Chapter 6—Impacts of historical mining in the Coeur d'Alene River Basin

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BACKGROUND

Mining began in the late 1880s in the Coeur d'Alene mining district in northern Idaho (fig. 1). Although only two mines, the Galena and Lucky Friday, currently are operating, more than 90 historical mines exist in this region (Bennett and others, 1989). Most of the mines are along the South Fork of the Coeur d'Alene River and its major tributaries (Bennett and others, 1989). Total production records indicate that this district ranks among supergiants (top 1 percent of world producers) for silver (34,300 metric tons Ag) and lead (7,290,000 metric tons Pb) and among giants (top 10 percent of world producers) for zinc (2,870,000 metric tons Zn) (Long, 1998a, 1998b).

Ore deposits in the district are steeply dipping quartz veins and siderite ($FeCO_3$) veins containing stratigraphically controlled Pb-Zn-Ag ore shoots in Precambrian rocks of the Belt Supergroup (Fryklund, 1964; Hobbs and others, 1965; Zartman and Stacey, 1971; Bennett and Venkatakrishnan, 1982; Leach and others, 1988; Criss and Fleck, 1990). The veins are separated into two major types by ore mineralogy: (1) lead- and zinc-rich veins having argentiferous galena (PbS) and sphalerite (ZnS) and (2) silver-rich veins having argentiferous tetrahedrite [$(Cu, Ag)_{10}(Fe, Zn)_2(As, Sb)_4S_{13}$] and minor galena and sphalerite. The vein types are spatially separated, may represent one or two ages of mineralization, and were deposited from fluids of metamorphic origin (Leach and others, 1998; Long, 1998a). Pyrite (FeS_2) is ubiquitous but variable in abundance in the veins. Most veins contain small amounts of chalcopyrite ($CuFeS_2$). Minor minerals include arsenopyrite (FeAsS) and pyrrhotite

$(Fe_{1-x}S)$. Host rocks are primarily quartzite and argillite, which contain some interbedded carbonate-bearing rocks. Studies at the Lucky Friday Mine indicate that wall rocks around veins are altered and typically contain 10 to 15 percent carbonate minerals. Concentric zonation with respect to three carbonate minerals [siderite $(FeCO_3)$, ankerite [$CaFe(CO_3)_2$], and calcite $(CaCO_3)$] is common in the altered wall rocks (Gitlin, 1986). The predominant gangue minerals are siderite and quartz. The absolute and relative abundances of sulfide and gangue minerals vary significantly between different vein systems.

Milling and ore concentration practices varied over time in the district because of changing technology and economics. Early ore separation methods, which included coarse crushing and gravity ("jig") mineral separation methods, were not very efficient. Jig tailings produced before 1915 ranged from coarse gravel to fine powder and were still very rich in metals. Development of more efficient flotation methods between 1915 and 1925 resulted in tailings with finer grain size (fine sand and finer) and lower metal concentrations. Most tailings were deposited directly into the Coeur d'Alene River and its tributaries before environmental regulations required the installation of tailings ponds in 1968. A preliminary accounting by Long (1998b) has estimated that 56 million metric tons of tailings containing 2,200 metric tons of Ag, 800,000 metric tons of Pb, and at least 650,000 metric tons of Zn were dumped into the river system. Stream transport, especially during major flood events, has redistributed and continues to redistribute metal-enriched sediment from its sources for distances of more than 240 km downstream throughout the channel of the South Fork and main stem of the Coeur d'Alene River and their floodplains, into Lake Coeur d'Alene, and into the Spokane River (Horowitz and others, 1993; Horowitz and others, 1995; Bookstrom and others, 2001; Box and others, 2001). Because the river gradient is steeper and the flow faster in the upper Coeur d'Alene River system, the major repositories of the discharged mine tailings were the channel and floodplain of the lower Coeur d'Alene River (that is, between Cataldo and Harrison) and Lake Coeur d'Alene.

The Bunker Hill lead smelter in Kellogg (see fig. 1) operated between 1917 and 1982 (Bennett and others, 1989). This smelter released more than 3,300 metric tons of Pb to the atmosphere between 1965 and 1981. An area of 54 km^2 surrounding the smelter was listed by the U.S. Environmental Protection Agency (EPA) as one of the nation's largest Superfund sites in 1983 (U.S. Environmental Protection Agency, 1994). The listing was prompted, in part, by very high levels of Pb in the blood of children living in Kellogg. A Natural Resource Damages (NRD) lawsuit filed by the Federal government and two Native American tribes is awaiting a decision after 2 months of court testimony in 2001. The EPA completed a 3-year Remedial Investigation/Feasibility Study (RI/FS) for the entire Coeur d'Alene Basin in 2001. The proposed plan, in its public comment period as of May 2002, recommends a 30-year, $300 million remedial program as the first increment of a longer remediation schedule. EPA is expected to issue a Record of Decision laying out its remediation plan in mid-2002. The State of Idaho has completed some remediation projects and is currently doing several more within the district but outside of the Superfund site.

Although our data encompass a wide range of elements, the following discussion of our work focuses on the behavior of Pb and Zn in the near-surface environment because of their importance to environmental and health issues in the Coeur d'Alene River basin. As discussed in the introductory chapter (ch. 1), we examine the results of our work in light of four questions:

1. What is known about the distributions, concentrations, and speciation of Pb and Zn in this river basin?
2. What is known about the processes that release Pb and Zn from their sources and then act to physically and biogeochemically redistribute them?
3. What is known about the impacts of Pb and Zn on biota and can we identify specific processes that influence bioavailability?
4. What additional work needs to be done to provide a more thorough understanding of Pb and Zn cycling in this basin?

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DISCUSSION OF MINING IMPACTS

What is known about the distributions, concentrations, and speciation of Pb and Zn in the Coeur d'Alene River basin?

Particulate Lead

Pb exists primarily in the particulate or solid phase rather than the dissolved phase. This is because of the low solubility of Pb minerals and the high affinity of dissolved Pb for metal oxide particles at neutral pH. Health problems in the basin for humans and wildlife are linked to high concentrations of particulate Pb in surface soils and sediment and to ingestion of those particles. Elevated concentrations of particulate Pb are associated with soils that formed over mineralized rocks in the area (Gott and Cathrall, 1980), tailings from mills that processed the mineralized rock (Long, 1998b), and atmospheric fallout from smelters that operated in the mining district (U.S. Environmental Protection Agency, 1994). There are no new sources of particulate Pb from smelters or tailings today because of closure of the smelters and environmental regulations that prohibit the dumping of tailings into rivers. However, historically produced particulate Pb from smelter fallout and mill tailings is constantly being redistributed by wind and water. Because Superfund work focused on cleaning up smelter fallout in houses and yards, the biggest remaining challenge is grappling with the environmental and health impacts of fluvially distributed tailings.

The origin of the fluvially deposited tailings is the historical milling and processing of ore within the district and subsequent disposal of tailings into the river system. The concentration of metals in tailings from mills in the Coeur d'Alene mining district decreased irregularly through time as ore concentration methods improved (fig. 2). Gravity separation or jigging was the ore concentration method used between 1885 and 1925. Data from the historical Morning Mill, the remnants of which are just west of Mullan, indicates that tailings contained between 4 and 9 percent Pb and Zn during this time (fig. 2). Flotation methods, used between 1925 and 1968, produced tailings containing lower metal concentrations (<1.5 percent Pb and Zn) (fig. 2).

The distribution of Pb as a function of depth in the sediments of the Coeur d'Alene River valley reflects the onset of mining and history of milling practices within the district (Bookstrom and others, 2001; Box and others, 2001). Before mining began in the late 1880s, the concentration of Pb was <30 ppm in the silty clay and fine sand of the basin (Bookstrom and others, 2001). Similar concentrations are observed today in the deepest portion of cores collected from transects across the river channel at Killarney (between Rose Lake and Harrison) and from the adjacent flood-plain (fig. 3). Changes in milling prac-tices over time also are reflected in the varying concentrations of Pb with depth across this transect. Sediments mixed with early jig tailings that were depos-ited before about 1925 have the highest concentrations of Pb (up to 36,000 ppm). A sharp drop in Pb concentration to less than 10,000 ppm, followed by a gradual upward decrease in Pb contents to 3,000-5,000 ppm, mark sediments from the era of flotation methods. A gradual upward coarsening trend from silt at the base to medium sand at the top is typical of the river channel and bank deposits. Deposi-tion rates are still high on the river banks (average of 0.8 cm/yr) and little, if any,

diminution of sedimentation rate or metal content in river bank or Lake Coeur d'Alene sediments has been noted since the dumping of tailings dumping into the river was stopped in 1968 (Horowitz and others, 1993; Box and others, 2001).

In sediments finer than 175 mm in the bed of the Spokane River, the Pb content ranges from background concentrations (<30 ppm) to about 2,500 ppm, whereas Zn concentrations vary from about 50 to 5,000 ppm (fig. 4). A mixing model suggests these sediments are composed of three types of material that have different sources: (1) background mate-rial with low Pb (20 ppm) and low Zn (50 ppm) concentrations, (2) material, possibly an authigenic flocculent, that is poor in Pb (50 ppm) and rich in Zn (5,000 ppm), and (3) material derived from the Coeur d'Alene River that has moderately high concentrations of both Pb (2,500 ppm) and Zn (4,000 ppm) (Box and Wallis, 2002).

Calculations of the volume of sediment and associated Pb in various areas of the river basin were recently done using digital maps of the South Fork and lower Coeur d'Alene River and chemical analyses of many sediment samples (Bookstrom and others, 1999; Bookstrom and others, 2001;

Box and others, 2001). These calculations indicate that there are 200,000±100,000 metric tons of Pb in the South Fork drain-age basin, 250,000±62,000 metric tons in the lower Coeur d'Alene River valley between Cataldo and Harrison, and 292,000±145,000 metric tons in Lake Coeur d'Alene. Estimates have not yet been made for the North Fork drainage basin or the Spokane River. About 99 percent of the Pb contained in these sediments was added as a result of mining-related activities. Of the Pb in the lower Coeur d'Alene River valley, approximately 59 percent is in the floodplain, 37 percent in the river channel, and 4 percent in the riverbanks. The estimated sum of Pb added to sediments of the South Fork River valley, Coeur d'Alene River valley, and Lake Coeur d'Alene (739,000 ± 305,000 metric tons) amounts to about 87 percent of the estimated Pb (850,000 ± 10,000 metric tons) that was dumped into tribu-tary streams by the mills in the mining district.

Dissolved Zinc

Although large amounts of particulate Zn reside in the Coeur d'Alene River basin, it is the dissolved form of Zn that governs water quality in this region because of its impact on the health of

biota, particularly fish. Because of this impact, we compare concentrations of dissolved Zn observed in the basin to the Criterion Continuous Concentration (CCC) for Zn, which is the highest concentration of total recoverable Zn to which aquatic life can be exposed for an extended period of time (4 days) without deleterious effects (U.S. General Services Administration, 1999). Within the basin, total recoverable Zn in water samples typically is equal to dissolved Zn (Brennan and others, 2000; Brennan and others, 2001). The CCC for Zn in Idaho is a function of the hardness of the water (U.S. General Services Administration, 1999). For example, for a range in hardness of 15 to 65 mg/L, as observed in the Coeur d'Alene River, the corresponding CCC for Zn ranges from 21 to 73 mg/L (U.S. General Services Administration, 1999). A water quality criterion for pH has also been set and ranges from 6.5 to 9 for freshwater (U.S. Environmental Protection Agency, 1999).

