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Reconstructing the history of mining and remediation in the Coeur d'Alene, Idaho Mining District using lake sediments

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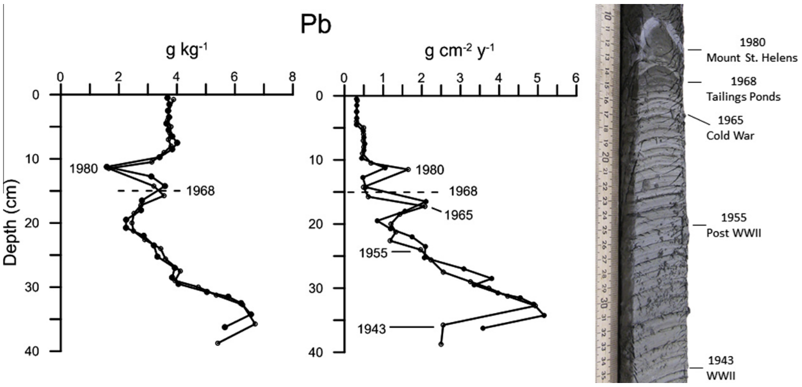
HIGHLIGHTS

- Lake Coeur d'Alene sediments are a record of mining contamination and remediation.
- Metal(loid) loading decreased after installation of tailings ponds.
- Arsenic concentrations show evidence of diagenesis.
- Sedimentary Cr and Pb concentrations remain at mining era levels.
- Improved management of tailings containing toxic Pb concentrations is required.

GRAPHICAL ABSTRACT



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ABSTRACT

Mining that began in the late 1800s intensified during World War II contaminating Lake Coeur d'Alene sediments with potentially toxic elements. We used 80 y of the sediment record to reconstruct metal(loid) loadings to the lake and quantitatively evaluate the effectiveness of tailings management. Sediment core analysis for pollen, chronological markers, and metal(loid)s permitted stratigraphic reconstruction showing that contaminant loading decreased after tailings pond construction, but that most metal(loid) concentrations exceed recommended limits. Arsenic concentrations (250–450 mg kg^{-1}) at the sediment–water interface are potentially toxic; however, low P concentrations in recent sediments (1.0–1.4 mg kg^{-1}) inhibit eutrophication and the concomitant release of soluble As. Zinc (3 g kg^{-1}), Cd (10 mg kg^{-1}), Ag (10 mg kg^{-1}), and Cu (90 mg kg^{-1}) concentrations are now lower than in sediments deposited during active mining, but remain an environmental concern. Sedimentary Cr and Pb concentrations have not changed in the last 50 y, because tailings continue to enter the lake. Although modern Cr concentrations (40 mg kg^{-1}) are unlikely to cause toxicity, current Pb concentrations (4 g kg^{-1}) exceed acceptable limits, creating challenges for remediation. Strategies to manage other mining-contaminated watersheds should include consideration of elemental differences when evaluating remediation effectiveness.

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1. Introduction

The Coeur d'Alene River Basin is home to one of the largest Superfund Sites in the United States, where soils and sediments are heavily contaminated by smelting and mining operations that began over a century ago. Mining in the area started with Au in the early 1880s, transitioning to Ag, Pb, and Zn with a boom of mill construction in 1888 that resulted in the dumping of waste materials containing large quantities Pb and Zn into the Coeur d'Alene River and its tributaries (National Research Council, 2005; Quivik, 2004). These waste disposal practices contaminated streams feeding into the Coeur d'Alene River, Lake Coeur d'Alene, as well as the floodplain (Fig. S1) (National Research Council, 2005).

Mine tailings began to cause environmental problems in the early 1900s, smothering downstream farmland and poisoning animals and plants (Casner, 1991). Complaints by residents prompted the construction of two impounding reservoirs in 1903, but downstream residents continued to experience environmental problems causing the Mining Association in 1932 to dredge the Coeur d'Alene River and transport the waste to an impound area (Quivik, 2004). Dredging was performed until 1968 when the last of the mills switched to using tailings impoundments.

In 1983 the U.S. Environmental Protection Agency (EPA) placed a 54 km^2 area, termed the Box, located near Smelterville, ID (Fig. S1) on the National Priorities List to address the impacts from mining contamination. This initiated an effort under the Comprehensive Environmental Response, Compensation and Liability Act to remediate contamination (National Research Council, 2005). Remediation of the Box that began in the early 1990s was expanded in 2002 to include the entire Basin excluding Lake Coeur d'Alene (National Research Council, 2005; U.S. EPA, 2000). Ongoing remediation is addressing both human health issues and environmental contamination through a 30 y interim remedy (U.S. EPA, 2002).

Despite remediation efforts, contaminated materials deposited to river banks and floodplains are remobilized and transported to Lake Coeur d'Alene with flooding and high flow events. Lake Coeur d'Alene retains some of these materials, while suspended sediments continue downstream through the Spokane River (Box et al., 2005; Donato, 2006). The deposition of materials on the lake bed provides a record of historical mining activities as well as depositional events occurring after the introduction of remediation, because little bioturbation occurs and sediment stratigraphy remains undisturbed (Horowitz et al., 1993; Kuwabara et al., 2000). Horowitz et al. (1992, 1993) were the first to comprehensively characterize the chemistry of Lake Coeur d'Alene, establishing that the sediments are enriched in metal(loid)s associated with mining inputs from the Coeur d'Alene River. Other research has determined that changing redox conditions within the sediments affect the mobility of elements (Balistrieri, 1998; Harrington et al., 1998; Kuwabara et al., 2000; La Force et al., 1999; Toevs et al., 2006, 2008). The bottom of the lake is oxic, transitions to suboxic conditions within the top few centimeters of the sediment–water interface, and is anoxic throughout the remaining sediment profile (Toevs et al., 2006). Toevs et al. (2008) established that depositional events bury what were once oxic sediments, transitioning them to an anoxic environment that alters metal(loid) solubility.

