rocks (Barksdale 1975). The Newby Group was intruded by the Alder Creek stock, which has been dated at 137 + 3 m.y. (Burnet 1976, Bunning 1990). Ore minerals were deposited possibly during the emplacement of the Alder stock (Barksdale 1975). Carbonate rocks are found in the drainage basin and the streams and rivers are thus hardwater in nature. There is extensive faulting and calcite-filled fractures in the area where the abandoned mine sites in this study are located. Alkalinity of the Methow River is 103 + 14 mg $L^{-1}$and the pH is 7.2 ± 0.5, which is typical of a system dominated by bicarbonate (Stumm and Morgan 1996).

## CAUSAL INFERENCE

A causal relationship between the presence of mining activities at the Alder Mine, Alder Mill and Red Shirt Mill sites and the accumulation of trace elements in groundwater and sediments is apparent when the results in this study were evaluated using the five epidemiological criteria recommended by Susser (1986) and Fox (1991): (1) coherence [i.e., does the cause-effect hypothesis conflict with existing knowledge or theory]. Coherence contains three elements: theoretical (and factual) fit, biological fit, and statistical fit (Susser 1986), (2) strength of association [i.e., what is the degree or size of an effect when exposed to a cause], (3) time order [i.e., does cause precede effect in time], (4) specificity [i.e., is effect caused by only one cause], and (5) consistency on replication [i.e., has the association been repeatedly observed by different persons, in different places, circumstances, and times].

## COHERENCE WITH THEORY

Findings that are plausible in terms of pre-existing theory support the causal hypothesis whereas inchoherence is indeterminate because there might be another explanation (Susser 1986). It is generally accepted that interactions between the atmosphere, hydrosphere and lithosphere are responsible for the mobilization and transport of mineral elements from ore deposits and processing wastes in the environment (Zajic 1969, Plumlee 1999). Findings that are in coherence with this theory are affirming (Susser 1986). The causal hypothesis will be supported if there is evidence of pyrite weathering and ARD dispersion and the deposition of trace elements in Methow River sediments.

## COHERENCE WITH BIOLOGY

The requirement that sediment metal deposition is in coherence with existing knowledge of biological systems will be evaluated in terms of the bacterial processes that affect the mobilization, transport and deposition of trace elements in mine waste environments.

## COHERENCE WITH STATISTICS

Monotonic relationships between cause and effect signal coherence and any response proportional to dose is strongly persuasive of a causal relationship. In this study, the evidence of a causal relationship will be based on whether gradients of sulfate concentration exist between the site of trace metal contamination in the Methow River and a source of metal sulfide oxidation at Alder Mill. The correlation of sulfate concentration with distance from the presumed source at station 14 northeast to the Methow River through stations 15, 16, and station 10 and southeast through stations 17, 18 and 12 was evaluated by regression analysis of log-transformed data using Minitab statistical software (version 9).

## STRENGTH OF ASSOCIATION

In epidemiology, the most common measure of strength of association is relative risk. In this study, ratios that compare trace element concentrations to ecotoxicological benchmarks (Hull and Suter 1994), referred to as concentration factors (CF), were used as indicators of relative risk. It was assumed that the stronger the relative risk for an element associated with abandoned mines the more likely the relationship is causal (Susser 1986).

## TIME ORDER

If the cause precedes outcome then causality is indeterminate, but if the order of the cause and the outcome is reversed, then it becomes a decisive criterion for rejection. Temporal changes in metal deposition in Alder Creek sediments below the Alder Mine were determined by taking a stream sediment core from an undisturbed depositional pool near station 13 (Fig. 1) following the method described by Church (1993). The concentrations of Cu was determined by ICP-AES and normalized to Al concentrations and plotted as a function of depth to correct for the decreasing concentrations of organic matter with depth and time then plotted as a function of depth.

## SPECIFICITY

To evaluate specificity, the range of metals in ARD, tailings water, groundwater and sediments was compared to the estimated ranges for the same elements at other natural and mine impacted sites. Ideally, an effect would have only one cause. Specificity in the cause of a given effect would support the causal hypothesis but its absence would not detract (Susser 1986).

The mean chemical compositions of AMD from 62 adits from eight deposit types and the composition of water from 12 natural seeps, reported by Plumlee et al. (1999), were used to estimate concentrations at unmined and mine impacted sites for comparison to ARD and tailings water concentrations from Alder Mine and Alder Mill. Ground water affected by open-pit mining reported by Plumlee et al. (1999) was used as a reference for Alder Mill groundwater data. Background values for sediment metal concentrations were based on the 90th percentile values from a USGS data base containing 292 data points for the “Methow 4” topographic quadrant (Boleneus and Chase 1999). The 90th percentile was estimated using the computer software program MTCAStat.