Dissolved Zn concentrations are plotted as a function of pH in figure 5 for different types of water (adit drainage, ground water from deep wells, porewater in the upper 30 cm of water-saturated sediments, water from tailings seeps, and river water) affected by ore deposits or mining wastes within the Coeur d'Alene River basin. Both pH and dissolved concentrations of Zn show large variations, and many samples, particularly of ground water, do not meet water quality criteria (Mink and others, 1971; U.S. Geological Survey, 1973; McCulley Frick and Gilman, 1994; Balistrieri and others, 1998; Golder Associates, 1998; TerraGraphics Environmental Engineering, 1998; Balistrieri and others, 2000; McCulley Frick and Gilman, 2000). Values of pH range from a low of 2.72 at the Kellogg Tunnel (adit drainage) to a high of 9.1 in the Coeur d'Alene River. Dissolved Zn concentrations range from 1.2 mg/L to 759 mg/L, and vary significantly at near-neutral pH values. Table 1 summarizes the range and median values for pH and dissolved Zn concentrations in the various waters. Except for water from the Kellogg Tunnel, ground water under tailings-bearing floodplain sediments and tailings piles has the lowest pH values and highest dissolved Zn concentrations. Porewater in metal-contaminated sediment mostly tends to be slightly acidic (median pH = 6.57) and can have moderately high dissolved Zn concentrations (up to 70 mg/L). Most adit drainage, except from the Kellogg Tunnel, has slightly alkaline pH values (median pH = 7.34) and moderately high dissolved Zn concentrations (up to 58 mg/L). Water from rivers is mostly near neutral and tends to have the lowest dissolved Zn concentrations, although the median value is still above the CCC.

Solid-phase speciation

We have conducted two studies on the speciation of metal-enriched particles in the Coeur d'Alene River valley. The intent was to look at changes in mineralogy and geochemical availability of particulate Pb and Zn as they are dispersed from their primary sources as sulfide minerals (galena and sphalerite) in the ore deposits and to determine how the redox characteristics of the depositional environment influence the mineralogy and geoavailability of Pb and Zn. Our conclusions are based on mineralogical and geochemical leach studies of the particles.

The first study looked at the speciation of Pb in particles from paired sites at three locations within the mining district. At each location, the paired sites are the floodplain, which contains tailings from the jig era, and the nearby river channel. Both types of

site are oxidizing environments. Mineralogical (R.L. Hooper and C. Rowe, unpublished data, 2000) and leach data using the methods of Gasser (Gasser and others, 1996) for these particles are shown in table 2. The Pb, Fe, and Mn contents of these samples vary substantially, considerably higher concentrations generally occurring in sediment from the floodplain. The mineralogical data indicate the importance of Fe and Mn oxides as host phases for Pb (also see fig. 6) and, in some cases, the formation of substantial amounts of Pb carbonates and sulfates. Trace amounts of sphalerite are present in all samples. The sequential extraction data are in accord with the mineralogical data in that they indicate large fractions of Pb associated with Fe and Mn oxides (that is, in the EDTA or HNO_3 leach) or, in the case of sample 205, anglesite (that is, in the $MgCl_2$ leach). Results from the leach simulating gastric conditions suggest that a major fraction of Pb in most of these samples would be mobilized in the human stomach. This work indicates that the speciation of particulate Pb changes from a sulfide mineral to Pb carbonates and sulfates or Pb associ-

ated with Fe and Mn oxides within a short distance (<10 km) from the ore deposits. These results are consistent with observations of mineralogical changes in Pb downstream from lead-zinc-fluorite-barite deposits in northeast England (Hudson-Edwards and others, 1996).

The second study looked at the speciation of Pb and Zn in particles as a function of depth from four different environments (river bed, levee banks, wetlands, and lateral lakes) in the lower Coeur d'Alene River valley using a combination of mineralogical and chemical techniques (SEM, TEM, and sequential leaches) (Hooper and Mahoney, 2000, 2001). Care was taken to maintain the redox characteristics of the samples during collection, storage, and analyses. A sequential extraction method (Tessier and others, 1979) was calibrated by determining the mineralogy after each extraction step (fig. 7). The individual steps in the sequential extraction scheme generally are not specific for given mineral phases. However, patterns of metal release, considering all of the extraction steps along with the calibration results, provide information about the dominant phases in the samples.

Periodic flooding transports primary ore minerals (sulfides) and secondary mineral phases (oxides and carbonates) from upstream tailings deposits into the lower river valley. Preliminary results of our analyses of particles in the lower river valley suggest that their mineralogy is very complex and that they contain considerable amounts of amorphous and nanocrystalline material. The fate of particles, which may involve mineral dissolution, metal mobilization and migration, and mineral precipitation, depends on the redox characteristics, permeability, organic content, and microbial activity of the depositional environment. Particles in the bed of the river below the sediment-water interface are in a reducing environment, which acts as a sink for detrital sulfides and carbonates (fig. 8). Authigenic Fe, Pb, and Zn sulfides appear to form near the sediment-water interface. Because of water-level changes throughout the year, particles in the levee environment, near the edge of the river, cycle between dry and wet conditions. This results in oxidizing zones containing oxide-coated grains interspersed with reducing zones dominated by detrital

and authigenic carbonate and sulfide phases. Unexpectedly, detrital sphalerite is present in oxidized levee samples, indicating that some fraction of the total amount of the mineral is resistant to oxidation. Sediment at the top of levees resides in oxidizing environments, and samples from these environments, contain small amounts of detrital galena (PbS) and greater amounts of cerrusite ($PbCO_3$) and Pb-Fe-Mn oxides (fig. 8). In some samples Pb is associated with Mn oxides, and in others it is associated with Fe oxides. Zn exists primarily with Fe-Mn oxides. The wetland environment is anoxic, and most of the particulate Pb and Zn exist as microcrystalline and nanocrystalline to amorphous authigenic sulfides associated with biofilms, rootlets, and bacteria. Anoxic conditions also exist in the sediments of the lateral lakes. Particles in the lateral lakes contain nanocrystalline inorganic and biogenic sulfides in the upper third of the metal-enriched sediment and increasing amounts of silt-size detrital sulfides (especially sphalerite) closer to the premining surface. In both the wetland and lateral lake environments, microbial activity is extremely effective in removing metals from the water and producing a nanocrystalline biofilm on particles that is characterized by ZnS and nonstoichiometric PbS, FeS, and mixed metal sulfides.

What is known about the processes that mobilize Pb and Zn from their sources and then act to physically and biogeochemically redistribute them?

Physical processes

Several physical processes play important roles in determining the distribution and concentration of Pb and Zn in the Coeur d'Alene River basin, including those involved in historical mining practices; hydrologic transport and seasonal fluctuations in water levels; sorting of particles by size fractions during flood events; mixing of different source waters; and transport of dissolved metals across the sediment-water interface by molecular diffusion. Each of these is discussed here.

The milling practices and subsequent disposal of tailings into the river system before 1968 were important factors in determining the present day geochemical characteristics of the basin. Long (1998b) estimated that 109 million metric tons of metal-enriched mill tailings were produced by jigging and flotation methods within the district. About 51 percent of those were disposed of in the Coeur d'Alene River and its tributaries, 37 percent were placed in impoundments or used as stope fill, and 12 percent were stockpiled along the floodplain. Hydrologic transport, especially during flood events, resulted in sorting of this metal-enriched material and in the deposition of fluvial tailings deposits not only within the mining district, but also throughout the lower Coeur d'Alene River valley, in Lake Coeur d'Alene, and in the Spokane River. There is a potential long-term source of metal-enriched material to the floodplain, Lake Coeur d'Alene, and the Spokane River because a large fraction of Pb (about 41 percent of Pb in the lower Coeur d'Alene River valley) resides or is stored in the river channel and riverbanks (Box and others, 2001) and is subject to movement during high flows.

Pb and Zn data for particles in the river bed and on the levee banks (Box and others, 2001) and for particles suspended in the water of the Coeur d'Alene River during two flood events (Box and others, in press) are used to illustrate the importance of sources of sediment to the river (fig. 9). Riverbanks and natural levees of the

Coeur d'Alene River and alluvial terraces of the South Fork have lower Zn than Pb concentrations because Zn is preferentially leached from sediments stored in oxidizing environments. In contrast, bed sediments in the river channel are more enriched in Zn than Pb. The major rain-on-snow flood of 1996 began suddenly, when Lake Coeur d'Alene was low and hydraulic head between the river and the lake was high. Floodwaters ran red with oxidized suspended sediment, and Zn/Pb ratios of suspended sediment were less than one, indicating that most of the suspended sediment was mobilized from oxidizing environments. By contrast, the major 1997 spring runoff flood began gradually and continued for about a month, with relatively clear waters in the upper basin, sluggish currents along the Coeur d'Alene River, and floodwater backing up from Lake Coeur d'Alene as it overfilled. During this 1997 and previous spring runoff floods, Zn/Pb ratios of suspended sediment were greater than one, indicating that fines, winnowed out of riverbed sediment, predominated over sediment from oxidizing environments. In both events, however, sandy riverbank deposits were derived from mobilization of nearby bed sediments.

Another physical process that influences the distribution of elements is mixing of different source waters. Adit drainage within the district that is enriched in dissolved elements mixes with rivers and creeks that have lower concentrations of elements (Balistrieri and others, 1998). The North Fork of the Coeur d'Alene River supplies less metal-enriched water and sediment to the lower Coeur d'Alene River than the South Fork at their confluence above Cataldo. Also, variations in metal loading along the South Fork and its tributaries suggest mixing of surface water with more metal-enriched ground water (Barton, 2002).

Dissolved Zn, other metals, and nutrients can be supplied to Lake Coeur d'Alene by inflowing rivers and by transport across the sediment-water interface (benthic flux). Benthic fluxes were determined from concentrations in the water at the bottom of the lake and in porewater in the sediment using Fick's First Law and time-series data from in-situ benthic flux chambers (Balistrieri, 1998; Kuwabara and others, 2000). The results indicate that transport of dissolved elements and species is controlled by molecular diffusion and that the magnitudes of the benthic fluxes of dissolved Zn, Cd, phosphate, and nitrogen species

into the water column of the lake are similar to fluxes supplied to the lake by the St. Joe and Coeur d'Alene Rivers.

Biogeochemical processes

Water-rock interactions act to mobilize and redistribute elements within the river basin. Microorganisms mediate many of these reactions. Oxidation reactions involving primary sulfide minerals in the ore deposits result in the release of metals, sulfate, and in some cases (for example, pyrite oxidation) acid to the water. This acidity can be neutralized by the dissolution of buffering minerals, primarily carbonates such as calcite or ankerite. The relative molar amounts of pyrite and carbonate minerals in the deposits and host rocks that react or the reacting pyrite-to-calcite ratio can be predicted from the composition of drainage from adits (Balistrieri and others, 1999; Balistrieri and others, 2002). The predicted reacting pyrite-to-calcite ratios (assuming precipitation of ferrihydrite) for deposits in the Coeur d'Alene mining district range from 0.02 to 0.5 for near-neutral drainage to about 1 for the acidic drainage from the Kellogg Tunnel at the Bunker Hill mine site (fig. 10). Data for drainage from other polymetallic vein

deposits in the Colorado Mineral Belt and the Humboldt River Basin, Nevada, are also shown in figure 10 for comparison (Plumlee and others, 1993; Plumlee and others, 1999; Nash, 2000). Theoretically, neutralization of acid generated during oxidation of one mole of pyrite requires between 2 and 4 moles of calcite (that is, reacting pyrite-to-calcite ratios between 0.25 and 0.5) (Cravotta and others, 1990). Data for water draining polymetallic vein deposits in Idaho, Colorado, and Nevada are consistent with the theoretical predictions, showing drainage pH values that range from near neutral to alkaline when reacting pyrite-to-calcite ratios for the deposits are <0.3.

The precipitation of secondary minerals such as carbonates (cerrusite and smithsonite), sulfates (Zn sulfate and anglesite), and oxides (Fe and Mn oxyhydroxides and Fe oxyhydroxysulfates) and adsorption of dissolved elements onto the secondary oxide phases occur after mobilization of species from the primary sulfide minerals. The identity and composition of these precipitates were determined using mineralogical, chemical, and modeling techniques. We conducted several sets of experiments that mixed surface water with ground water, adit drainage, or porewater and assessed the ability of thermodynamic models to predict the precipitation of mineral phases and adsorption of metals onto metal oxide phases (Paulson and Balistrieri, 1999; Tonkin and others, 2002) using PHREEQC (Parkhurst and Appelo, 1999) and a database containing sorption parameters for elements onto hydrous ferric oxide (Dzombak and Morel, 1990).