Previous investigations on Lake Coeur d'Alene sediments have characterized the extent of contamination and provided an understanding of geochemical relationships controlling metal(loid) solubilities; however, direct comparison of pre-remediation with post-remediation metal(loid) deposition to the lake has not been performed (Horowitz et al., 1992; Toevs et al., 2006). Such assessment is critical given that the last extensive sediment survey was conducted in 1990 and remediation efforts in the Basin have continued (Horowitz et al., 1992, 1993; National Research Council, 2005).

Our objective was to determine if remediation activities have quantitatively and qualitatively altered sediment deposition to Lake Coeur d'Alene by using detailed sediment stratigraphy to calculate historical trends in elemental concentration and loading. We have used an 80 y sediment record to assess the effectiveness of remediation, providing an unprecedented evaluation of how a mine-impacted site responds to decades of remediation efforts. The results of our investigation are applicable in guiding the management of numerous other mining-contaminated watersheds whether by way of active remediation strategies or by allowing for natural attenuation (Cidu et al., 2011).

2. Materials and methods

2.1. Sediment core collection and sectioning

Sediment samples were collected using a K-B gravity core sampler (Wildlife Supply Company, Yulee, FL) from Peaceful Point in Lake Coeur d'Alene, a site chosen based on previous research that showed extensive mining contamination from the Coeur d'Alene River (Horowitz et al., 1992, 1993; Toevs et al., 2006). Upon retrieval, cores were capped and placed in air-tight boxes filled with liquid N_2. Once on shore, the air-tight boxes were purged using N_2 and stored frozen until analysis. Core samples showed a distinct banded section in their lower portion and a light grey layer above the banded section (Fig. 1) in which glass particles indicative of volcanic ash from Mount St. Helens (Farlow et al., 1981) were identified microscopically.

The cores were removed from the tubes while frozen and split in half vertically using a band saw. The ash layer was sectioned from the cores as a discrete segment. The cores were sectioned upward toward the most recent sediments in 1 cm segments. Below the ash layer the cores were sectioned in 1 cm segments until the banded portion. Once the banded portion was reached, segments were cut along the dark layers of the banding to the bottom of the cores (Fig. 1). To ensure sufficient sample size for analysis, some segments contained multiple bands and ranged from 1–4 cm in thickness. Two cores were sectioned, one having a length of 37 cm and yielding a total of 28 segments and a second with a length of 47 cm yielding 32 segments.

A 3-cm segment of the banded section from a third core was chosen for pollen sampling. One sample was taken from each of the four dark layers, two from the most recently deposited light layer, and three from each of the two remaining light layers for a total of 12 samples.

2.2. Pollen analysis

A modified Faegi and Iversen method (Faegri et al., 2000) was used in which samples were mixed with HF and digested for 1 week, agitated with muriatic acid, and rinsed with deionized water. A detergent was added and samples were mixed with acetic anhydride plus H_2SO_4. Samples were rinsed with deionized water followed by acetic acid prior to staining using Saffranin O and ethanol. Samples were treated with increasing concentrations of ethanol (50%, 75%, and 100%) mixed with Saffranin O, the stain was drained, and toluene and silicon oil were added. Samples were dried at 200 °C for 1 week and pollen grains counted using a microscope.

Identified pollen grains were sorted by pollinating season: winter (December to early March); spring (late March through May); summer (June through August); and fall (September through

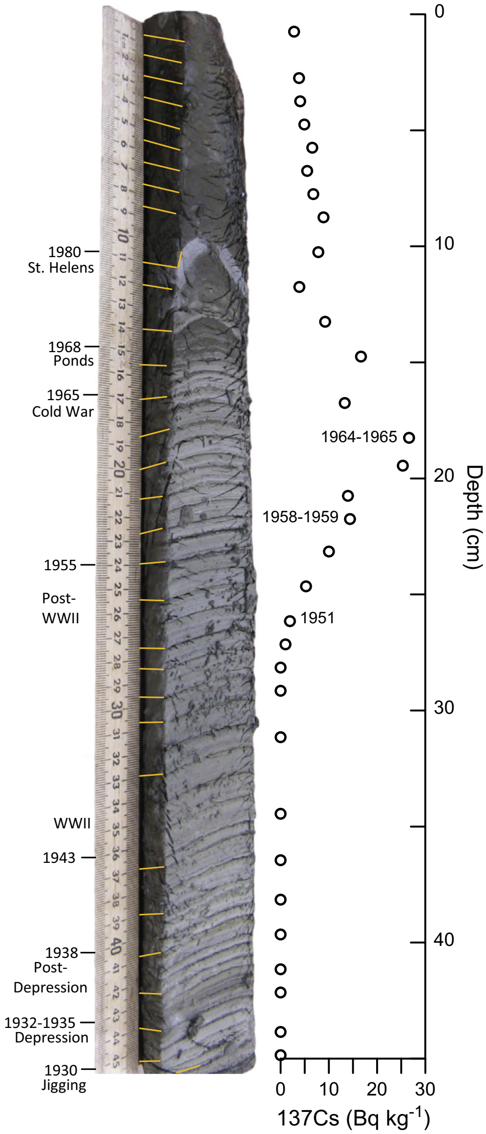

Fig. 1. Sediment core from Lake Coeur d'Alene showing important dates, orange lines indicating at which depths it was sectioned, and Cs-137 concentrations.