## CONSISTENCY

Past studies have shown that drainage compositions vary as a function of deposit geology, climate, mining method used, and mineral processing method used (Plumlee 1999). It has also been shown that the composition of ARD varies predictably within mines and across districts (Waitt et al. 1980, Wildeman et al., 1974). However, no systematic examination of ARD compositions from mines with similar deposit types and ore types within a deposit type has been found and it is not possible to predict the exact composition of water that will develop in a particular mine. Because of these limitations, consistency was not determined and will be considered indeterminate with regards to the causal hypothesis.

## SAMPLING AND ANALYSIS

Mineralogy and weathering in the Alder Mill tailings impoundment was determined by sampling a 3 m core from station 14 at 25 cm intervals (14 samples). Samples were analyzed using scanning electron microscopy and an energy dispersive system (SEM-EDS). The relative proportion of hornblende, as well as the surface etching features on pyrite, were used to determine the weathering of minerals under acidic soil conditions (Lang 2000). A polyvinyl chloride (PVC) monitoring well was installed to the saturated zone of the tailings impoundment at station 16 in October 2000 and water from the saturated zone of the tailings impoundment was sampled monthly between October and December 2000 for metals. Trace metal and As concentrations were determined by ICP-AES and HG-AFS, respectively.

In order to characterize ARD from Alder Mine adit at station 1 (Fig. 1), samples were collected once monthly from May to December 2001 and analyzed for metals by inductively coupled plasma-atomic emission spectrophotometry (ICP-AES). Tailings water from Alder Mine waste rock at station 1 was characterized by collecting three samples of leachate using zero-tension lysimeters. The lysimeters were constructed from 3.5 x 90-cm PVC pipe with 0.625-cm holes drilled in a longitudinal row at the bottom 50-cm of the lysimeter. Three lysimeters were installed in August 2000 along a vertical transect near the center of the three largest waste piles at Alder Mine. The lysimeters were installed using a steel drive-point with an outside diameter equal to the inside diameter of the PVC. One end of the drive-point had a cap used to drive the lysimeter into the mine waste pile. The end of the drive point extended 5-cm and was tapered to a point. When completely inserted the drive-point was removed leaving the lysimeter in place with the holes oriented upwards. The lysimeters were also inserted so they sloped out at an angle of 2° and were capped to retain ARD. One sample of ARD from each lysimeter was collected as soon as the site was accessible following snowmelt in the spring (April 2001), by removing the PVC cap and collecting the leachate in a water sample container.

Sodium chloride (NaCl) injections and geogenic sulfate ($SO_4$) were used to budget the ARD entering Alder Creek at station 5 (Fig. 1). In this study, chloride was injected at Station 1 and sulfate, produced geogenically from sulfide mineral oxidation, was used to indicate ARD contamination. Both chloride and sulfate were assumed to be conservative with respect to adsorption (Stream Solute Workshop 1990). This assumption suggests that the sulfate to chloride ratio would remain constant unless additional inputs of $SO_4$ in groundwater contaminated by additional inputs of ARD, would occur causing the sulfate to Cl ratio to increase.

Solute was injected into the ARD discharge stream at Station 1. ARD flow was diverted to a 227 L plastic reservoir containing 68 kg NaCl, which was dissolved to a final concentration of 300 g $L^{-1}$ (180 g Cl $L^{-1}$). Samples were taken from hand driven 3.8 cm (1.5 inch) PVC wells driven to the bedrock at stations 2 and 3 (Figure 1) and from a similar well 1m deep at the end of the subsurface ARD flow path, 3 m prior to its confluence with Alder Creek (Station 4). Groundwater samples were collected once hourly for 12 hours then again at 24 hours. Groundwater samples were refrigerated and analyzed for $SO_4$ and Cl by ion chromatography (IC). Chloride transport was also monitored using *in situ* electrical conductivity readings. Sulfate concentration was also measured at 22 sites along the Methow River above station 10, the Twisp River, Poorman Creek and their triputaires to estimate area sulfate background concentrations as well as at stations 10, 12, and 14-17 to determine whether sulfate gradients exist between Alder Mine and the Methow River.

Mineralogy and trace element contamination in Methow River was determined by comparing trace element concentrations in sediments below the mines (Fig. 1, stations 10-13, n=40) to results for sediments above the mine (Fig. 1, stations 6 -9, n=16). Sediment samples were collected using plastic scoops at a shallow depth (<5 cm) and immediately wet sieved in ambient water through a 63µm sieve. Samples were dried to constant weight at 90°C.

## GENERAL ANALYTICAL METHODS

Samples of water and sediment were analyzed at the University of Washington, College of Forest Resources Analytical Laboratory in Seattle, Washington. Dissolved metal concentrations (0.45µm filtered) were determined by ICP atomic emission spectrophotometry (ICP-AES; Thermo Jarrell Ash ICAP 61E, EPA Method 3050). Ion chromatography (Dionex DX120) was used for the analysis of sulfate and chloride. Samples were analyzed for As by Hydride Generated Atomic Fluorescence Spectrophotometry (HG-AFS) (Corns et al., 1993). A Piccolo Model HI 1295 temperature compensated digital pH meter was used to measure pH. Standardization was performed daily before and after use.