Many important conclusions resulted from this work. First, thermodynamic modeling successfully predicted observed pH changes, precipitation of ferrihydrite, and removal of Cd, Cu, Pb, Zn, and, in some cases, As in the mixing experiments (fig. 11). Second, the relative efficiency of removal of metals by adsorption onto Fe oxide is Pb>Cu>> Zn~Cd. Third, Fe oxide is a stronger adsorbent than Al oxide, and adsorbed organic matter is an important adsorbent for Zn and Cd. Fourth, the adsorption characteristics of ferrihydrite and schwertmannite can be described by the same set of adsorption parameters (that is, site density, surface area, and adsorption complexation constants). Fifth, more metal is removed by adsorption if Fe oxides that precipitate during the mixing of acidic ground water and near-neutral surface water remain suspended in the water (transported scenario) rather than being separated from the water and remaining in the aquifer (retained scenario) along a flow path. Because pH increases along the flow path, greater metal removal occurs in the transported than in the retained case because the zone of precipitation of Fe oxide, which occurs at a lower pH, is not separated from the zone of adsorption of metals onto Fe oxide, which occurs at a higher pH.

The influence of organic matter diagenesis on redox state has been demonstrated in porewater studies in the sediments of Lake Coeur d'Alene and in sediments along the river's edge and in marshes of the lower Coeur d'Alene River valley (Balistrieri, 1998; Balistrieri and others, 2000). Organic matter decomposition occurs using a thermodynamically predictable sequence of oxidants (oxygen, nitrate, Mn oxide, Fe oxide, and sulfate) and results in redox conditions that range from oxic to suboxic, or to anoxic and sulfidic as depth increases in the sediment (Froelich and others, 1979). Redox state, in turn, influences the mobility of elements, particularly Zn, because of the release of associated elements during reduction of oxide phases under suboxic conditions and the insolubility of authigenic metal

sulfide phases under anoxic and sulfidic conditions. Porewater data from sediments in the lower Coeur d'Alene River valley suggest that Zn is more mobile (that is, higher concentrations in porewater) under oxidizing than under reducing conditions, most likely because of formation of authigenic Zn sulfides under anoxic and sulfidic (reducing) conditions.

Modeling of coupled physical and biogeochemical processes

Metal distributions and concentrations in the environment are a result of the interaction of many physical transport processes and biogeochemical reactions. Understanding the dominant processes is critical for successful design of remediation activities and for long-term management of ecosystems affected by human activities. Development of mathematical models that describe metal cycling in such systems synthesizes our understanding of how the system works by identifying and describing dominant processes and potentially allows for sensitivity tests to assess how a system might respond to perturbations. Models can also assess our understanding of system behavior by comparing observations and predictions during and after remediation activities. One such model describing the behavior of dissolved Zn in Lake Coeur d'Alene is discussed here.

We used a mass balance approach to examine various processes that control the concentration of dissolved Zn in Lake Coeur d'Alene (L.S. Balistrieri and P.F. Woods, unpublished data, 2002). Lake Coeur d'Alene is treated as a single, completely mixed system (that is, a one-box model) (fig. 12). The following equation describes changes in dissolved Zn concentrations in the lake as a function of time (dC_{Zn}/dt):

$$dC_{Zn}/dt = I_{Zn} + P_{Zn} - O_{Zn} - R_{Zn} \qquad (1)$$

where I_{Zn} accounts for all external inputs of dissolved Zn to the lake, P_{Zn} accounts for all internal sources of dissolved Zn to the lake, O_{Zn} accounts for fluxes of dissolved Zn out of the lake, and R_{Zn} accounts for internal removal of dissolved Zn from the water column. All terms have units of mg/L per day.

Dissolved Zn enters the lake through river inlets (Coeur d'Alene, St. Joe, and St. Maries Rivers) and leaves through a single outlet (Spokane River). These processes are depicted by the I_{Zn} and O_{Zn} terms in equation 1. Benthic fluxes of dissolved Zn, represented by the P_{Zn} term in equation 1, act as an additional source of dissolved Zn to the lake, whereas scavenging of dissolved Zn to particulate Zn and sedimentation, depicted by R_{Zn}, removes dissolved Zn from the water column of the lake.

Calculations were done using the computer program AQUASIM (Reichert, 1994), which allows for simulations of aquatic systems. Discharge and dissolved concentrations in the rivers for three water years (WY1999-2001; note that water year 2000 runs from October 1, 1999 to September 30, 2000) were used (Brennan and others, 1999; Brennan and others, 2000; Brennan and others, 2001) (fig. 13). Discharge during the 3 water years was variable; WY2000 had 90 percent of the discharge of WY1999, whereas WY2001 had only 37 percent of the discharge of WY1999.

Several assumptions were made in the modeling:
1. The inflow is equal to the outflow; in other words, the volume of the lake does not change over time. This assumption is a good approximation because the lake volume changes by less than 9 percent throughout the year (Woods and Beckwith, 1997).

2. The volume of the lake is 2.8 x 10^{12} L and the surface area of the lake-bottom sediment is 1.08 x 10^{12} cm^2 (Woods and Beckwith, 1997).

3. The exchange of dissolved Zn across the sediment-water interface is by molecular diffusion; therefore, a molecular diffusion coefficient is used to describe this process. This assumption is supported by the work of Kuwabara and others (2000). The average value of the molecular diffusion coefficient of dissolved Zn at bottom water temperatures in Lake Coeur d'Alene is 0.279 cm^2 per day (Li and Gregory, 1974; Balistrieri, 1998).

4. A range in the concentration of dissolved Zn in the porewater just below the sediment-water interface is used to calculate the input of dissolved Zn to the lake by benthic fluxes. Dissolved Zn concentrations of 1,070 (25th percentile), 1,210 (median), and 1,650 (75th percentile) mg/L are used, based on 10 published values (Balistrieri, 1998; Kuwabara and others, 2000); these concentrations do not vary seasonally in the model calculations.

5. Scavenging of dissolved Zn to particulate Zn and subsequent sedimentation is described by a first-order rate coefficient (k_{scav}), and scavenging of dissolved Zn derived from the riverine input is the same as scavenging of dissolved Zn derived from the benthic flux source. In other words, there is no difference in the chemical behavior or speciation of dissolved Zn from the two sources.

Model results depend on the formulation of the model (for example, the processes considered and their parameterization) and the measured data that are used. Assuming that all of the important processes are incorporated into the model, then the most reliable data are the physical characteristics of the system such as lake volume and surface area of sediment, the measured discharge and dissolved Zn concentrations for the inflows and outflow, and the molecular diffusion coefficient for dissolved Zn. The least well known data are the porewater concentrations of dissolved Zn, which determine the benthic flux, and the parameterization of the removal of dissolved Zn from the water column. Little information is available on spatial values and no information on seasonal values of dissolved Zn in the porewater just below the sediment-water interface in Lake Coeur d'Alene. The removal of dissolved Zn from the water column is assumed to be by transformations to the particulate phase and settling of particles. No sediment trap data are available to support this assumption. In addition, this removal is assumed to follow first-order kinetics. Limited information from in situ microcosm studies in lakes suggests that removal of dissolved metals from the water column follows a first-order rate equation (Santschi and others, 1986; Anderson and others, 1987).

Model results indicate that the relative importance of inputs of dissolved Zn to Lake Coeur d'Alene from rivers and benthic flux varies through the year and from year to year (fig. 14A,B). The benthic flux contribution to dissolved Zn concentrations in the lake was larger than the river contributions during October of the first two water years (WY99-WY00); otherwise, contributions from the inflowing river dominated. During WY01, which was a low-discharge year, the supply of dissolved Zn to the lake by benthic flux dominated during the first 6 months (October through March), whereas the supply from inflowing rivers was dominant

during the subsequent 4 months (April through July). Benthic flux was the primary input of dissolved Zn to the lake for the remainder of the water year. Low discharge results in less input of dissolved Zn to the lake from rivers and a higher proportion of input from benthic flux. In addition, the relative importance of sources of dissolved Zn to the lake will change as cleanup efforts within the mining district and lower Coeur d'Alene River valley proceed.

Values of the first-order scavenging rate coefficient that are needed to fit the measured dissolved Zn concentrations in the outflow (Spokane River) range by a factor of 46, from 0.0005 to 0.023 per day (fig. 14*C*). The highest values of this coefficient were determined in the third or fourth quarter of the water year and slightly precede the minimum in dissolved Zn concentration. For comparison, values of scavenging coefficients for dissolved Zn from whole-lake experiments and microcosm studies using radiotracers range from 0.03 to 0.06 per day (Santschi and others, 1986; Anderson and others, 1987). These values are at the high end of values determined by the modeling of dissolved Zn in Lake Coeur d'Alene.

What processes are responsible for variations in the scavenging rate coefficient? Scavenging rate coefficients encompass the partitioning of metal between dissolved and particulate phases and the settling velocity or flux of particles (Sigg, 1985). Partitioning between dissolved and particulate phases can be described by a distribution coefficient and is a function of the particle type, particle concentration, pH, ionic strength, and temperature of the system. Scavenging rate coefficients are largest when dissolved metals have a strong affinity for particulate phases and the flux of particles in the system is large. Some insight into variations of scavenging rate coefficients for Zn is given by work done in a lake in Switzerland (Sigg and others, 1996). Although they examined a relatively pristine lake relative to Lake Coeur d'Alene (Lake Greifen, Switzerland, where Zn concentrations are 0.65-2.6 mg/L), the chemical behavior of Zn should be similar in the two lakes. Using sediment trap data, they found that the sedimentation of Zn (or transformations from dissolved to particulate phases and subsequent settling) was related to sedimentation of algae and manganese dioxide. Because primary productivity is seasonal, they observed corresponding seasonal variations in sedimentation of Zn. About 87 percent of the dissolved Zn that enters Lake Greifen is trapped within the lake, compared to 56 percent in Lake Coeur d'Alene. Sigg and others (1996) concluded that biological mechanisms of uptake and binding are significant for the removal of dissolved Zn from the water column in Lake Greifen. The largest scavenging rate coefficients for dissolved Zn determined for Lake Coeur d'Alene occur during periods when the maximum in biological productivity would be expected. Further work is needed to understand the mechanisms and the role of biology in controlling transformations of dissolved to particulate Zn in Lake Coeur d'Alene.

What is known about impacts of Pb and Zn to biota, and can specific processes that influence bioavailability be identified?

The health impacts of mining in the Coeur d'Alene River basin on humans and other biota are highly dependent on the phase of the metal. The critical phase for Pb is the particulate form,

whereas for Zn it is the dissolved form.

Some of the highest levels of Pb in the blood of children in the United States were measured in the Coeur d'Alene mining district around the Bunker Hill smelter and the eventual Superfund site (fig. 15). The primary pathway of Pb into human blood is ingestion of Pb-enriched particles that are soluble in the stomach. Solubility of the particles depends on the speciation of Pb in the solid phase (Ruby and others, 1992; Gasser and others, 1996). In 1974, one year after a fire destroyed the air emission controls on the Bunker Hill smelter stack, 98 percent of children 1 to 9 years old in the area around the smelter had blood Pb levels >40 mg/dL (U.S. Environmental Protection Agency, 1994). Emergency response actions (for example, education about hygiene, smelter closure, and yard remediation) resulted in lower blood Pb levels, most of which are now below the maximum recommended level of 10 mg/dL. However, recent studies of blood Pb levels in children living outside of the Superfund site, but within the Coeur d'Alene River basin, indicate that about 15 percent of children between the ages of 9 months and 9 years have higher than recommended levels of Pb in their blood (TerraGraphics Environmental Engineering and others, 2001). Warnings of potential human exposure to high concentrations of metals in sediment and fish and related health impacts are posted at recreational beaches along the lower Coeur d'Alene River, Coeur d'Alene Lake, and Spokane River.

High concentrations of Pb in surface sediments within the basin and dissolved Zn in rivers also have proved harmful to terrestrial and aquatic wildlife. The metal-enriched marshes within the lower Coeur d'Alene River valley are prime resting and feeding areas for migratory birds, and deaths related to Pb poisoning during feeding in this area have been reported for waterfowl (Beyer and others, 1998). High dissolved Zn concentrations in the South Fork of the Coeur d'Alene River and its tributaries have prevented the re-establishment of a viable fishery, despite attempts to improve fish habitat in streams (T. Maret, unpublished data, 1999).