November). The percentages of winter, spring, summer, and fall pollen in each sample were calculated. Multiple samples obtained from each light band were treated as replicates and averaged. Pollen grains in the light and dark bands of the cores' banded sections were compared using a paired difference student's *t*-test and *p*-values of less than 0.05 were considered significant.

2.3. Radiocesium analysis

Frozen core segments were freeze dried and weighed for both radioisotope and elemental analyses. Samples were subjected to radioisotope analysis for Cs-137 by low-background gamma analysis. Shielded "Broad Energy" intrinsic germanium detectors (BE5030, Canberra Industries, Meriden, CT) were used with ultra-low background cryostats and remote detector chambers. Sample geometry was a 12 mL petri dish (BD Falcon 50 × 9 mm with tight lid) in which 10 g of sediment was counted for 24–48 h. The detectors were calibrated for Cs-137 efficiency using a solution containing a certified value (Eckert & Ziegler Isotope Products, Valencia, CA). Typical 1-sigma analytical errors were 4–9% depending in part on photopeak areas accumulated. The amount of Cs-137 activity in each segment was used to date the segments assuming that concentrations peaked in 1963–1964 (Appleby, 2001).

2.4. Sediment deposition

For the periods 1968–1980 and 1980–2010, the amount of deposition was divided by the number of years in the period. The years of deposition were calculated from the surface sediments to the ash layer using an average estimate of 0.33 cm of deposition per year. The ash layer was considered to include one year, 1980. Years of deposition of sediments deposited between the ash layer and the 1963 Cs-137 peak were calculated using an average estimate of 0.23 cm of deposition per year. Years of deposition within the banded section were based on the number of bands assuming that each dark/light band pair represents a single year.

2.5. Elemental analysis

The same samples used for age dating were sent to Acme Analytical Laboratories Ltd. (Vancouver, British Columbia (ISO 9001:2000 certified)) for total elemental analysis. Samples were heated in HNO_3–$HClO_4$–HF and taken to dryness, and the residue was dissolved in HCl and analyzed using ICP-ES. Dry bulk density for each segment of both cores was calculated by oven drying a known volume of sediment at 105 °C. Dry bulk density values for each segment were used to determine an average bulk density for each 5 cm depth increment (Table S1). Loading of each element was calculated using the following formula:

$$\frac{\text{concentration} \times \text{bulk density} \times \text{thickness of section}}{\text{years of deposition}}$$

2.6. Statistical analysis

Sediments deposited between 1968 and 2010 were divided into groups by depth to determine changes in elemental loading resulting from remediation efforts in the Basin post-installation of the tailings ponds. Details of the statistical analyses can be found in the Supplementary material.

3. Results and discussion

3.1. Pollen analysis

Thirty-two types of pollen (Table S2), 14 types of spores, three types of algae, as well as organismal remains were identified within the sediment samples. The organismal remains were observed in higher quantities in the dark than the light layers. There were no observed trends in the counts of spores and algae.

The percentage of winter pollen was higher in the light (44.9%) than the dark layers (19.5%) ($p = 0.01$), while summer pollen was higher in the dark (52.0%) than the light layers (21.4%) ($p = 0.00006$) (Fig. S2). There was no significant difference between the light and dark layers in spring and fall pollen, but there was a trend for more spring pollen in the light (27.2%) than the dark layers (18.9%) and more fall pollen in the dark (9.7%) than the light layers (6.4%).

The difference in deposition of seasonal pollen in the light and dark layers indicates the bands present in Lake Coeur d'Alene sediments are varves as previously presumed (Horowitz et al., 1995) and can be used to date the banded portion of the core (Ojala et al., 2012). The greater thickness and lighter color of the light layers coupled with a higher percentage of winter and spring pollen suggest these layers were deposited during winter and spring floods. The presence of summer and fall pollen in higher percentages in the dark layers indicates they were deposited during the drier seasons.

3.2. Age dating

The ash layer was determined to be composed of Mount St. Helens ash based on previous observations (Horowitz et al., 1993) and its elemental composition compared to that reported for material ejected in the eruption (Balistrieri, 1998; Farlow et al., 1981). Mount St. Helens erupted in 1980 (Lipman and Mullineaux, 1981), thus providing an age marker within the core at a depth of approximately 11.5 cm (Fig. 1). Previous research performed in 1990 and 2002 in the area of Peaceful Point (Horowitz et al., 1993; Toevs et al., 2006, 2008) was used to establish approximate time points within the 11 cm upper portion of the core by comparing the amount of sediment above the Mount St. Helens' ash layer and assuming an average deposition rate.

Radioisotope analysis showed the first detectable amount of Cs-137 near sediment depths of 27 cm indicating the initiation of large-scale above-ground weapons testing that began in 1951 (Figs. 1 and S3). This is consistent with the date associated with this depth as determined by varve counting. Cs-137 deposition increased after 1951, reaching high levels in 1958-1959, followed by the highest fallout rates in 1963–1964 (17 cm). The use of Cs-137 date assignments and varves in the cores indicate that the 37-cm core includes sediments that date to 1941 and the 47-cm core includes sediments deposited in 1924. Banding in the cores ceases at depths near 15 cm, corresponding to 1968 when mines implemented the use of tailings impoundments.