The mineralogy of tailings and sediments were determined by treating samples with hydrogen peroxide to remove organic matter. A subsample was treated with citrate buffer and sodium dithionite to remove iron oxides. The sand fraction was removed using a 270-mesh (63µm) sieve. Particle size separation by sedimentation was employed to remove the clay fraction. Oriented clay mounts from samples with organic matter and oxides removed were analyzed by XRD. Clay mounts of samples with only the organic matter removed were analyzed by IR. Samples of silt with only the organic matter removed were analyzed by SEM, EDS and microprobe. The relative proportion of hornblende, as well as the surface etching features, were used to determine the weathering of heavy minerals under acidic soil conditions (Lang 2000).

XRD analyses of sediment samples were performed using a Scintag model XGEN-4000 with Scintag software (DMSNT, version 1996) that includes the ICPD international database. A Jeol TSM-330-A scanning electron microscope that includes SQ/SSQ software was used for scanning electron imaging (SEI) and EDS. Microprobe analysis was performed on a Jeol model 733 with Geller Automation EDS software. IR analysis was performed using a Perkin Elmer 1600 Series FTIR model spectrophotometer. XRD analyses was performed at the U.S. Environmental Protection laboratory at Manchester**,** Washington. All other analyses were performed in the analytical laboratory at the College of Forest Resources, University of Washington, Seattle, Washington.

The sequential extraction procedure used was a modified version of the Tessier et al. (1979) method. Sequential chemical extractions were performed on 1 g samples using 40 g of the following six solutions and conditions: (1) 0.1 M $Ca(NO_3)_2$ + 0.05 M $AgNO_3$ for 16 h (exchangeable), (2) 1M NaCHCOO at pH 5 for 5 h (carbonates), (3) 0.1 M $NH_2)OH•HCl$ + 0.1M $HNO_3$ for 30 min (Mn oxides), (4) 0.1M $Na_4P_2O_7$ for 24 h (organics), (5) 0.4M $NH_2OH•HCl$ in 25% v/v $CH_3COOH$ and mix periodically for 6 h in a boiling water-bath (Fe oxides), and (6) concentrated $HNO_3/HClO_4$ using the method for total (residual).

Solutions were centrifuged at about 4000 x g for 20 min and decanted. Samples were washed with 40 g of 0.025 M $Ca(NO_3)_2$ for 5 min after extracting fractions 1 to 5. Washings were discarded.

## DATA ANALYIS

Metal concentrations in Methow River sediments were presented as the mean. The students t-Test was used to compare the mean concentrations of metals above and below Twisp. Differences were considered significant at $p<0.05$. The concentrations of metals in sediments were compared to ecotoxicological benchmarks derived from primary literature by Hull and Suter (1994) for the exposure of benthic organisms to sediments.

## RESULTS

### COHERENCE WITH THEORY

Weathering, transport and deposition of trace metals was studied to determine whether the production of ARD and the mobilization and transport of mineral elements from ore deposits and processing wastes was occurring.

### WEATHERING

Quartz and pyrite were the most common minerals in tailings samples analyzed by energy dispersive x-ray analysis (microprobe). The minerals encountered at trace levels were epidote, chlorite, and tephra. Primary minerals such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and galena (PbS) were not detected. Framboidal spheres of Si, Al and Fe containing As, Cu, and Zn were observed suggesting these elements probably occur in tailings as secondary colloidal minerals or inorganic crystals with amorphous coatings (Fig. 2). Banding and overgrowth of Fe-oxides on quartz and pyrite was extensive indicating that oxidation and reprecipitation had occurred and FeS had been leached out of the pyrite and redeposited as amorphous hydrous iron.

Operations at the Red Shirt and Alder Mills reduced pyrite-containing ore to particles <50µm in diameter. SEM analysis of ore and tailings particles showed evidence of increased weathering in mill waste samples compared to particles from the interior of ore samples that were shielded from atmospheric conditions. Pyrite from crushed ore samples showed minimal signs of weathering compared to particles of milled ore in tailings samples (Fig. 3) that have an increased surface area, pitting, rounded corners, and amorphous coatings. At the Alder Mill and Red Shirt Mill sites, weathering decreased with depth. Easily weathered hornblende was absent down to a depth of 150 cm and from 175-250 cm hornblende increased from 2 to 20% of the grains analyzed by SEM-EDS (Fig. 4).

