

## Research Article

# Trace Element Concentration and Speciation in Selected Mining-Contaminated Soils and Water in Willow Creek Floodplain, Colorado

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Long-term mining activities in the mountains around Creede, Colorado have resulted in significant contamination in soils and water in the Willow Creek floodplain. Total major and trace were determined for soils and water and sequential chemical extraction for soils. Objectives were to determine concentrations and potential reactivity of trace elements and investigate their relationship with other soil and water properties. Water trace elements showed significant variability among sites, ranging from 347 to 12108  $\mu\text{g/L}$ . Relative trend showed  $(\text{Zn} > \text{Sr} > \text{Ba}) > (\text{Mn} > \text{W} > \text{Cd}) > (\text{Sn} > \text{V} \approx \text{Ni} \approx \text{Cu} > \text{Co}) > (\text{Ag})$ . Soil trace elements showed significant short-range spatial variability, ranging from 2819 to 19274 mg/kg. Relative trend showed  $(\text{Pb} \approx \text{Zn} > \text{Mn} > \text{Ba} > \text{P}) > (\text{As} > \text{Cu} > \text{Sr} > \text{V} > \text{Cd} > \text{Sb} \approx \text{Ag}) > (\text{Co} \approx \text{Cr} > \text{Mo} \approx \text{Sn} \approx \text{Ni}) > (\text{Be} \approx \text{W} > \text{Se} \approx \text{Hg})$ . Predominant fractions were oxide, specifically-sorbed/carbonate bound, and residual. Water soluble and exchangeable fractions showed  $(\text{Zn} \approx \text{Cd}) > \text{Pb}$  and  $\text{Cd} > \text{Zn} > \text{Pb}$ , respectively. Mobility factors for highly contaminated soils showed  $\text{Cd} \approx \text{Zn} > \text{Pb} > \text{Cu} > \text{As}$ .

## 1. Introduction

The measurement of the total extractable pool of trace elements has been commonly used to assess the environmental levels or background amounts of trace elements in soils and water [1–7]. Selective fractionations or “geochemical partitioning” have been used to evaluate the potential reactivity of these elements [8–11] and are widely used in soil pollution studies, providing qualitative evidence about trace element reactivity and indirectly of their bioavailability [12–15]. Trace element bioavailability in soils is a complex phenomenon, affected by many factors such as total concentration, pH, organic matter, clay, and redox conditions [7, 16–20]. Trace element toxicity in waters is strongly affected by site-specific water quality factors such as pH, hardness, and other dissolved constituents [21, 22]. An assessment of trace element fate, bioavailability, and transport (e.g., surface and groundwater) is required in order to predict potential contamination and impact upon soil and water quality.

Historic mining activities in the mountains around Creede, Colorado, began around 1889 and continued until 1985. Underground mining of silver and base metals has resulted in Zn and Cd contamination of ground and surface water in and along the broad floodplain of Willow Creek below Creede [23]. Willow Creek, a tributary to the Rio Grande, is polluted from drainage from various mine adits and rock piles upstream of Creede and by leachates from a gravel-capped tailings pile below [23]. Ores common to this area contain Cd which occurs mainly in the Zn sulfides sphalerite and wurtzite and is recovered with Zn usually from polymetallic ores containing Pb and Cu [24].

Major and trace element concentrations (Al, Cd, Cu, Fe, Mn, Pb, and Zn) in river systems are of interest because of their many natural and mine-related sources and their impact on aquatic life through a variety of mechanisms, including both acute and chronic toxic effects of aqueous metals as well as from metal exposure in soils and sediments [22, 23, 25–37].

To assess, monitor, and revitalize the Willow Creek watershed, the Willow Creek Reclamation Committee (WCRC) partnered with numerous state and Federal agencies, including the US Environmental Protection Agency (USEPA); US Forest Service (USFS); US Geological Service (USGS); Colorado Department of Public Health and Environment (CDPHE); Colorado Division of Minerals and Geology; the US Department of Agriculture, Natural Resources Conservation Service (USDA-NRCS), and others. Assessment reports produced by WCRC and/or its partners include [22, 38–43].