3.3. Sediment deposition and metal loadings

Historical production rates of total ore, Pb, and Zn are compared to sedimentation rates in Fig. 2. Maximum sedimentation rates of approximately 0.8 g cm^{-2} y^{-1} occurred at the end of WW II and during the post-WW II boom from about 1945–1950 at the same time that total ore production was at a maximum (Bookstrom et al., 2004). As total ore production decreased from 1950–1960, sedimentation rates showed an analogous decline. A peak in Pb production and a spike in sedimentation in 1964 were followed by a distinct drop in sedimentation in 1968 to 0.2 g cm^{-2} y^{-1} with the installation of tailings ponds. Sedimentation rates have remained relatively low at near 0.1 g cm^{-2} y^{-1}, except when ash was deposited from the 1980 eruption of Mount St. Helens.

Historical events and mining trends can be identified in elemental concentration and loading depth profiles of the sediments. Discussion of any changes in elemental concentrations with depth must consider how sediment texture and origin influence observed profiles. Particle size analysis indicates that sediment within the depth range sampled contains 80–90% silt (Toevs et al., 2008), thus making it unlikely that textural differences play a major role in explaining elemental concentration changes with depth. Origin of the materials as related to operations used during the period of active mining would have influenced historical elemental concentrations of the silt-sized materials deposited to the lake bottom. However during the more recent period of decreased mining activity and after the installation of tailings ponds, elemental concentrations of the sediment are controlled by characteristics of the eroded materials. Box et al. (2005) have shown that recent sources of the sediment are metal-enriched materials mobilized from the stream channel or floodplain depending on the size of the flood event.

Elemental concentration and loading depth profiles of the sediments demonstrating these historical events and mining trends are exemplified by Fe and S (Fig. 3). The deposition of Mount St. Helens' ash in 1980 caused an obvious change in Fe concentration and loading. Installation of tailings ponds in 1968 produced a dramatic decrease in loading for both Fe and S, consistent with a decrease in sedimentation rates. Times of peak ore production as occurred in 1930, 1938, 1943–1955, and 1965 (Fig. 1) are also obvious in loading profiles for Fe and S (Fig. 3). The maximum in S concentration that occurred in 1930 is particularly important, because it represents a period of intense mining activity when a relatively inefficient method of ore separation, jigging, was commonly used (Fig. 1) (Bookstrom et al., 2004). Changes in Fe concentration caused by remobilization and precipitation reactions are only evident in the sediment profile from 0–10 cm where oxidized sediments from 0–5 cm transition to reduced conditions that occur below 5 cm (Toevs et al., 2006) (Fig. 3), a trend best illustrated by As and Mn.

Changes in As and Mn (Fig. 4) concentration profiles demonstrate pronounced evidence of diagenesis resulting from redox differences in sediments from 0–10 cm. The concentration of As

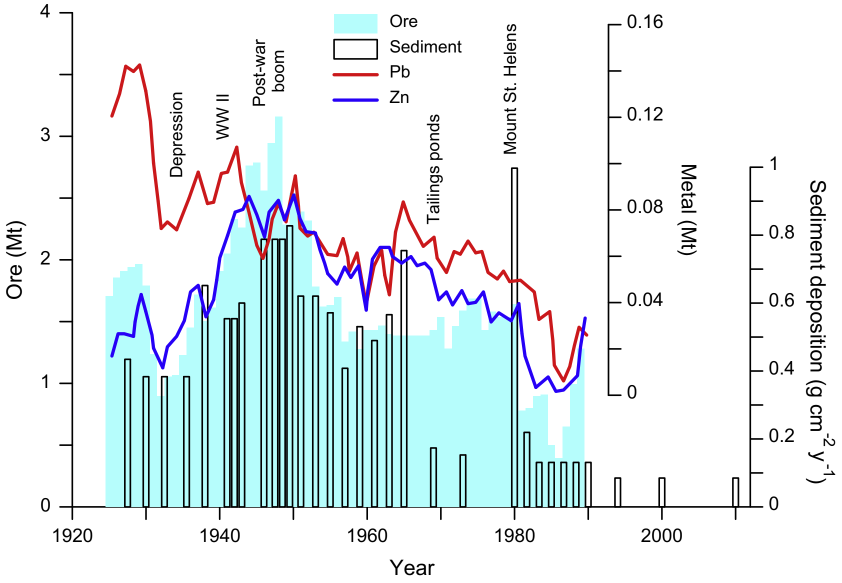

Fig. 2. Historical trends of ore (light blue bars), Pb (red line), and Zn (blue line) production as compared to the amount of sediment deposited (open bars) to Lake Coeur d'Alene. Historical data adapted from Bookstrom et al. (2004).