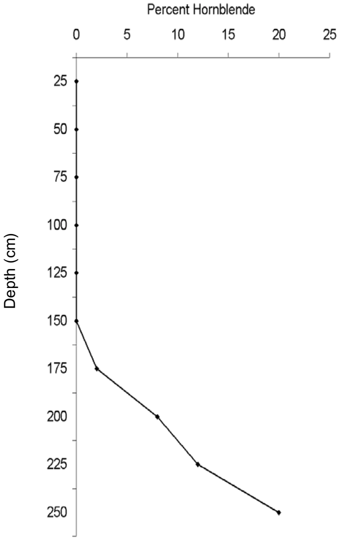

*Figure 4. Percent hornblende with depth in core from Alder Mill tailings pile.*

## TRANSPORT

Sodium chloride (NaCl) injections were used to determine whether there was hydrologic continuity between the ARD at station 1 and Alder Creek at station 5 and to characterize the rate of flow. At a distance of 322 m between the adit and Alder Creek, peak and electrical conductivity and Cl in water samples was detected in Alder Creek 10 hours following tracer injection at the mine adit, indicating the subsurface rate of flow at the Alder Mine was approximately 32 m hr $^{-1}$. Chloride injection data were also combined with measurements of geogenic sulfate in subsurface water samples (Stations 1-5) to determine whether ARD from the adit at station 1 was supplemented by additional subsurface inputs of ARD from the tunnel or ARD leached from the waste rock. Although Cl concentrations declined from 612 mg L$^{-1}$ where it was injected into the ARD stream at station 1 to 14 mg L$^{-1}$ at station 5, concentrations of geogenic $SO_4$ were relatively constant and ranged from 649-743 mg L$^{-1}$ with no detectable trend. Consequently, the mean $SO_4$ to Cl ratio increased from 1 to 46 (Fig. 5).

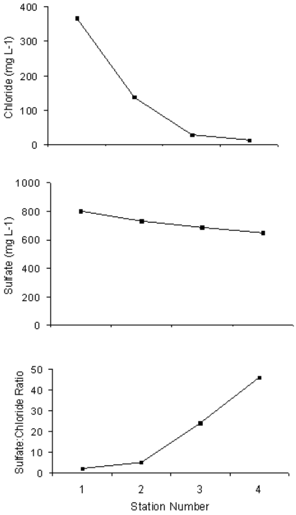

*Figure 5. Chloride, injected at station 1, and geogenic sulfate concentrations between Alder Mine adit at station 1 and Alder Creek at station 4. (A) Peak chloride concentrations at stations 1-4. (B) Peak sulfate concentrations at stations 1-4. (C) Increasing sulfate to chloride ratio indicates ARD contaminated groundwater is added to discharge from adit as station 1.*

## ABIOTIC DEPOSITION OF IRON AND TRACE ELEMENTS

Abiotic deposition of trace elements was characterized by the sequential analysis of Methow River sediments and observing the relative concentrations of trace elements in the Fe-oxide, Mn-oxide, carbonate and exchangeable fractions. Results showed that 43% of copper resided in the Fe-oxide fraction (Fig. 6). Iron-oxide coatings containing trace elements were also confirmed using SEM-EDS (Figure 7). The EDS spectrum shows Si was the major constituent when the electron beam from the SEM-EDS analysis was directed at an uncoated place on the sediment particle. When the electron beam was redirected to an area with an amorphous coating an Fe peak appeared. The spectrum shows that the coating also contained Mg, Br, Na, K, Ca, Ti, and K in addition to the dominant Fe peak.

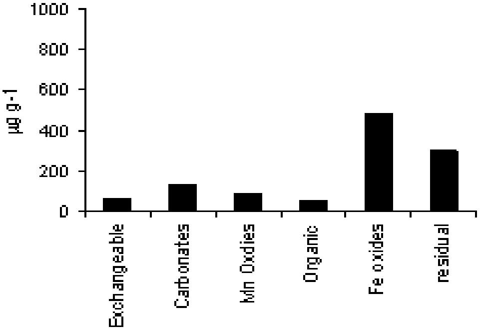

*Figure 6. Sequential extraction results showing copper concentrations in different fractions of Methow River sediments at station 11.*

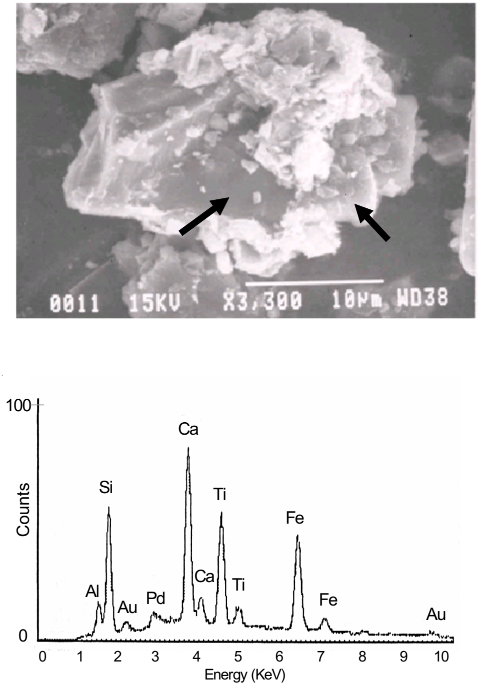

*Figure 7. SEM micrograph and EDS spectrum showing quartz particle from Methow River sample and coating that contains Ti.*

## COHERENCE WITH BIOLOGY

In addition to the abiotic deposition of Fe and sorbed micronutrients, there is evidence that deposition is also a result of biotic processes. Red hematite-colored tubules that measure < 1∝m in diameter and from a few to over 100 µm in length were observed on sediment particles near groundwater upwellings in the Methow River (Fig. 8). Although SEM-EDS analysis is not quantitative, peak height reflects the relative proportions of the constituents. The spectrum for the tubules suggest the tubules are composed of Fe-oxides.