The USDA-NRCS designed a sampling scheme to help assess contamination of Willow Creek from nonpoint sources of metals from historical mining activities. In August 2005, USDA-NRCS collected and analyzed soil and water samples from Willow Creek. Initial intent of sampling was to provide background survey levels to help guide potential future samplings for more intensive investigations and later expanded to provide comment on potential soil metal/metalloid bioavailability. This paper reports the results of this investigation. The objectives of this study were as follows: (1) to determine the concentrations and potential reactivity of trace elements using total analysis and sequential chemical fractionation so as to (a) determine the extent and variability of trace element dispersal along the creek and (b) investigate the relationship between trace element concentrations and their potential reactivity with other soil and water properties as well as vegetation or lack thereof along the stream. Knowledge and understanding of these relationships are important to researchers when evaluating trace element data for use in predictive models for environmental purposes. In addition to the geochemistry, detailed site descriptions and other basic soil and water characterization were considered necessary to aid in the interpretation and application of these elemental data.

## 2. Materials and Methods

**2.1. Study Area.** The Willow Creek watershed is an area of 103 km<sup>2</sup> in Mineral County, Colorado in the northern San Juan Mountains. Willow Creek is formed by the confluence of the East and West Willow Creeks and is a tributary of the Rio Grande River. The City of Creede (Figure 1) and most of the Creede Mining District are located within the watershed. The Creede Mining District is in the central part of the San Juan Volcanic Field. Principal metals produced in the Creede District included Ag, Pb, Zn, Cu, and Au. Production of these metals was from veins along faults that formed during subsidence of the Creede caldera.

Bedrock geology is dominated by igneous rocks related to extensive tertiary volcanism, with ashflow tuffs the common rock in the watershed above Creede and the dominant rock for mineral deposits in the mining areas along the East and West Willow Creeks [41]. The area beneath Creede and southward to the confluence of Willow Creek and the Rio Grande is predominately the Creede Formation which is mostly lake and river deposits of reworked ash, sand and gravel, and travertine deposits from numerous mineral hot springs forming after the eruption of the Creede Caldera [41]. Much of the older rocks in the lower part of the water-

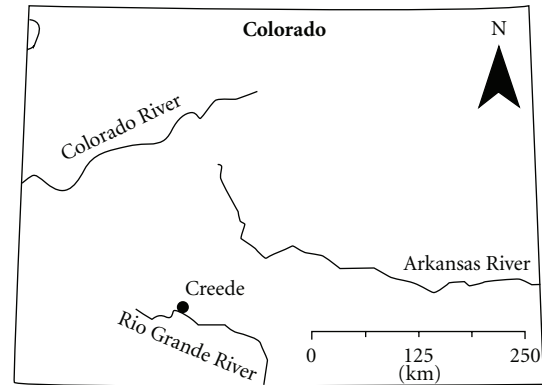


FIGURE 1: City of Creede, Colorado, part of the historic Creede Mining District, is located within the Willow Creek watershed. Willow Creek is formed by the confluence of the East and West Willow Creeks and is a tributary of the Rio Grande River.

shed, especially along the waterways, are covered by Quaternary alluvium from Willow Creek and the Rio Grande [44].

The Willow Creek watershed has a 1.6 km vertical relief and is characterized by steep slopes and distinct vegetative communities. Due to the substantial elevation variability, the climate within the watershed is diverse, affecting the vegetative communities, stream flow magnitude and timing, water temperature, ground-water recharge, and other watershed characteristics [41]. The Willow Creek watershed crosses four major life zones from the high mountains to the Rio Grande Valley, with the origin of Willow Creek in the Alpine Zone (tufted hairgrass-sedge and willow), in the sub-Alpine Zone (Engleman spruce, sub-Alpine fir, Thurber fescue grassland), in Montane Zone (aspen, Douglas Fir, and bristlecone pine), and in the Foothills Zone (Arizona fescue grasslands) [41]. In Creede, the annual average precipitation, temperature, and snowfall are 335 mm, 16°C, and 122 cm, respectively, with the highest and lowest precipitation in August and December and the highest and lowest temperature in July and January, respectively [41]. The largest volume of snow or rain is at the highest elevations. Aquatic resources within the watershed are primarily streams but also include wetlands and riparian areas.