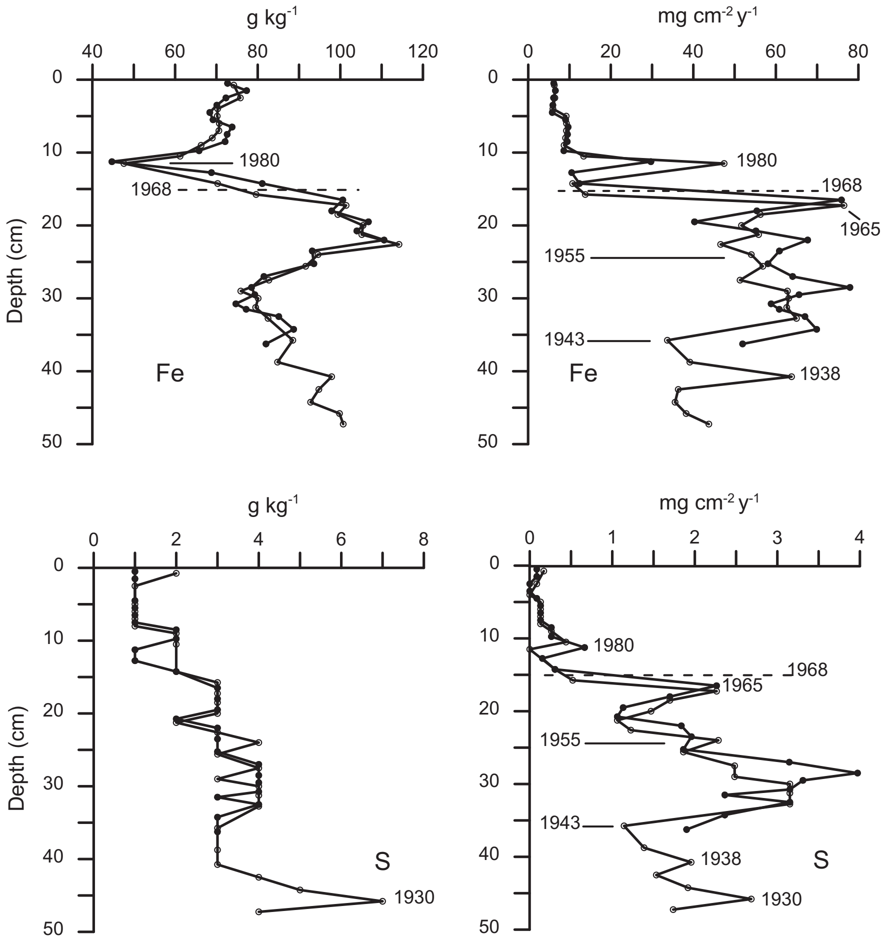

Fig. 3. Iron and S concentrations and loadings with depth in two Lake Coeur d'Alene sediment cores. Identified dates as estimated by Cs-137 age dating, varve counting, and the eruption of Mount St. Helens are noted.

increases from 100.0 mg kg^{-1} at a depth of 5 cm to 465.0 mg kg^{-1} within the oxidized zone of sediment that extends 5 cm below the sediment–water interface (Fig. 4) (La Force et al., 1999; Toevs et al., 2006). These concentrations greatly exceed the 50% probability level of toxicity (32.61 mg kg^{-1}) as defined by logistic regression models used by EPA to identify potentially hazardous sediments (U.S. EPA, 2004). Similarly, Mn concentration increases from about 6 g kg^{-1} at 5 cm to 10 g kg^{-1} at the sediment–water interface (Fig. 4). Soluble Mn and As mobilized in reduced zones of the sediment diffuse toward the oxic sediment–water interface where they precipitate in the oxic environment that exists to depths of about 5 cm (Toevs et al., 2006). High concentrations of Mn and Fe oxides within the oxidized zone serve to sorb As (Ying et al., 2012) preventing its release into the overlying water and producing concentrations of As within the ranges reported by others (Harrington et al., 1998; Horowitz et al., 1993). Despite the elevated concentrations of As and Mn in the top 5 cm of sediment, loading of these elements decreased with installation of the tailings ponds in 1968 (Fig. 4).

Loading profiles of As and Mn show similar trends to those for Fe and S, but the possibility of diagenetic reactions altering As and Mn distributions makes depth-date assignments less certain. For example, maximum As concentrations occur at a shallower depth (24 cm) (Fig. 4) as compared to S (29 cm) (Fig. 3) despite the probable association of these elements within the original ore (Toevs et al., 2008). Similarly, As mobilization and upward diffusion may explain occurrence of a broad concentration maximum at approximately 43 cm in sediments deposited during the time of the Great Depression, instead of a distinct spike in concentration at 45 cm as observed for S (Fig. 3). Mn loading trends appear to be less affected by diagenetic reactions given their similarity to those for Fe, most notably a spike in loading at 40 cm (Fig. 4) representing a 1938 peak in ore production (Fig. 2).

Phosphorus concentrations in sediments deposited after 1980 likewise show diagenetic alteration controlled by redox changes with depth (Fig. 4). Similar to As and to a lesser extent Fe, P shows a maximum at approximately 2 cm below the sediment–water interface (Fig. 4). Fe oxides sequester P in the oxidized zone of the sediment that extends to 5 cm, a phenomenon that has been reported to result in an exponential decline in P concentration as sediments transition from oxidized to reduced conditions (Rydin, 2000). Peaks for P, As, and Fe concentrations at the same depth indicate that upward diffusing soluble ions from the reduced zone below 5 cm precipitate in oxidized sediments present at 2 cm. Lower concentrations at the sediment–water interface for P as well as for Fe and As imply precipitation occurs rapidly enough to limit additional diffusion and that elemental concentrations at the sediment–water interface are controlled by oxide solubilities. In contrast, higher solubilities of Mn oxides (Balistrieri et al., 1992; Martin, 2005) allow greater diffusion and consequently, highest Mn concentrations occur at the sediment–water interface (Fig. 4).