## COHERENCE WITH STATISTICS

The response of sulfate concentrations in surface- and groundwater samples with distance from the mine was used to determine whether there was a correlation between the hypothetical cause (e.g., Alder Mill) and the effect (e.g., ARD contamination). From stations 14 northeast to stations 15, 16 and 10, the decline in sulfate concentrations correlated with distance (r = -0.93, $p<0.05$) (Table 1). Sulfate concentrations also correlated with distance away from stations 14 southeast to stations 17, 18 and 12 (r = -0.96, $p<0.05$). Background sulfate concentration in Methow River tributaries not impacted by the Alder Mine was 2 ± 1 mg L$^{-1}$.

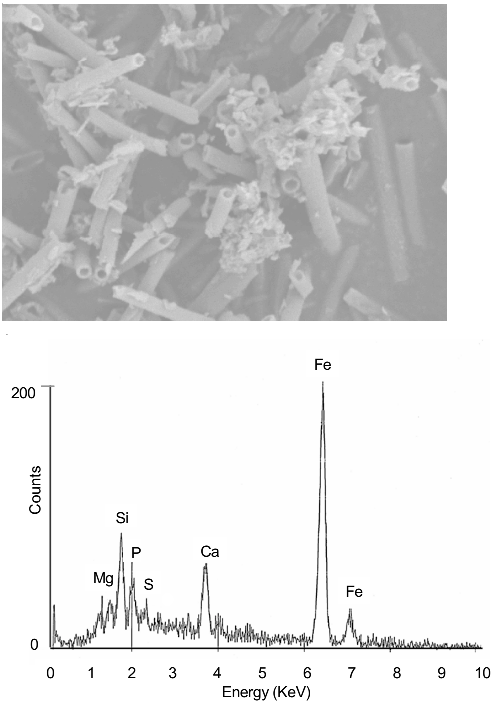

*Figure 8. Scanning electron micrographs of Methow River sediments showing abandoned Fe-oxide sheaths from iron-depositing bacteria and EDS spectrum showing composition of mineralized sheaths (above) and abandoned Fe-oxide sheaths from iron-depositing bacteria and EDS spectrum showing composition of mineralized sheaths (below)*

## STRENGTH OF ASSOCIATION

The ratios comparing trace element concentrations to ecotoxicological benchmarks, referred to as concentration factors (CF) were used as indicators of relative risk and a measure of strength of association. The concentrations of Al, As, B, Ba, Cd, Cr, Cu, Mn, Pb, and Zn were greater in the Methow River below Twisp and the abandoned mine sites (stations 10-13) than above (stations 6-10, $p < 0.05$, Table 2). Four trace elements that exceeded toxicity benchmark values, ranked in order of their concentration factor were, Cd (9) > Cu (5) > Mn (1.3) > Pb (1.3) (Table 2).

## TIME ORDER

To determine whether recent metal deposition exceeds historic background deposition, Cu concentrations in a sediment core at were measured 2 cm increments. When normalized to Al to correct for variations in organic carbon content with depth it was apparent that there were two periods of accumulation. In the earlier period that corresponded to fractions below 14-20 cm, Cu accumulation was lower than in the upper portions of the core that correspond to more recent periods of deposition (Figure 9). These data serve as a record of temporal changes in trace element deposition and show that relatively low background metal accumulation rates were followed in time by an increase in Cu contamination.

## SPECIFICITY

When the concentrations for Cd, Cu, Pb and Mn in ARD, tailings seeps, groundwater, and river sediments were compared to data sets from mineralized areas not impacted by mining, the ranges overlapped and there was no apparent specificity.

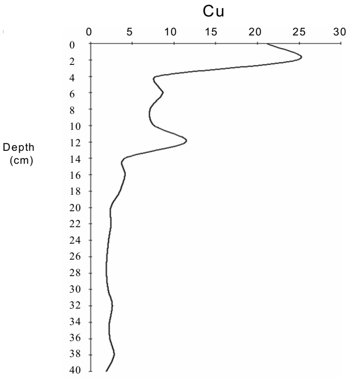

*Figure 9. Zinc and Cu concentrations in sediment core from Alder Creek at 2 cm increments. Concentrations were normalized t Al to compensate for changes in organinc matter with depth.*

## DISCUSSION

## SPECIFICITY

The hypotheses that trace element contamination is caused by an abandoned mine or mill site is often attacked for the lack of specificity in the suspected cause and it is often argued that contamination could be from natural background sources instead. It must be remembered, however, that specificity is an affirmative criterion that adds plausibility to a causal claim, but if absent it does not detract from the hypothesis (Susser 1986). The concentration of metals in ARD, tailings seeps, groundwater, and river sediments were not specific to either mine impacted or natural sites and the range of concentrations that have been reported suggest that specificity is generally low in regards to the effects of mining on the concentrations of these elements.