Factors that affect the geoavailability and, ultimately, bioavailability of Pb are linked to the speciation of Pb in the solid phase, which depends on the redox conditions of the depositional environment. The impact of Zn on biota depends on the mobilization of this element from metal-enriched tailings and subsequent transport and reaction between ground water and surface water.

What are the major gaps in knowledge remaining from this research?

1. Quantitative and predictive dynamic models are needed that provide an understanding of the underlying mechanisms controlling the transport, reaction, and fate of Pb, Zn, and other elements in the Coeur d'Alene River basin and other large-scale systems affected by mining activities. Sensitivity tests with such models would provide information on the response of large-scale systems to natural and human-induced perturbations, would identify data gaps, and could be used to direct remediation and management of the systems.
2. The interrelationships among processes and factors responsible

for chemical speciation, mobilization, and transport of Pb, Zn, and other elements in the environment (geoavailability) and the uptake of Pb, Zn, and other elements by biota (bioavailability) need to be further defined.

3. The role of microorganisms in determining chemical speciation, geoavailability, and bioavailability for Pb, Zn, and other elements needs to be further evaluated.

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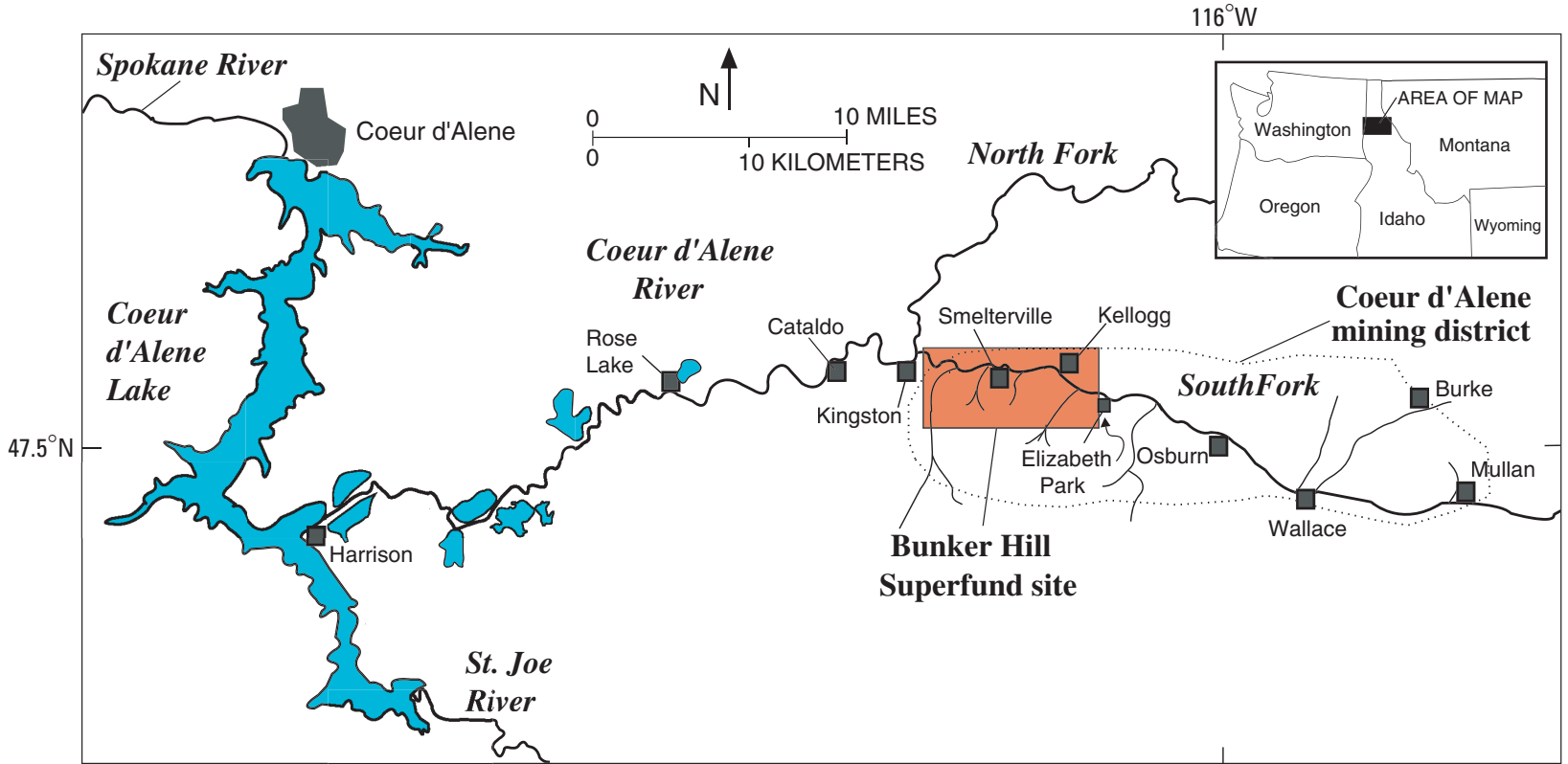
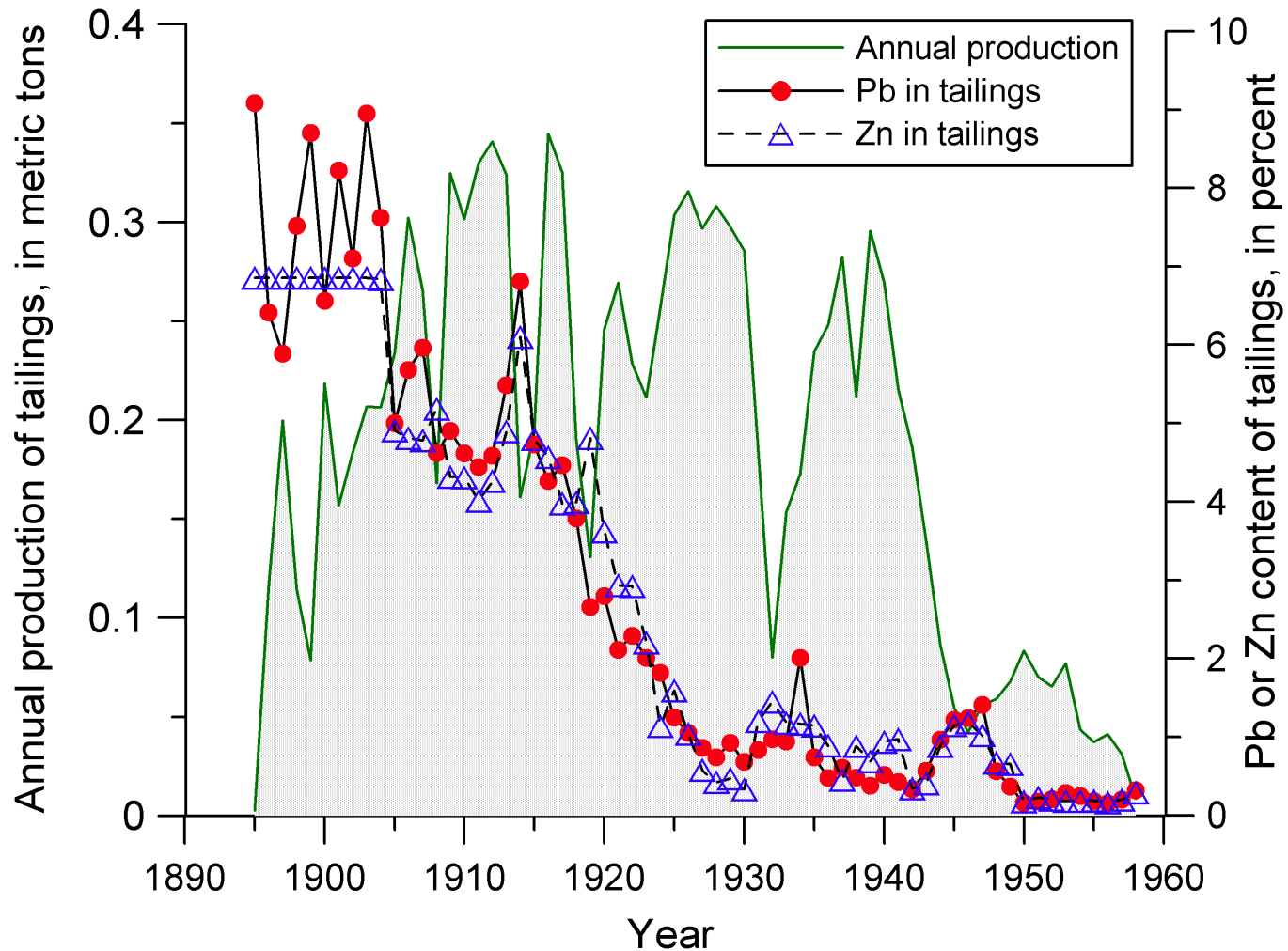Figure 1.—Index map of the Coeur d'Alene River basin. The dark squares are towns.

Figure 2.—Annual production in metric tons and percent metal content of tailings produced at the Morning Mill from 1895 to 1958. Unpublished data from K. Long, U.S. Geological Survey.
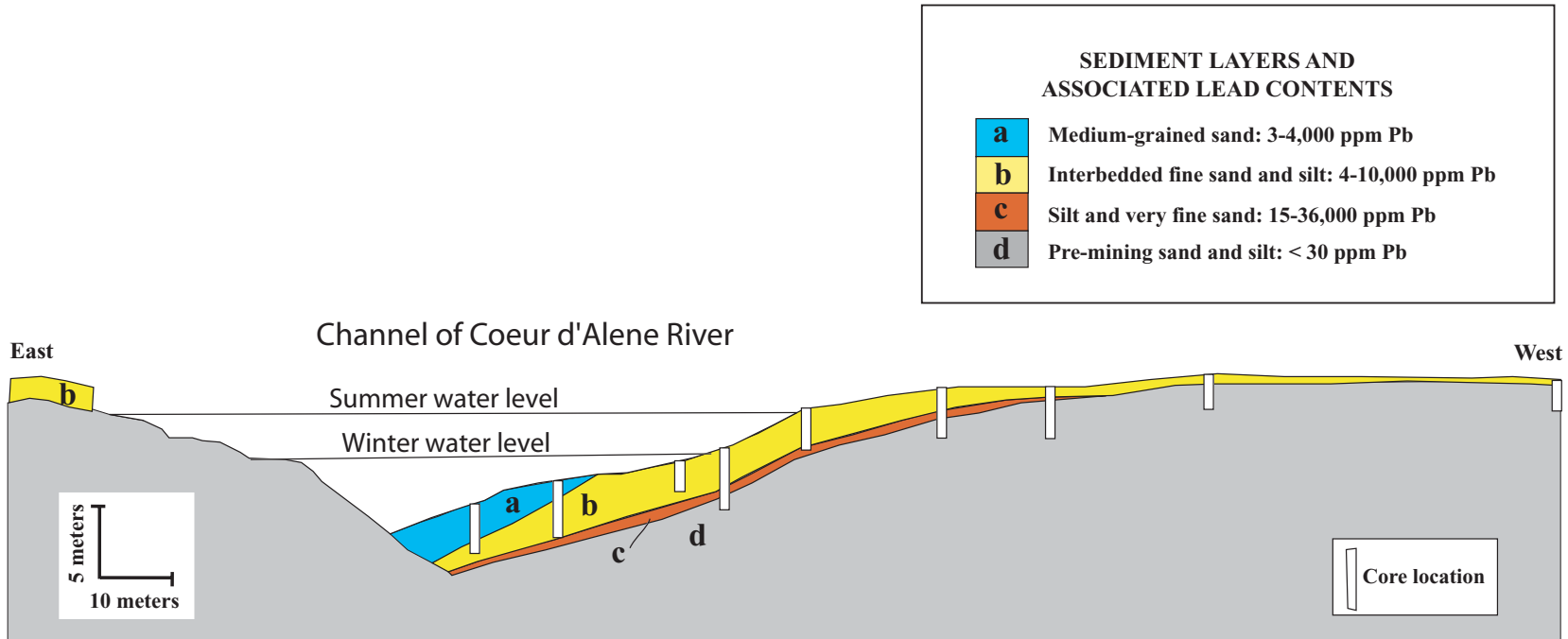
SEDIMENT LAYERS AND ASSOCIATED LEAD CONTENTS