Also notable in the P sediment profile is a peak in concentration in the anoxic environment at 15 cm that is nearly as high as the maximum concentration occurring at 2 cm where P sorption occurs on oxides (Fig. 4). The peak in P concentration at 15 cm corresponds with installation of the tailings ponds in 1968, indicating

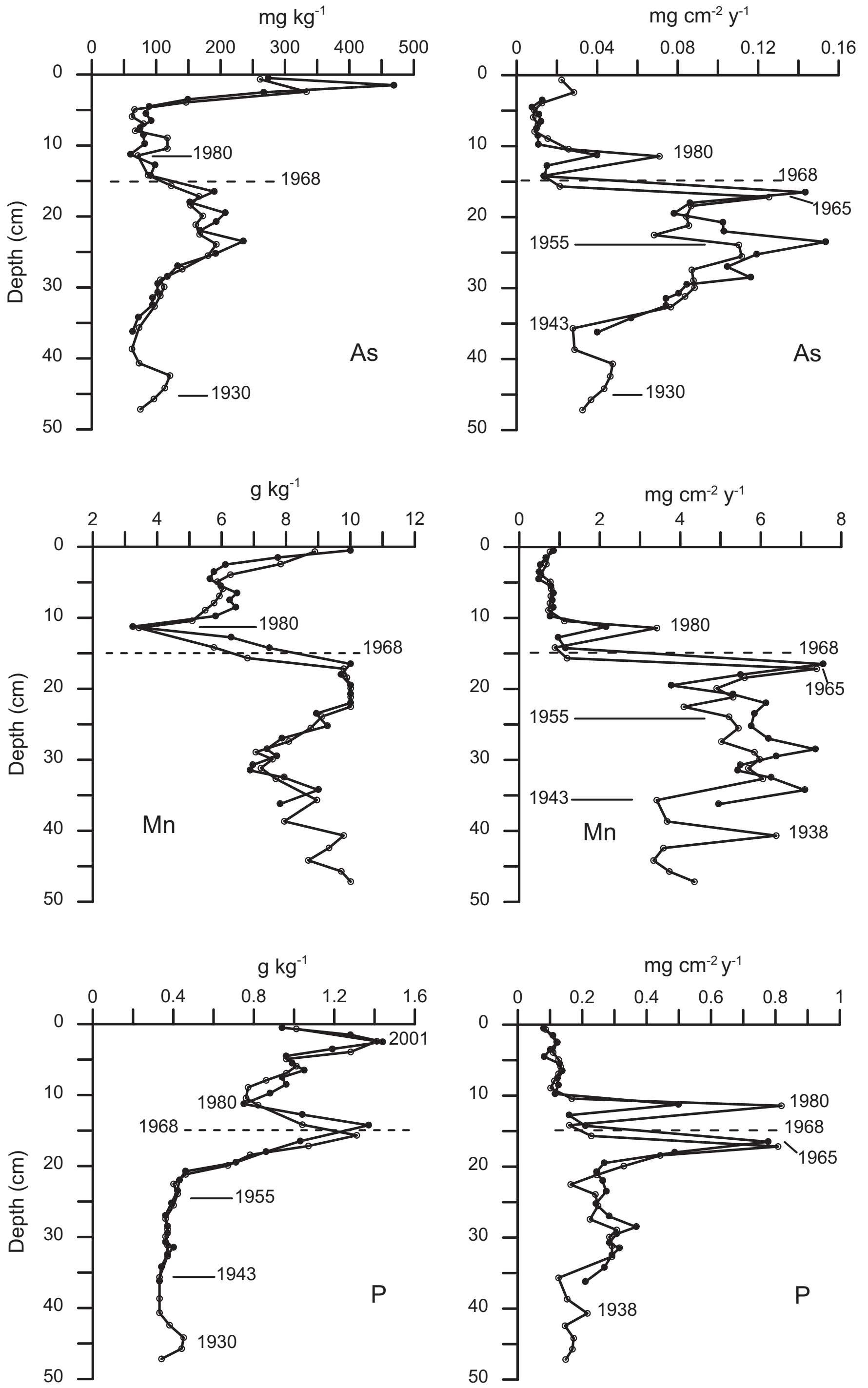

Fig. 4. Arsenic, Mn, and P concentrations and loading with depth in two Lake Coeur d'Alene sediment cores. Identified dates as estimated by Cs-137 age dating, varve counting, and the eruption of Mount St. Helens are noted.

that although total sediment loading was reduced, the smaller sized sediment particles not trapped by the ponds possessed a greater P concentration. P concentrations decreased in the ash layer at 11.5 cm, but P concentrations in the most recently deposited sediment remain two to three times higher than those in sediment at 24–36 cm deposited during an active mining period from 1943 to 1955 (Figs. 2 and 3).

The presence of P in Lake Coeur d'Alene is of concern for its role in eutrophication of the lake since primary productivity is P limited (State of Idaho Department of Environmental Quality, 2009; Woods and Beckwith, 1997). Anoxic conditions resulting from eutrophication within the hypolimnion could cause reductive dissolution of metal oxides and the release of associated metal(loid)s into the water column. Total P in the top 5 cm of sediment ranges from 0.94 to 1.44 g kg^{-1}, staying within the range of 0.5–1.6 g kg^{-1} that was measured in 1992 when the lake was determined to be oligotrophic (Woods and Beckwith, 1997). In 2009 the lake was still classified as oligotrophic (State of Idaho Department of Environmental Quality, 2009) and while concentrations of P in lake sediments do not directly indicate trophic status, total P concentrations in this range are low compared to those reported for sediments of other oligotrophic lakes (Carey and Rydin, 2011).

Additionally, P loading has decreased since the installation of tailings ponds, remaining near an average of 0.12 mg cm^{-2} y^{-1} since 1980 (Fig. 4). Noteworthy is a P loading peak at 17 cm of 0.8 mg cm^{-2} y^{-1} that corresponds to a peak in ore production during the Cold War (1965) (Figs. 1 and 2).