**2.2. Sampling Strategy: Soils and Water.** Soils are naturally variable, their properties changing horizontally across the landscape as well as vertically down the soil profile. Soil map units derived from changes in topography, underlying geology, and dominant vegetation type can be used for horizontal subdivisions, with soil horizons as subdivisions of vertical change [45]. Environmental and/or anthropogenic disturbances introduce additional variation into natural landscapes. In the field, the US soil survey has routinely used pedon sampling to obtain representative samples [46, 47]. In environmental studies as with soil survey, intuitive sampling often forms the basis of exploratory sampling which may be used for qualitative assessment of soils where impact or damage is visible or anticipated [45, 47, 48]. Pedon sampling has been used in studies when the area affected is known and/or usually visible, and the types of contaminants are

either known or unknown [11, 49–51]. Replicate sampling is often included in sampling plans for water quality, the primary purpose of which is to identify and/or quantify the variability in all or part of the sampling and analysis system [52]. Amount and composition of water samples vary strongly with small changes in location along water body [53]. The primary objective of water sampling is the same as with soil sampling, that is, to obtain a representative sample. For the reasons stated above, the approach to the USDA-NRCS exploratory soil/water sampling at Willow Creek (Aug 9–11, 2005) utilized pedon sampling in the collection of soil samples and water samples replicated on different day (sequential) and same day (concurrent) for laboratory characterization.

All water and soil samples were collected from sites located downstream of Creede on the Willow Creek floodplain. Water sampling was performed in a unidirectional manner with the water flow. Willow Creek has been substantially diverged from its presettlement form due to mining activities [43]. At the time of sampling, Willow Creek was in a braided form. Water sampling was conducted during low-flow conditions when the metal-loading pattern not only shows the metal sources entering the streams on a continual basis but also those sources contributing to high concentrations during the low-flow winter months when mine drainage is less diluted by other water sources and the most toxic conditions likely occur [22, 35, 38]. It was observed that flow conditions in some areas of Willow Creek were free flowing, whereas in other areas, flow was physically obstructed causing water to pool and stagnate, suggesting stream waters had both oxidizing and reducing conditions at the time of sampling.

Water samples were collected from seven sites over a three-day period. Two sites (Westfork and Eastfork) were collected at higher elevations than other sites and are referred to as “baseline” or “reference” samples. Some water samples were collected in conjunction with the pedon sampling [47] and as such bear the same name as the soil. Table 1 provides the names for the water samples and their soil survey identification numbers, with embedded codes indicating concurrent and/or sequential sampling. For example Creek water shows the soil survey numbers S05CO-079-003A-1 through S05CO-079-003C-3, with the A through C representative of sequential samples and 1 through 3 representative of concurrent samples.

Study soils have aquic conditions, undergoing periods of saturation and reduction [54]. Sampling in August during low-flow conditions provided a good representation of more oxidizing conditions in study soils compared to other times of the year with high-flow rates (high precipitation or snowmelt). Soil surface materials were collected from ten sites, including two sites (Spruce and Railroad), where additional underlying materials were collected. Figure 2 shows sites of these sampled soils. Table 2 provides longitude and latitude for sites and also shows soil name, soil survey identification number, and sampling depth (cm).

### 2.3. Field and Laboratory Characterization: Soils and Water

**2.3.1. Soil and Water Sampling.** Soils were described, sampled, and analyzed using standard USDA-NRCS soil survey

methods [47, 55]. Water samples were collected using standard USDA-NRCS [47] and USGS [56–58] sampling protocols, expedited for transport to the laboratory, and analyzed using standard USDA-NRCS soil survey laboratory methods [47].