a Medium-grained sand: 3-4,000 ppm Pb

b Interbedded fine sand and silt: 4-10,000 ppm Pb

c Silt and very fine sand: 15-36,000 ppm Pb

d Pre-mining sand and silt: < 30 ppm Pb

Channel of Coeur d'Alene River

East

West

Summer water level

Winter water level

5 meters

10 meters

Core location

Figure 3.—Stylized cross section showing the Pb content of sediments in cores from the floodplain and channel of the Coeur d'Alene River near Killarney (between Rose Lake and Harrison). Data from Box and others (2001).
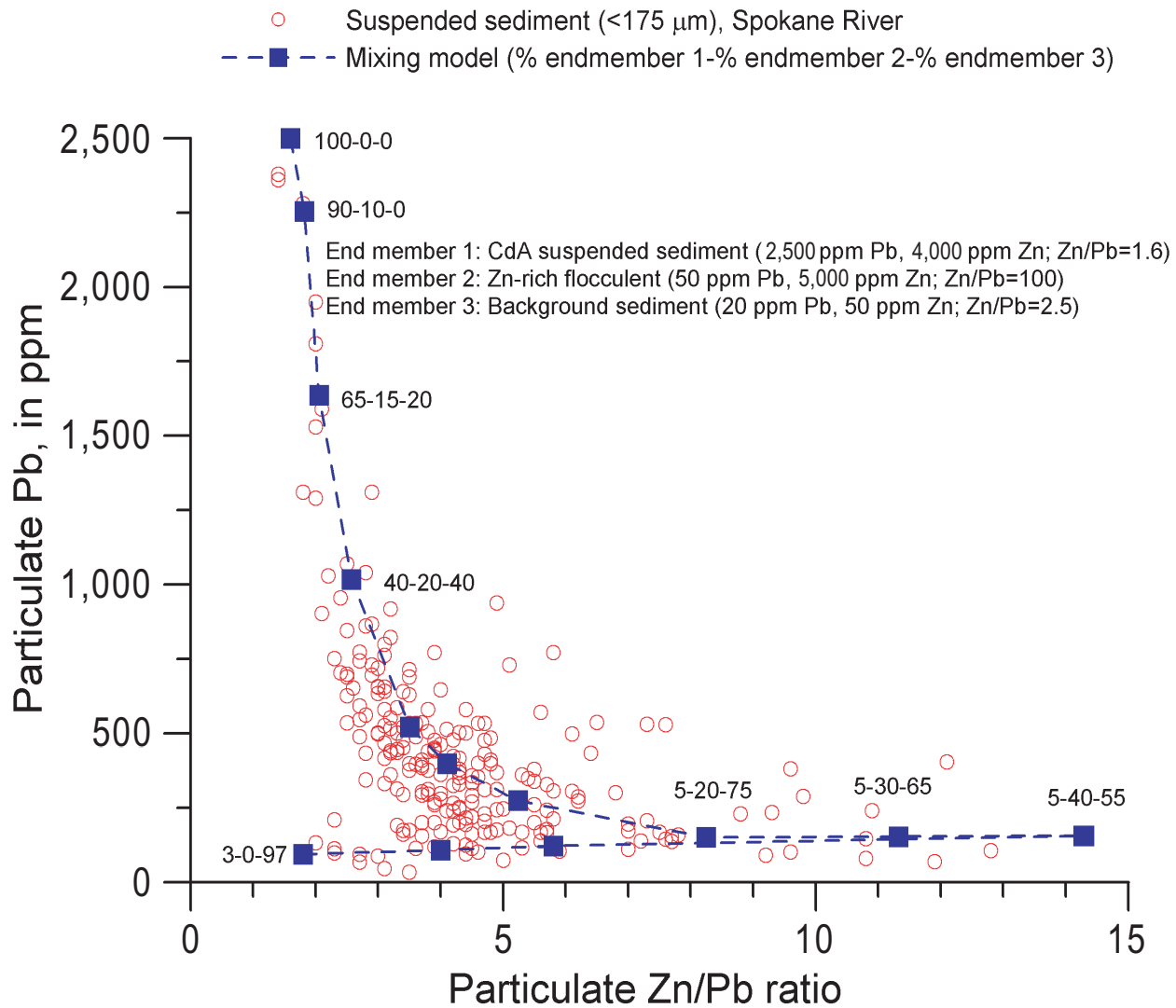
Figure 4.—Pb concentrations and Zn/Pb ratios in the <175 mm fraction of bed sediment in the Spokane River compared to results of a mixing model involving three different sources of sediment.
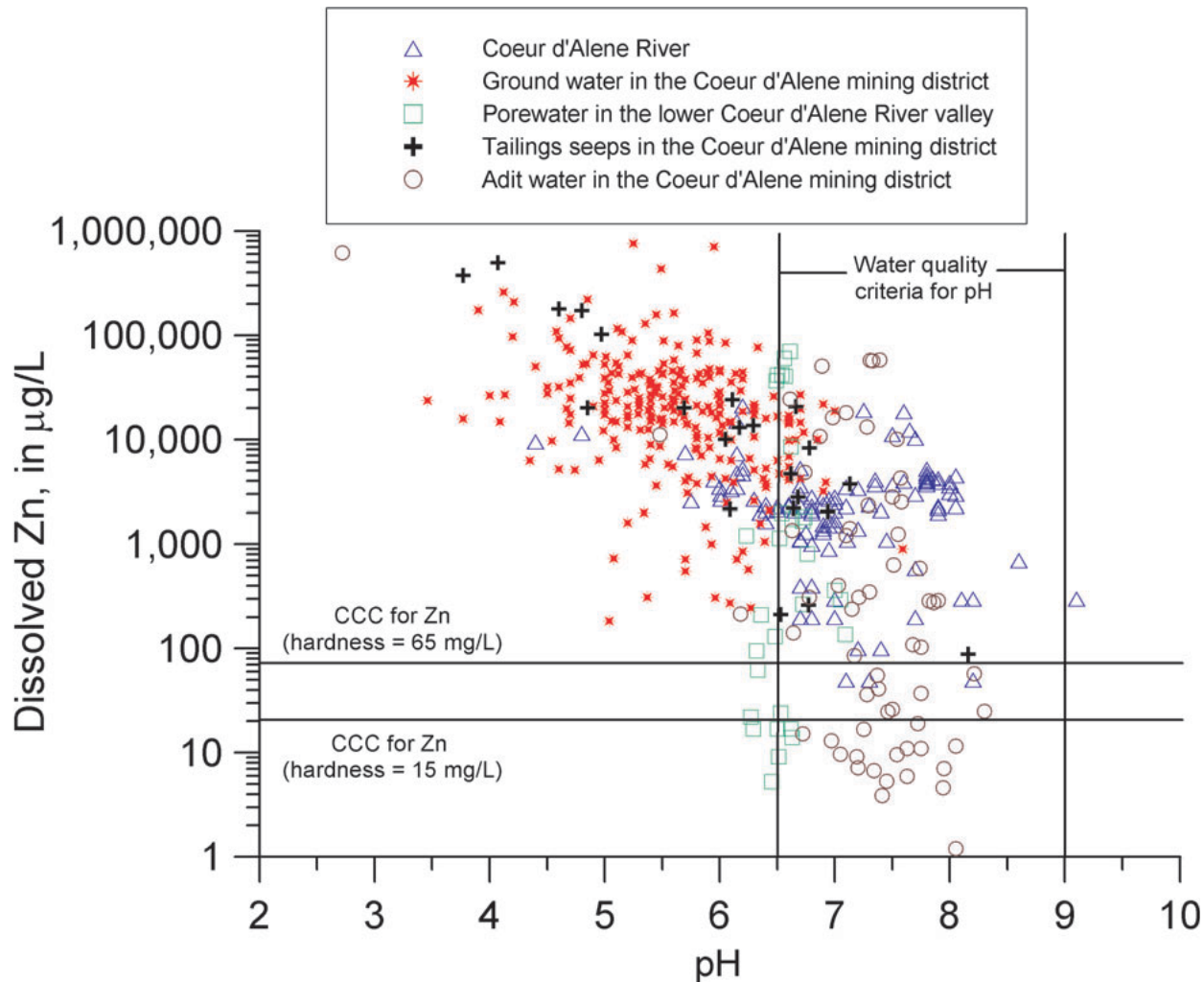
Figure 5.—Dissolved Zn concentrations and pH values in river water, ground water, porewater, tailings seeps, and adit drainage in the Coeur d'Alene River basin. Also shown are water quality criteria for pH and Criterion Continuous Concentration (CCC) for Zn, which is the highest concentration of total recoverable Zn to which aquatic life can be exposed for an extended period of time (4 days) without deleterious effects in Idaho water. See text and table 1 for data sources.
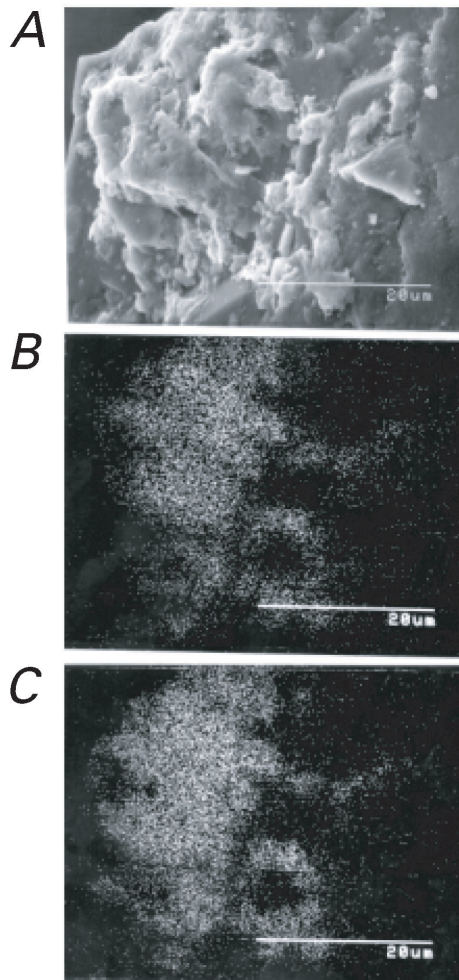
Figure 6.—Scanning electron microscope (SEM) image and X-ray intensity maps of a single detrital silicate grain coated with Pb/Fe/Mn oxide from the surficial floodplain soil in Smelterville Flats. *A*, SEM image. *B*, X-ray intensity map of Pb. *C*, X-ray intensity map of Mn. Images suggest that Pb is primarily associated with Mn oxide.
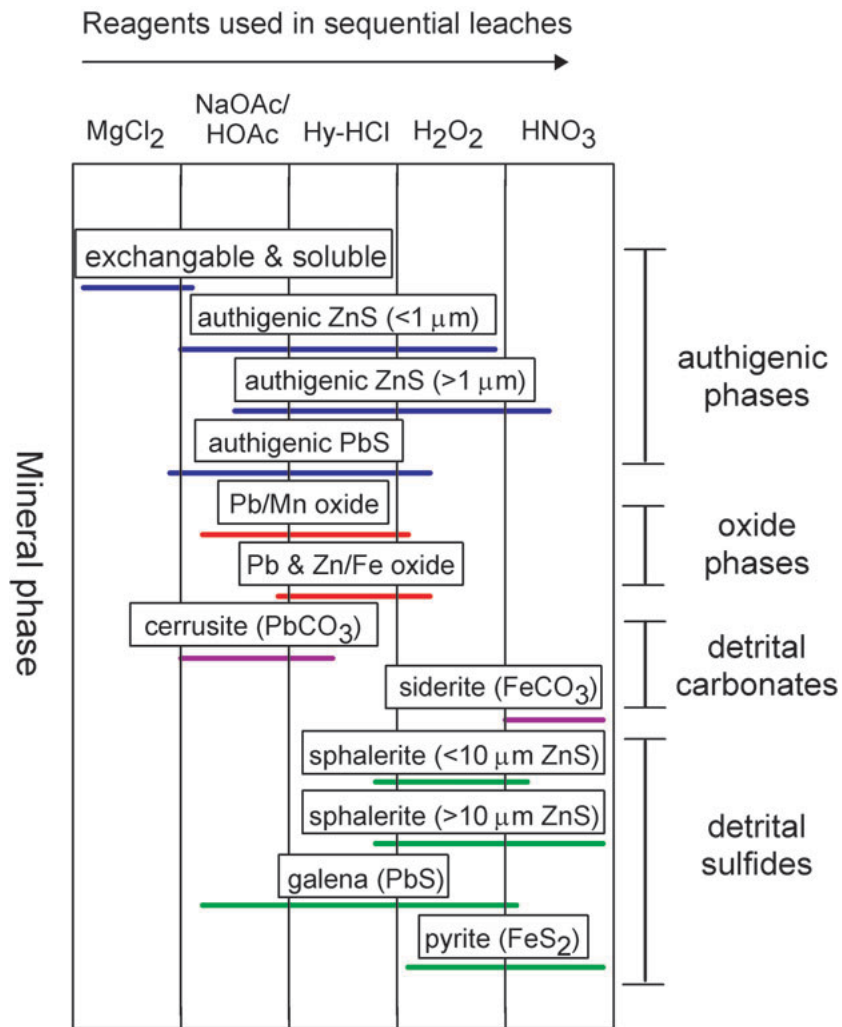
Figure 7.—Calibration of a sequential extraction scheme based on the method of Tessier and others (1979) by mineralogical analyses after each extraction step of particles collected in the Coeur d'Alene River basin.