Unlike P, Cd (Fig. 5) and Zn (Fig. S4) show trends for decreased concentration and loading post 1980. Despite these trends, concentrations exceed the 50% probability level of toxicity (U.S. EPA, 2004). The average sediment concentration of Cd from 1980 to 2010 of 25.3 mg kg^{-1} is almost 10 times greater than the 50% probability level of 2.49 mg kg^{-1} (U.S. EPA, 2004). The average Zn concentration from 1980 to 2010 of 3326 mg kg^{-1} is almost 10 times greater than the 50% probability level of 384 mg kg^{-1} (U.S. EPA, 2004). Also important are the maxima in both Cd and Zn concentrations at approximately 15 cm that correspond, as in the case with P, with installation of the tailings ponds in 1968. Observations that sediment loading decreased during this time period and concentrations of Cd and Zn in the sediment increased, again indicate that the tailings ponds reduced the amount of materials deposited as sediment, but that concentrations of these elements in the smaller, higher surface area particles was greater. However unlike P, decreasing concentrations and loading of Cd and Zn since 1980

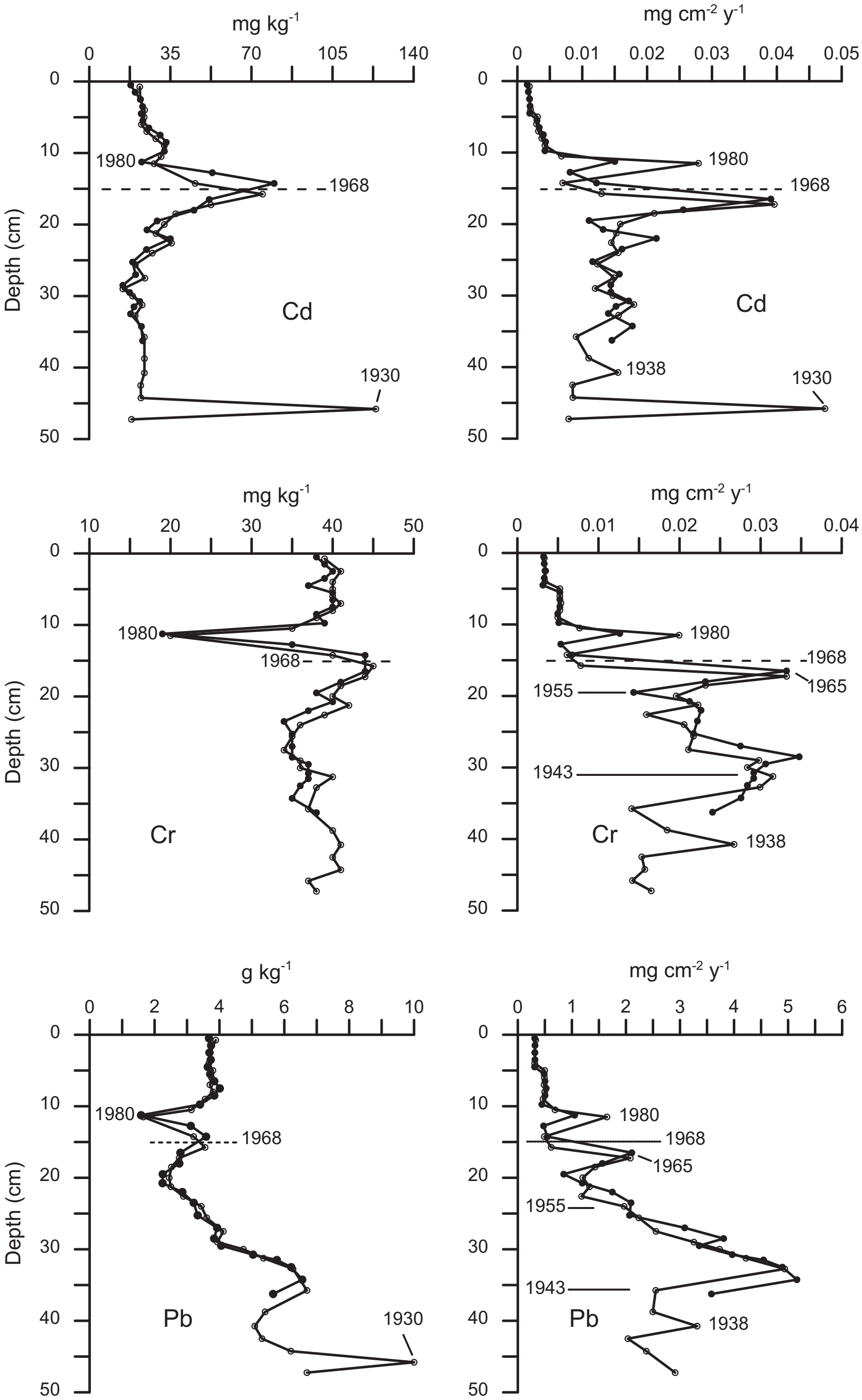

Fig. 5. Cadmium, Cr, and Pb concentrations and loading with depth in two Lake Coeur d'Alene sediment cores. Identified dates as estimated by Cs-137 age dating, varve counting, and the eruption of Mount St. Helens are noted.

indicate that improved environmental quality is expected with time.