*Table 1. Sulfate gradient between Alder Mill and the Methow River. Northeast from station 14 are stations 15, 16 and 10 and southeast from station 14 are stations 17, 18, and 12. Regression analyses were performed on log-transformed data.*

| **Station** | **Mean Sulfate Concentration mg $L^{-1}$** | **n** | **Station** | **Mean Sulfate Concentration mg $L^{-1}$** | **n** |
|---|---|---|---|---|---|
| 14 | 669 | 12 | 14 | 669 | 12 |
| 15 | 81 | 10 | 17 | 214 | 10 |
| 16 | 44 | 10 | 18 | 7 | 10 |
| 10 | 2 | 10 | 12 | 3 | 10 |
| $r^2$ | 96 | | | 93 | |
| p | 0.02 | | | 0.03 | |

The chemical composition of natural and mine-derived ARD is controlled by deposit geology and biogeochemical processes (Plumlee et al. 1999). Geologic features that control the composition of ARD include the presence of acid-generating iron sulfides, other metal sulfides, and acid-consuming carbonates but since reactivity of the minerals is a function of grain size as well as the trace-element content of the deposit, mineral processing results in the greater range of concentrations observed in mine waters. The range in concentrations of metals in ARD, tailings seeps, and groundwater overlapped with natural seeps and was not specific to mine impacted sites. The lack of specificity is indeterminate and does not affirm a causal hypothesis.

## COHERENCE WITH THEORY

### WEATHERING AND TRACE ELEMENT MOBILIZATION

At the Alder Mill there were three observations that suggested there is a temporal variation in oxidation and pore water chemistry that is influenced by seasonal hydraulic flushing: (1) evidence that the mine waste dump at Alder Mill is divided into a leached horizon above 250 cm and an accumulation horizon below. The absence of hornblende down to a depth of 150 cm and its increase between 175 and 250 cm provides evidence of weathering from the surface down to a depth of approximately 250 cm. (2) the banded formation of weathered tailings particles, and (3) rounded corners, pitting, and amorphous coatings indicating pyrite is being weathered.

These results agree with the generally accepted knowledge that the sulfide minerals weather leading to the generation of ARD containing dissolved metals and sulfate (Paulson and Balistrieri 1999). Also, in addition to the geology of the mineral deposit, climate, hydrology and biogeochemical processes, which are known to determine the composition of natural waters draining sulfide mineral deposits, the reactivity of sulfide minerals is also a function of grain size and the trace-element content of the minerals. The mining and milling processes that reduces sulfide mineral particle sizes, increases surface area of iron sulfide minerals exposed to the oxidation process and increases the production of ARD (Plumlee et al. 1999).

### TRANSPORT OF DISSOLVED TRACE ELEMENTS IN SURFACE- AND GROUNDWATER

Water is the prime transporting vehicle and is responsible for the dispersion of trace elements from their source (Zajic 1969). When subjected to erosion, weathering, oxidation, leaching, and groundwater transport, trace elements can become dispersed over large areas. The observation that the subsurface flow of ARD appears to be unrestricted between Alder Mine (station 1) and Alder Creek (station 5) is consistent with observations related to bedrock morphology. The presence of faulting and calcite-filled fractures in the area where the abandoned mine sites are located suggests that calcite fracture fillings are being dissolved by the acid mine waters infiltrating from the surface. Pyrite oxidation, which results in acid mine waters, dissolves carbonate minerals resulting in modifications of the hydrologic character of the bedrock (Balistrieri et al. 1999, Hoch 2000). Once calcite-cemented fractures open the porosity, the reactive character of the rock can potentially be increased resulting in the dissolution, transport, and dispersion of additional trace element contaminants. The increase in the ratio of sulfate to chloride between the adit at site 1 and Alder Creek site 4 suggest there are additional inputs of ARD along the subsurface flow path.