RIVER CHANNEL (8-10 cm depth)
Total extractable Pb = 14,000 ppm
Total extractable Zn = 11,850 ppm

LEVEE TOP (25-27 cm depth)
Total extractable Pb = 2,360 ppm
Total extractable Zn = 3,240 ppm

WETLAND
Total extractable Pb =
   3,180 ppm (0-1 cm depth)
   3,470 ppm (58-60 cm depth)
Total extractable Zn =
   5,500 ppm (0-1 cm depth)
   3,500 ppm (58-60 cm depth)
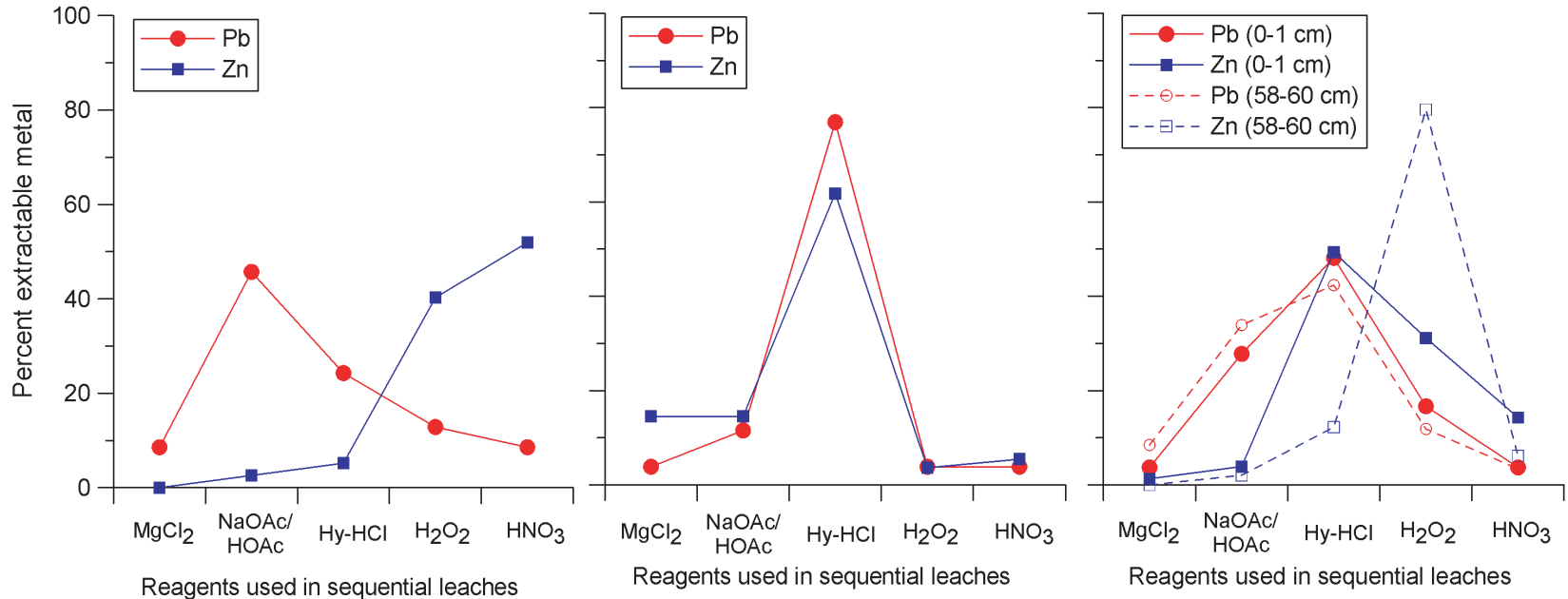
Figure 8.—Sequential extraction results for samples collected in the river channel, on top of levee banks, and in wetlands in the lower Coeur d'Alene River valley.
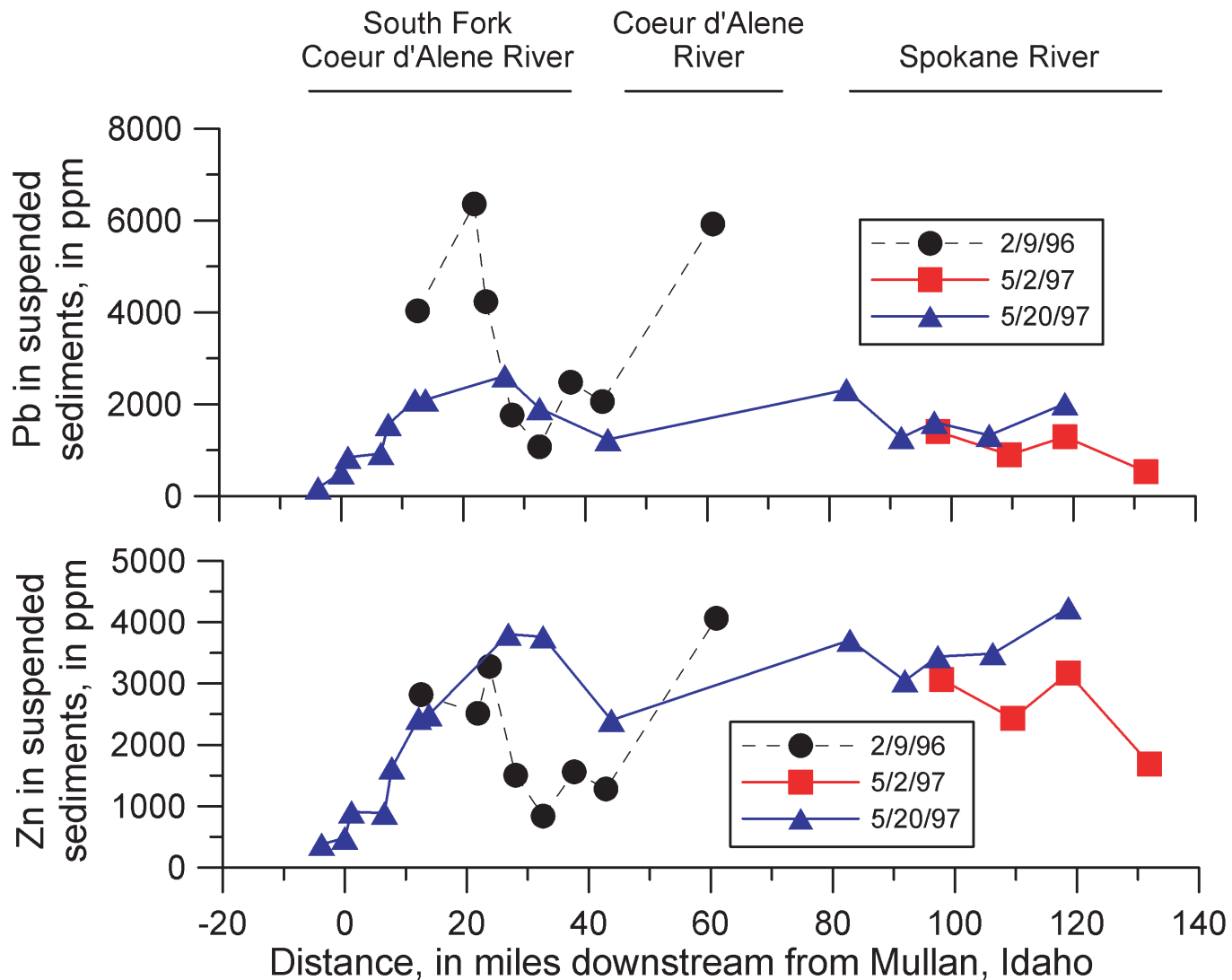
Figure 9.—Comparisons of the Pb and Zn contents of suspended sediments during the spring floods in 1996 and 1997 in the Coeur d'Alene River basin. The 1996 flood was larger than the 1997 flood.
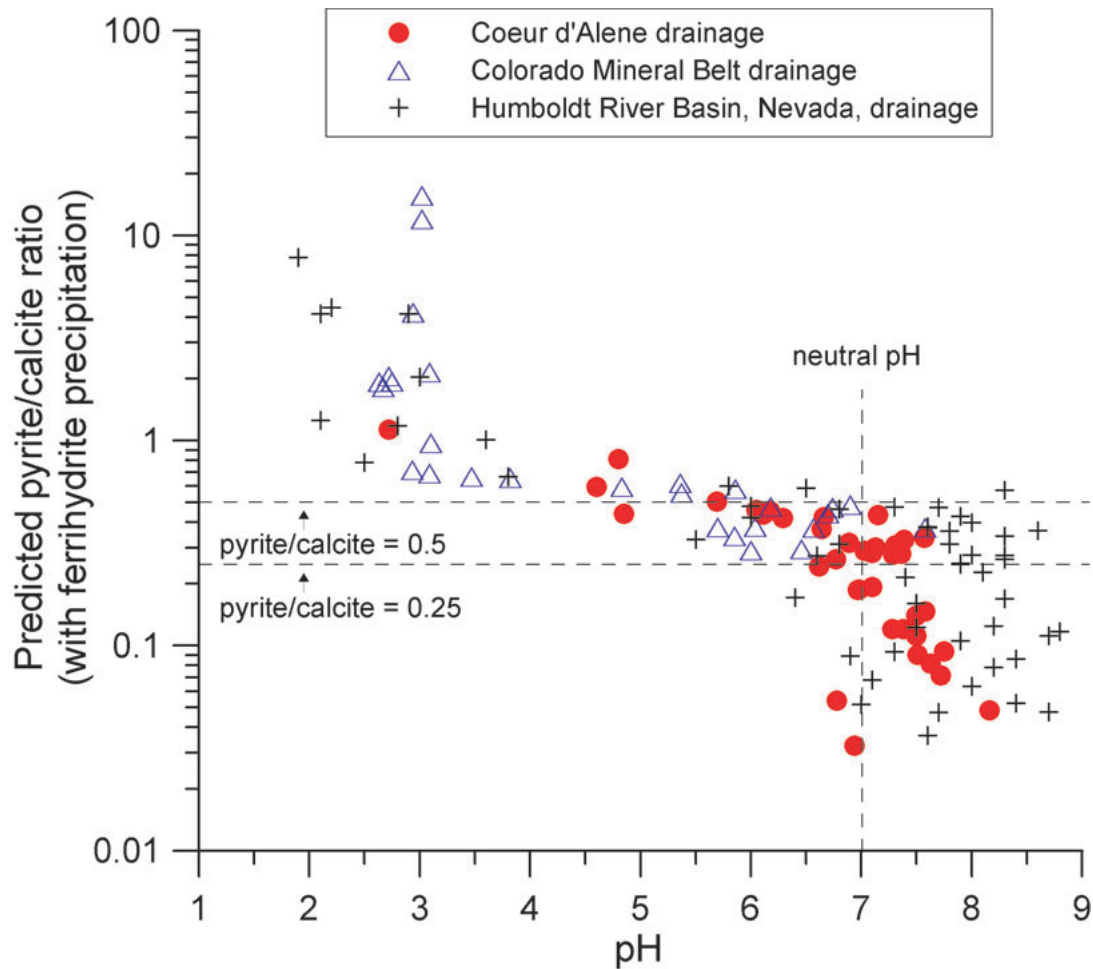
Figure 10.—Comparisons between the predicted ratio of reacting pyrite-to-calcite minerals (considering pre-cipitation of ferrihydrite and calculated as pyritic SO4/(Ca + Mg) in drainage) and pH in drainage from polymetallic veins in the Coeur d'Alene mining district, the Colorado Mineral Belt, and Humboldt River Basin, Nevada. See text for data sources.
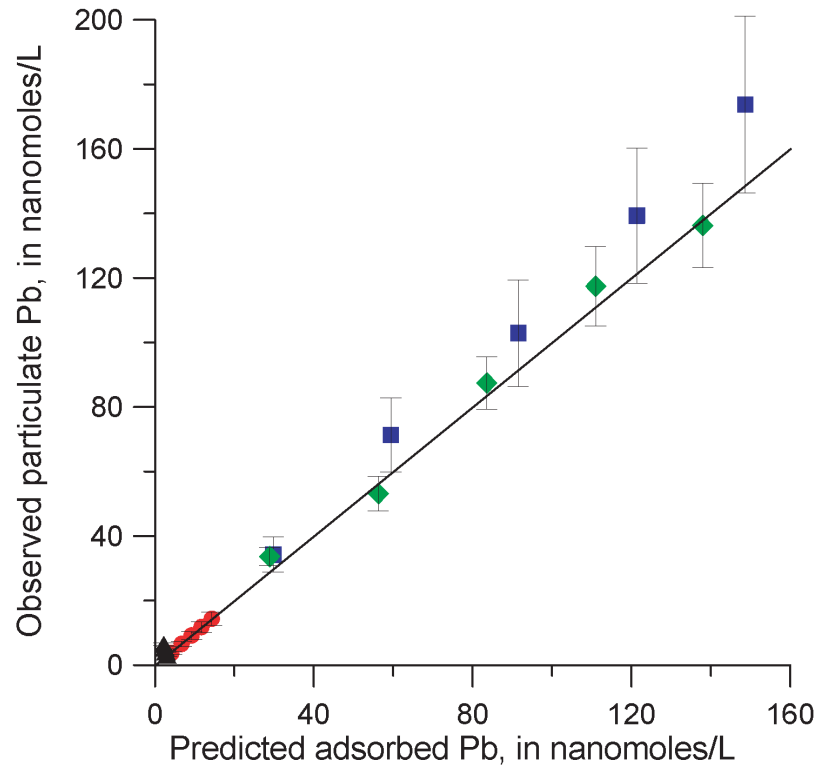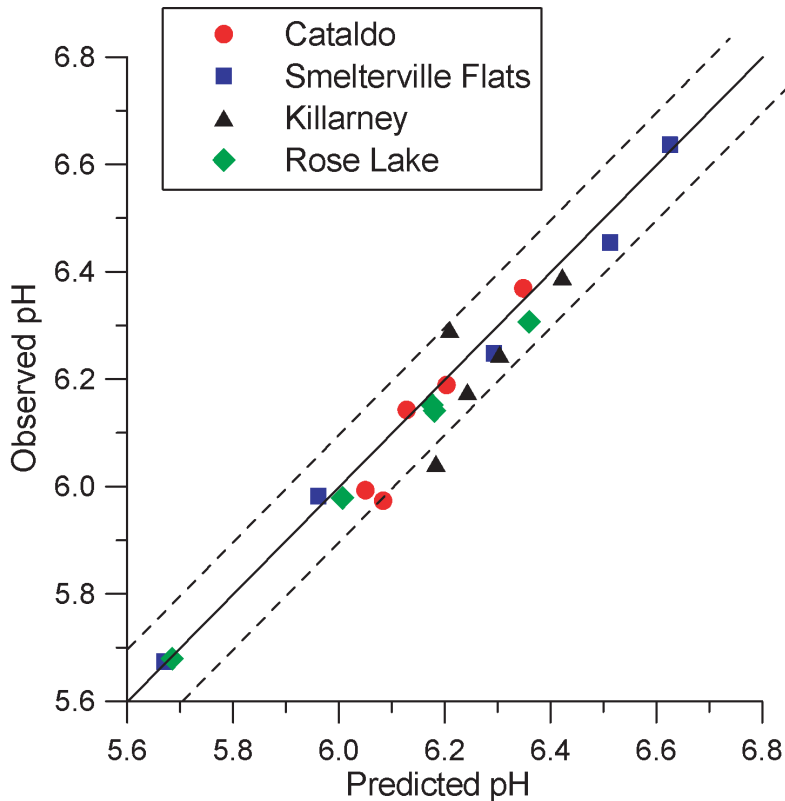