Obvious in the historic record are spikes in both Cd (Fig. 5) and Zn (Fig. S4) concentration and loading at 45 cm, the same depth as similar maxima recorded for S (Fig. 3). Since Cd and Zn tend to be associated with S in tailings (Balistrieri et al., 2002; Toevs et al., 2006), it is likely that increased ore production using inefficient processing methods caused these 1930 maxima in concentration and loading observed for all three elements (Fig. 1). As with previously noted elements, Cd and Zn show a loading peak at 17 cm that corresponds to the 1965 Cold War ore production increase (Figs. 1 and 2).

Similar to Cd and Zn, Ag and Cu loading have decreased since 1968 indicating that placement of the tailings ponds has been beneficial with respect to sediment deposition of these two elements. However although concentrations of Ag and Cu decreased after 1968, values have stayed relatively stable since 1980 (Fig. S4). Concentrations of Ag exceed the 50% probability level of observing toxic effects with an average of 9.3 mg kg^{-1} after 1980 and concentrations of Cu are between the 25% and 50% probability levels with an average of 86 mg kg^{-1} (U.S. EPA, 2004).

A marker for Ag and Cu is the spike in loading at 40 cm (1938) (Fig. S4), a depth at which both Fe and S (Fig. 3) show similar local maxima. This loading increase corresponds to an increase in Ag ore production to greater than 340 t y^{-1} around 1936–1939 (Bookstrom et al., 2004). The association of both Ag and Cu with Fe and S (Balistrieri et al., 2002) would explain the increased loading of all elements during that time period.

Both Cr and Pb are critically important, because post-1968 concentrations have not declined as compared to concentrations recorded for sediments deposited from the end of the post-WW II boom until 1968 (24–15 cm) (Fig. 5). Installation of tailings ponds and other remediation efforts have thus, not noticeably decreased incoming sediment Cr and Pb concentrations. Between 1958 and 1968 Cr concentrations averaged 41 mg kg^{-1}, while concentrations after 1980 averaged 39 mg kg^{-1} (Fig. 5). Pb concentrations have increased since 1980, staying consistently between 3 and 4 g kg^{-1}. In the 10 years prior to installation of the tailings ponds, Pb concentrations averaged 2.7 g kg^{-1} and after 1980 the average concentration dramatically increased to 3.7 g kg^{-1}. Relatively high Cr and Pb concentrations contrast with the loading profiles of both elements that show decreasing trends (Fig. 5). Extensive contamination present in the stream channel of the South Fork of the Coeur d'Alene River and the associated floodplain continues to produce silt-sized materials with relatively high and consistent concentrations of Pb and Cd that are deposited to the lake bottom.

The logistic regression model shows there is a 25% probability of observing toxic effects when 76 mg kg^{-1} of Cr is present in sediments (U.S. EPA, 2004). This concentration is almost twice that of Cr measured in recent sediments, indicating a low probability of observing toxic effects despite the lack of a Cr decrease as compared to older sediments. In contrast, recent sediment concentrations of Pb are almost 23 times greater than the 50% probability level of 161 mg Pb kg^{-1}, thus indicating a high likelihood of observing negative effects on sediment biota. These effects are expected to continue given Pb's limited solubility and the calculation that in a typical year only 9% of total Pb entering the lake is transported out of the lake through the Spokane River (Clark et al., 2004). Unlike Cd and Zn where 52% and 70% of the lake inputs, respectively, are transported out of the lake in soluble form (Clark et al., 2004), relict mine tailings with potentially toxic Pb concentrations will continue to be deposited and retained in the sediment.

Loading and concentration data for additional elements including Al, Ba, Be, Ca, Co, K, La, Mg, Na, Nb, Ni, Sb, Sc, Sr, Th, Ti, V, Y, and Zr that were not previously discussed above can be found in Fig. S5. Historical markers and trends observed with these elements are consistent with those described in detail above.

4. Conclusions

The decrease in contaminant loading after 1968 corresponds with the installation of tailings ponds that reduced sediment deposition to Lake Coeur d'Alene. Unfortunately, concentrations of many of the contaminants in the sediment deposited since 1980 remain above acceptable limits. Arsenic concentrations at the sediment–water interface have a high probability of causing toxic effects, thus posing a management challenge given that diagenesis is responsible. While P concentrations in recent sediments are higher than during active mining, they remain sufficiently low as to prevent eutrophication. This indicates that an aerobic zone at the sediment–water interface is likely to persist and that metal release predicted to occur with the onset of anaerobic conditions is unlikely. Although Cd and Zn show a decrease in concentration with time, the concentrations within recent sediments are still high enough to cause toxic effects. With additional sediment deposition it is possible that improved environmental quality will occur with respect to these two elements. Ag and Cu concentrations are lower than measured in sediments deposited during the period of active mining; however, concentrations of both elements are not declining and additional remediation emphasis specifically targeting these elements will be required. Cr and Pb are the contaminants of greatest concern, because their concentrations have not decreased since the period of active mining despite decreased loading. Cr is a potential problem with concentrations in recent sediments returning to levels similar to those measured in sediments deposited during active mining. However, Cr concentrations in recent sediments have a low probability of causing toxic effects. In contrast, Pb concentrations are a cause for concern, because they are higher in recent sediments than those deposited during the period of active mining and they are at levels expected to cause toxic effects. Decreasing the high concentration of Pb in materials deposited to Lake Coeur d'Alene should be a primary target for future remediation efforts. Without a concerted effort on remediation to prevent silt-sized (Toevs et al., 2008), Pb-laden particles from entering the lake, Pb concentrations in the sediment will remain at toxic levels with substantial potential to cause negative environmental impacts.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.04.055.

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