*Table 2. Mean concentrations of trace elements in sediments below mines (stations 10 - 13) that exceded the mean concentrations above the mines (stations 6 - 9).*

| Trace Elements | Mean Concentration Station 1 | Mean Concentration Station 1 | Mean Concentration Above | Mean Concentration Below | Aquatic Biota | Concentration | t-Test |
|---|---|---|---|---|---|---|---|
| **Elements** | **AMD** | **Leachate** | **(Stations 6-9)** | **(Stations 10-13)** | **Benchmark** | **Factor** | **p =** |
| Al | 16673 | 815 | 10794 | 17249 | 58030 | <1 | 0.00 |
| As | 206 | 33 | 0 | 7 | 12 | <1 | 0.00 |
| B | 339 | 0 | 39 | 51 | NA | NA | 0.01 |
| Ba | 6 | 43 | 67 | 146 | NA | NA | 0.00 |
| Cd | 2713 | 9 | 5 | 9 | 1 | 9 | 0.02 |
| Cr | 53 | 10 | 22 | 35 | 56 | <1 | 0.00 |
| Cu | 12776 | 737 | 18 | 146 | 28 | 5.2 | 0.00 |
| Mn | 9169 | 1078 | 305 | 580 | 460 | 1.3 | 0.00 |
| Pb | 461 | 0 | 30 | 43 | 34 | 1.3 | 0.00 |
| Zn | 197944 | 2009 | 59 | 107 | 159 | <1 | 0.00 |

## ABIOTIC DEPOSITION OF IRON AND TRACE ELEMENTS

Oxidation and reduction (redox) and pH are major environmental variables that determine the mobility of iron and trace elements in water. The combined effects of Eh and pH on the speciation of Fe is best illustrated in an Eh/pH diagram (Alloway 1995) that shows that Fe oxides are either dissolved by either decreasing pH or Eh or flocculate when they increase. When pH is approximately equal to the point of zero net proton charge (pH 8) the iron oxyhydroxide particles are not repelled, which causes them to flocculate and settle out (Langmuir 1999). With increasing Eh and pH, Fe oxides precipitate as coatings on soil and sediment particles. Precipitation of Fe is initially in the form of gelatinous hydrated iron oxide [Ferrihydrite, $Fe_5(O_4H_3)_3$] which gradually dehydrates with aging to more stable forms such a goethite.

Ferrihydrite coprecipitates other ions and acts as a scavenger adsorbing metal cations and cations (e.g., $Cd^{2+}$, $Cu^{2+}$, $Pb^{2+}$, and $Mn^{2+}$) and anions (e.g., $AsO_4{}^{3-}$) (Hem 1977, Benjamin 1981, Belzile and Lebel 1986). In this study Cu was in the Fe-oxide fraction where it exceeded toxicity benchmark values. The formation of Fe-oxide coatings on sediment particles in the Methow River was confirmed by SEM-EDS analyses.

## COHERENCE WITH BIOLOGY

The deposition of Fe and sorbed micronutrients due to biotic processes is the result of iron-depositing bacteria that scavenge toxic metals from aqueous solutions (Ghiorse 1984, Schultze-Lam 1996). It is not unusual for bacteria to precipitate an amount of metal equal to or exceeding their cellular weight (Schultz-Lam et al 1996, Tessier et al. 1988, Beveridge 1989). The microtubules of Fe-oxide detected by SEM and analyzed using EDS resembled the sheaths formed by the iron-depositing bacteria described by Mulder and Deinema (1992), which strongly suggests that microorganisms are involved in the formation of these secondary mineral deposits.

Bacteria have long been recognized for their ability to deposit Fe-oxide. Iron-depositing bacteria include Gallionella, Sphaerotilus, Clonothrix, and Leptothrix. The occurrence of Fe-depositing microorganisms suggests that they may be important in the accumulation of Fe-oxides that occur frequently as coatings, concretions, flocculent particles, and surface films in sedimentary environments. In low-nutrient, Fe-containing enrichment cultures, Leptothrix, a gram-negative aerobic heterotroph, has been shown to synthesize and vacate iron-encrusted sheaths very rapidly, leaving behind large masses of empty sheaths.

According to Schultze-Lam (1996), adsorption occurs due to the overall anionic charge of bacterial surfaces imparted by the macromolecules (i.e., acidic polysaccharides, proteins, and polysaccharide-protein-lipid complexes) that make up their capsule.

## COHERENCE WITH STATISTICS

Sulfate concentrations decreased along two gradients that were sampled northeast from station 14 to station 15, 16, and 10 and southeast from station 14 to stations 17, 18, and 12. All sulfate concentrations exceeded estimated background concentrations. The correlation of sulfate concentrations with proximity to the source of metal sulfide oxidation is strongly persuasive of a causal relationship and suggests that ARD is being dispersed from the Alder Mill to the Methow River.

## STRENGTH OF ASSOCIATION

When both confidence factors (CF) and confidence in the toxicity threshold values are considered, contamination of Methow River sediments by Cd, Cu, Mn, and Pb appears to be strongly associated with sediments in the Methow River below the abandoned mines. A large amount of data exists for Cd, Cu, and Pb and there is a relatively high degree of confidence in their toxicity threshold values (Jones and Suter 1997). The only data for Mn relates to severe effects levels and so there is only a moderate degree of confidence in the threshold values for Mn (Persaud et al. 1993).