Figure 11.—Comparison of measured and predicted values of pH, and of Pb adsorbed on Fe precipitates formed, during the mixing of Coeur d'Alene River water and porewater from metal-enriched sediments near the river's edge in Cataldo, Smelterville Flats, Killarney, and Rose Lake. Errors bars on measured particulate Pb data are propagated error in calculating particulate concentrations from initial and final dissolved Pb concentrations in the mixing experiments. Model predictions were made using PHREECQC (Parkhurst and Appelo, 1999) and a sorption database for ferric oxide (Dzombak and Morel, 1990).
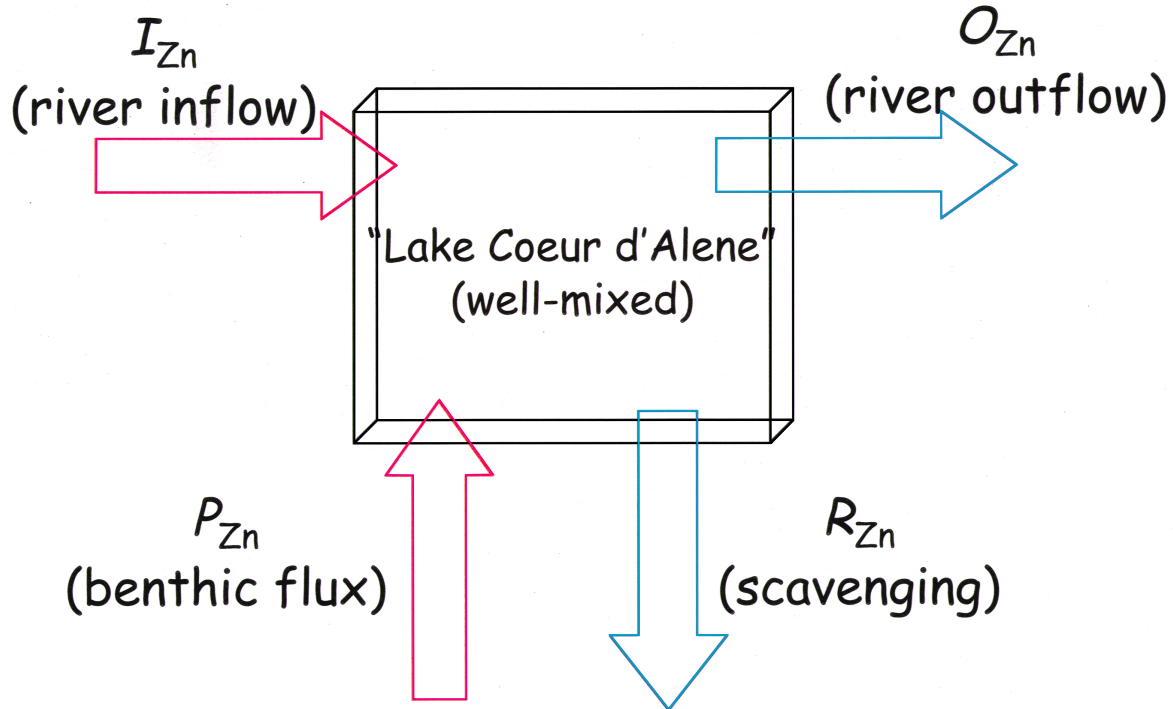
Figure 12.—A one-box model depicting the processes considered in modeling dissolved Zn concentrations in Lake Coeur d'Alene.
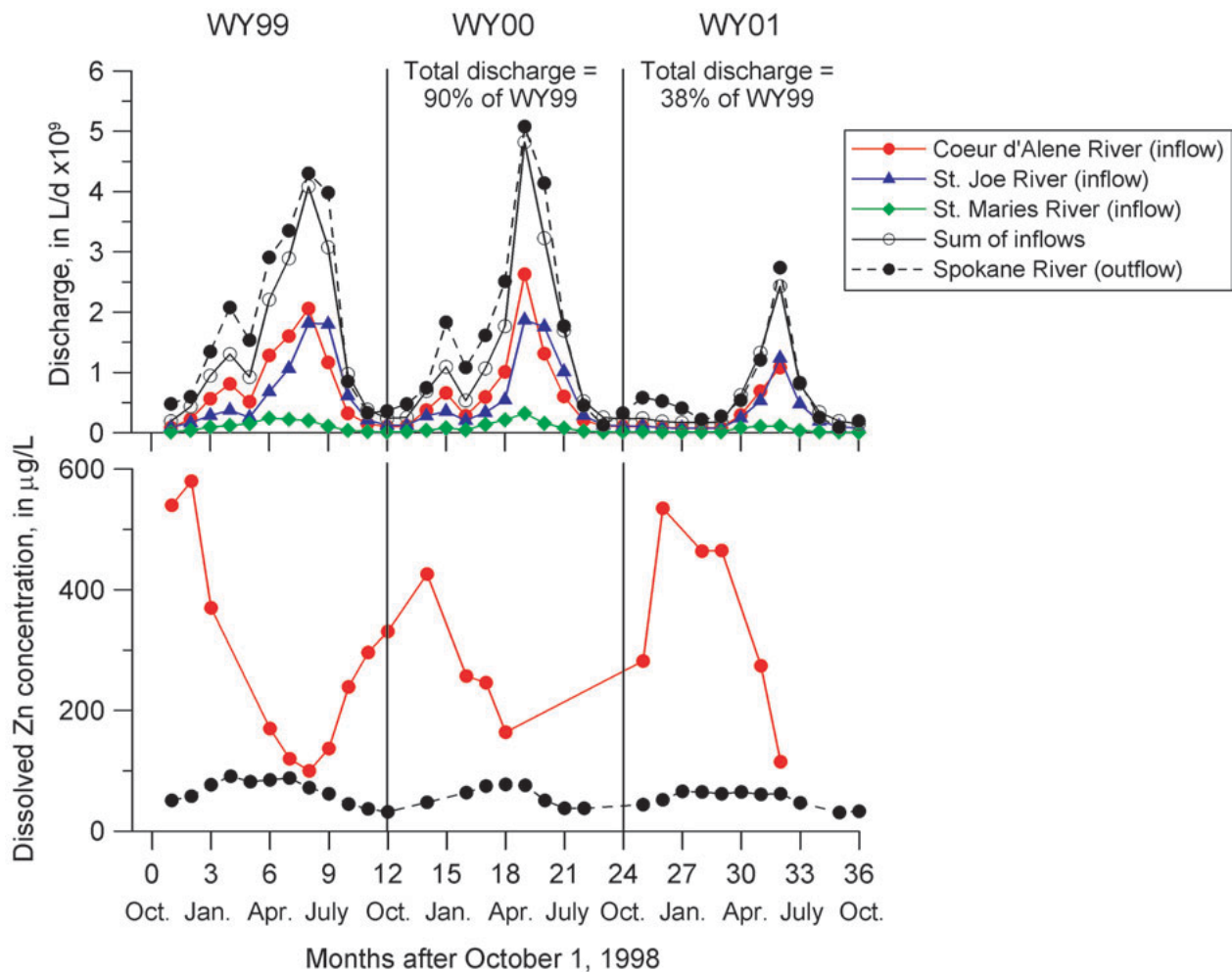
Figure 13.—Discharge data and dissolved Zn concentrations for rivers entering and leaving Lake Coeur d'Alene during water years (WY) 1999-2001. Concentrations of dissolved Zn in the St. Joe and St. Maries Rivers are not shown and typically were below published detection limits of <1 or <20 mg/L (note: detection limits varied over time); when detected, concentrations in these rivers were <4 mg/L.

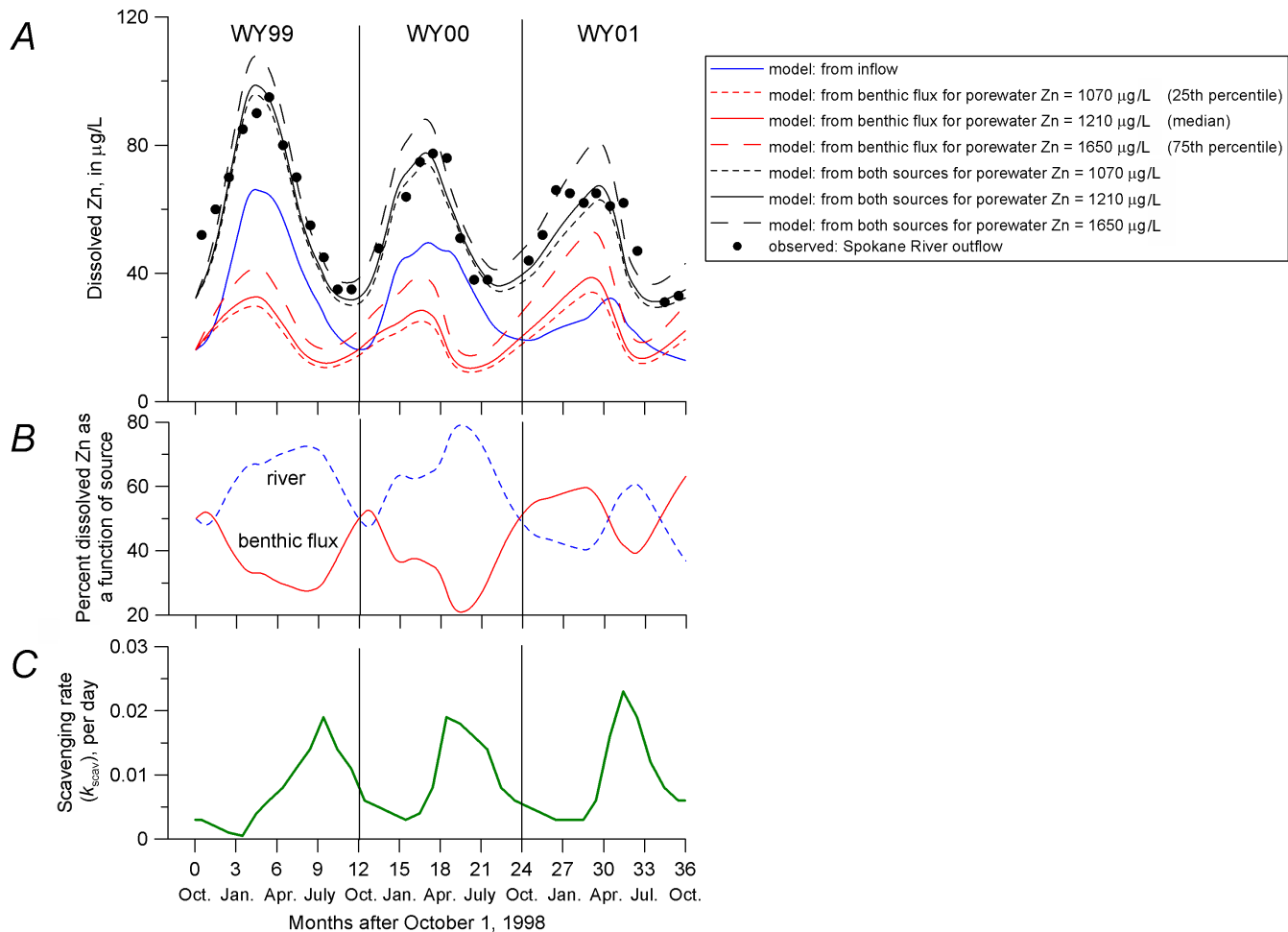# Measured and modeled dissolved Zn concentrations

Figure 14.—Results of box model calculations for dissolved Zn in Lake Coeur d'Alene. *A*, Comparisons of measured and modeled dissolved Zn concentrations as a function of water years (WY) 1999 through 2001, taking into account variable discharge and dissolved Zn concentrations in the inflow and outflow and benthic fluxes. Concentrations of dissolved Zn as a function of time in the St. Joe and St. Maries Rivers were assumed to be constant at a value of 1.5 mg/L for the model runs. *B*, Relative contributions of dissolved Zn to the lake from inflowing rivers and from benthic flux. *C*, Model values for the scavenging rate coefficient (kscav) that fit observed dissolved Zn concentrations in the outflow.
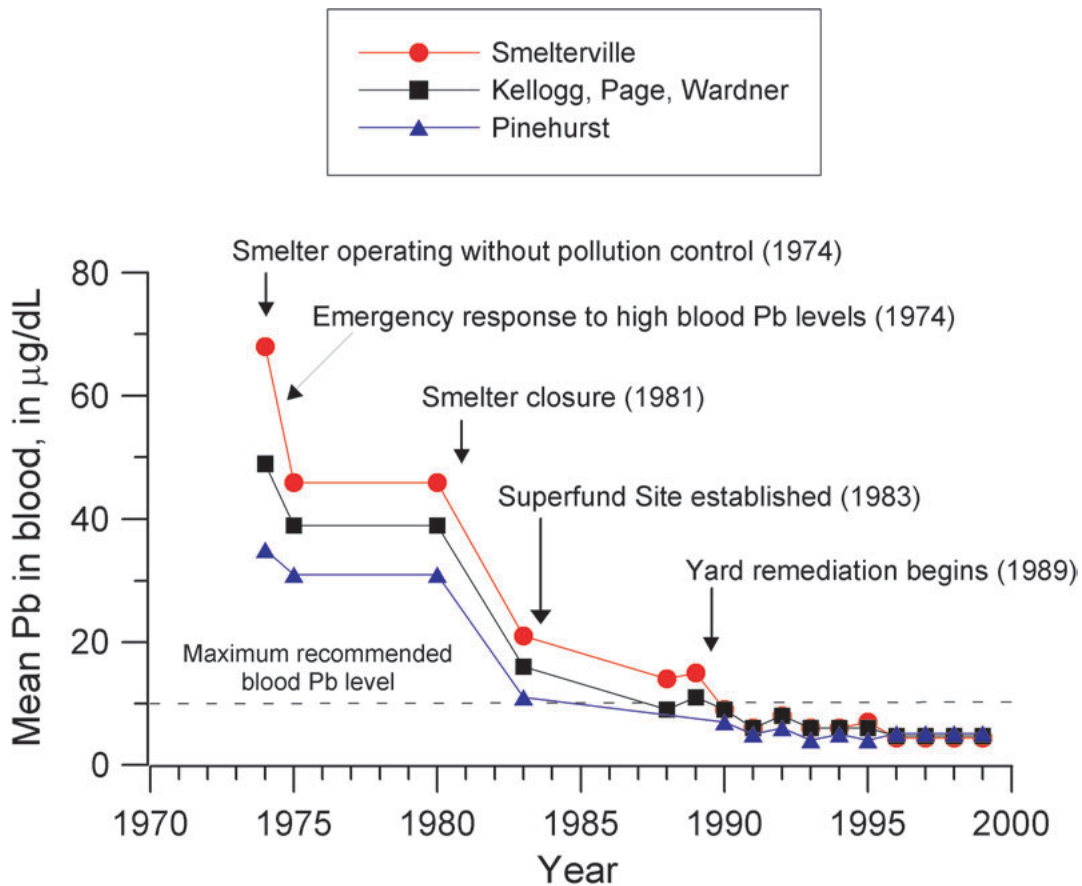
Figure 15.—Concentrations of Pb in the blood of people living within the Bunker Hill Superfund site as a function of time. Data from U.S. Environmental Protection (EPA) web page (www.epa.gov), search on Bunker Hill Superfund. The U.S. Environmental Protection Agency (EPA) and Centers for Disease Control and Prevention (CDC) determined that concentrations of Pb in blood at or above 10 mg/dL present risks to the health of children.

Table 1.—Range and median values of pH and dissolved Zn concentrations in waters in the Coeur d'Alene (CdA) River Basin.

[Data sources: Mink and others, 1971; U.S. Geological Survey, 1973; McCulley Frick and Gillman, 1994; Balistrieri and others, 1998; Golder Associates, 1998; Terragraphics Environmental Engineering, 1998; S.E. Box, unpublished data, 1999; Balistrieri and others, 2000; McCulley Frick and Gilman, 2000.]

Water type	Number of samples	pH		Dissolved Zn (mg/L)	
		Range	Median	Range	Median
Ground waters	246.	3.5-7.6	5.61	0.18-759	38.
Tailings seeps	26.	3.8-8.2	5.93	0.09-498	66.
Porewaters	30.	6.2-7.1	6.57	0.005-70	10.
Adits:					
Kellogg Tunnel	1.	2.7		615	
All other adits	61.	5.5-8.3	7.34	0.001-58	5.8
CdA River	117.	4.4-9.1	7.05	0.05-21	3.4

Table 2.—Summary of mineralogical and leach studies of particles in the Coeur d'Alene mining district.

Location	Smelterville Flats	Smelterville Flats	Osburn Flats	Osburn Flats	Upper Woodland Park	Upper Woodland Park
Environment	floodplain	channel	floodplain	channel	floodplain	channel
Sample number	201	202	203	204	205	206
Total Pb (ppm)	18,500.	5,760.	34,600.	4,665.	123,800.	5,670.
Total Fe (%)	16.	5.3	17.	7.9	14.	7.3
Total Mn (ppm)	11,720.	3,765.	17,530.	5,160.	2,485.	3,275.
SEM/EDS and XRD[1]						
Bulk - metallic minerals						
Major		dispersed Pb, Mn-Pb ox	Pb-Mn ox	Cer, Pyr	Ang	Pb-Fe ox, dispersed Pb
Minor	Mn-Pb ox, Pb-Mn-Fe ox	Zn-Pb-Fe ox		Pb-Fe ox, Mn-Pb ox	Fe-Pb ox, dispersed Pb	
Trace	Sph, Cer, Pyr	Sid, Cer, Sph	Sid, Pyr, Sph, Cer	Sid, Cer, Sph	Sph	Sid, Cer, Sph, Ang
Sequential extraction[2]						
% Pb in MgCl$_2$ leach	4.6	13.	5.5	3.3	39.	9.8
% Pb in NaOH leach	1.7	13.	1.6	11.	17.	16.
% Pb in EDTA leach	18.	35.	16.	35.	32.	35.
% Pb in HNO$_3$ leach	78.	38.	75.	50.	10.	40.
Gastric leach[3]						
% Pb	44.	73.	39.	61.	16.	76.
% Fe	.7	4.7	.7	2.3	.8	3.5
% Mn	4.5	26.	5.5	17.	1.2	30.

[1]Mineral abbreviations: ox = oxide, Sph = sphalerite (ZnS), Cer = cerrusite (PbCO$_3$), Pyr = pyrite (FeS$_2$), Sid = siderite (FeCO$_3$), Ang = anglesite (PbSO$_4$)
[2]Sequential extraction leaches (Gasser and others, 1996)
   1 M MgCl$_2$: easily soluble minerals such as Pb sulfate (Ang)
   0.5 M NaOH: organically complexed Pb and Pb carbonates (Cer)
   0.05 M Na$_2$EDTA: specifically adsorbed Pb, Pb oxides, Pb phosphates, and some amorphous Fe/Mn oxides
   4 M HNO$_3$: Pb sulfide (galena) and remainder of Fe/Mn oxides
[3]Gastric leach: 0.1M HCl/0.1M NaCl for 1 hr at 37°C (Gasser and others, 1996)