## TIME ORDER

Data in this study on the effects of mine waste on aquatic and terrestrial fish and wildlife habitat near the Methow River south of Twist were collected 48 years after the cessation of mining. The combination of metal analyses and radiometric dating would have made the historical reconstruction of contamination possible (Valetta-Silver 1992). Even in the absence of pre-mining background data or radio-isotope data to determine exact age and depositional history of the deposits sampled in the core, the time-order of Cu accumulation in Alder Creek sediments supports the cause-effect hypothesis. The sediment profile for Alder Creek suggests historical changes in Cu accumulation occurred and that there were two periods of accumulation. In the lower fraction, which correlates with the earliest period, Cu accumulation was lowest. Copper accumulation increased in the fractions above 20 cm, which correlate with the later period. The cored material came from an area that is assumed to have a relatively fast sedimentation rate and was apparently undisturbed thus supporting its reliability.

## CONSISTENCY

Past studies have shown that drainage compositions vary as a function of deposit geology, climate, mining method used, and mineral processing method used (Plumlee 1999). It has also been shown that the composition of ARD varies predictably within mines and across districts (Waitt et al. 1980, Wildeman et al., 1974). However, no systematic examination of ARD compositions from mines with similar deposit types and ore types within a deposit type has been found and it is not possible to predict the exact composition of water that will develop in a particular mine. Because of these limitations, consistency was not used as a criterion in this study.

*Table 3. Rejection of the hypothesis that a causal relationship exists between the presence of mining activities and the accumulation of trace elements at concentrations that are potentially harmful to human health and fish and wildlife habitat in the Methow River Valley using the criteria strength, consistency, and coherence.*

| Criteria | Supports | Detracts | Indeterminate |
|---|---|---|---|
| Coherence with Theory | + | | |
| Coherence with Biology | + | | |
| Coherence with Statistics | + | | |
| Strength of Association | + | | |
| Time Order | + | | |
| Spedificity | | + | |
| Consistency | | + | |

## CONCLUSION

Coherence with theory is supported by observations that the tailings pile at the Alder Mill is divided into a leached horizon above and an accumulation horizon below approximately 250 cm. There are banding formations on weathered tailings particles, and pyrite particles are rounded, pitted and covered in amorphous iron-oxide coatings indicating that oxidative weathering of iron sulfide minerals is occurring (Table 3). These results agree with the generally accepted knowledge that the weathering of sulfide minerals generates ARD containing dissolved metals and sulfate and that the mining and milling processes that reduces sulfide mineral particle sizes, increases surface area of iron sulfide minerals and increases the production of ARD. Coherence was also supported by the observation that the subsurface flow of ARD appears to be unrestricted between Alder Mine (station 1) and Alder Creek (station 5), which is consistent with the idea that water is the prime transporting vehicle and is responsible for the dispersion of trace elements from their source and that when subjected to erosion, weathering, oxidation, leaching, and groundwater transport, trace elements can become dispersed over large areas. The formation of Fe-oxide coatings on sediment particles in the Methow River, confirmed by SEM-

EDS analyses, is in agreement with redox theory which predicts that with increasing Eh and pH, Fe oxides precipitate as coatings on soil and sediment particles and the Fe-oxides coprecipitates other ions and acts as a scavenger adsorbing metal cations and cations (e.g., $Cd^{2+}$, $Cu^{2+}$, $Pb^{2+}$, and $Mn^{2+}$).

The occurrence of Fe-depositing microorganisms in Methow River sediments is in coherence with theory because bacteria have long been recognized for their ability to deposit Fe-oxide (Table 3). The deposition of Fe and sorbed micronutrients due to biotic processes is the result of iron-depositing bacteria that scavenge toxic metals from aqueous solutions and occur frequently as coatings, concretions, flocculent particles, and surface films in sedimentary environments. Coherence with statistics also supports the causal hypothesis (Table 3) because the correlation of sulfate concentrations with proximity to the source of metal sulfide oxidation is strongly persuasive of a causal relationship and suggests that ARD is being dispersed from the Alder Mill along hydrologic pathways that lead to the Methow River.

Concentration factors, which are measures of relative risk, indicate the association of contamination in Methow River sediments by Cd, Cu, Mn, and Pb is strongly associated with the presence of abandoned mine (Table 3). A sediment profile for a tributary of the Methow River below the Alder Mine suggests historical changes in Cu accumulation occurred and that there were two periods of accumulation, which support the causal hypothesis that trace metal deposition associated with the presence of abandoned mine sites increased over background levels (Table 3).

The lack of specificity is indeterminate (Table 3) and does not affirm a causal hypothesis because the range in concentrations of metals in ARD, tailings seeps, and groundwater overlapped with natural seeps and were not specific to mine impacted sites. Also, because there has been no systematic examination of ARD compositions from mines with similar deposit types, and ore types within a deposit type, it is not possible to predict the exact composition of water that will develop in a particular mine. Because of these limitations, consistency was indeterminate with regards to the causal hypothesis (Table 3).

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