**2.3.2. Soil Analyses.** Bulk soil samples were air-dried, homogenized, and sieved to <2 mm in the laboratory to remove rock fragments. Samples received standard laboratory characterization performed on air-dried <2 mm soil with resulting data reported on an oven-dry basis. Particle-size analysis was determined by sieve and pipette methods, following pretreatments to remove organic matter (OM) and soluble salts, and chemical dispersion with sodium hexametaphosphate. Total C, N, and S were determined by dry combustion. Soil pH 1:1 soil:water was determined. Exchangeable cations (Ca, Mg, K, and Na) were extracted with buffered (pH 7.0)  $\text{NH}_4\text{OAc}$  and measured by atomic absorption spectrometry (AAS). Cation exchange capacity (CEC-7) was determined by Kjeldahl titration of the  $\text{NH}_4$ -saturated soil. Base saturation by CEC-7 was determined by dividing the sum of  $\text{NH}_4\text{OAc}$  extractable bases by CEC-7 and multiplying by 100. Acidity was extracted by  $\text{BaCl}_2$ -TEA, pH 8.2. Exchangeable Al was extracted with 1 M KCl and determined by inductively couple plasma emission spectrometry (ICP-AES) on samples with pH < 5.5. If electrical conductivity (EC) for 1:2 soil water extract was > 0.25 dS/m, a saturated paste extract was prepared and analyzed for cations (Ca, Mg, Na, and K) by AAS and anions (F, Cl,  $\text{PO}_4$ , Br, OAc,  $\text{SO}_4$ ,  $\text{NO}_2$ , and  $\text{NO}_3$ ) by ion chromatography and carbonate and bicarbonate ( $\text{CO}_3$  and  $\text{HCO}_3$ ) by acid titration. Dithionite-citrate extracts were analyzed for Fe, Al, and Mn ( $\text{Fe}_d$ ,  $\text{Al}_d$ , and  $\text{Mn}_d$ , resp.) by AAS. Sodium pyrophosphate extracts were analyzed for Fe, Al, Si, and Mn ( $\text{Fe}_p$ ,  $\text{Al}_p$ ,  $\text{Si}_p$ , and  $\text{Mn}_p$ , resp.) by AAS. Acid oxalate extracts were analyzed for Fe, Al, and P ( $\text{Fe}_o$ ,  $\text{Al}_o$ , and  $\text{P}_o$ , resp.) by ICP-AES. Optical grain counts were conducted on the coarse-silt (0.02–0.05 mm), very fine sand (0.05–0.10 mm), or fine-sand (0.10–0.25 mm) fraction. Crystalline clay minerals (<2  $\mu\text{m}$ ) were identified by X-ray diffraction analysis.

**2.3.3. Soil Elemental Analyses.** Soil samples for major and trace element analysis were prepared metal-free by grinding approximately 10 g of <2 mm soil in a silicon nitride ball mill to <74  $\mu\text{m}$ . Major elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Sr, Ti, and Zr) were determined on soil samples (0.25 g) by microwave digestion (180°C for 9.5 min) combined with 4 mL HF + 9 mL  $\text{HNO}_3$  + 3 mL HCl. Following digestion, boric acid was added to neutralize HF (2.5% in 100 mL final volume) and extracts analyzed by ICP-AES. Total extractable (TE) trace elements (Ag, As, Ba, Be, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Sr, V, W, and Zn) were determined on soil samples (0.5 g) by microwave digestion (180°C for 7 min) using aqua regia (9 mL  $\text{HNO}_3$  + 3 mL HCl). Elements extracted by this method are designated as TE, and the sum of all elements extracted by this method are designated  $\text{SUM}_{\text{TE}}$ . In order to simplify presentation of study results, Mn, P, and Sr are included as trace elements.

**2.3.4. Soil Sequential Fractionations.** Sequential chemical fractionations were based on the procedure of Tessier et al.

TABLE 1: Selected chemical properties of study waters.

Water site	Soil survey no.	EC (dS/m)	pH	Ca	Mg	Na	K	CO <sub>3</sub>	HCO <sub>3</sub>	F	Cl	PO <sub>4</sub>	Br	OAc	SO <sub>4</sub>	NO <sub>2</sub>	NO <sub>3</sub>	
				mmol(+)/L								mmol(-)/L						
Gravelbar water	S05CO-079-001A	0.16	6.6	0.9	0.1	— <sup>a</sup>	tr <sup>b</sup>	—	0.4	—	tr	—	—	—	1.0	—	—	
Gravelbar water	S05CO-079-001B	0.17	6.6	0.8	0.1	—	tr	—	0.4	—	tr	—	—	—	1.0	—	tr	
Gravelbar water	S05CO-079-001C	0.16	6.9	0.8	0.1	—	tr	—	0.4	—	tr	—	—	—	1.0	—	—	
Cottonwood water	S05CO-079-002A	0.22	6.6	0.7	0.1	—	0.1	—	0.2	tr	0.1	—	—	—	1.6	—	tr	
Cottonwood water	S05CO-079-002B	0.22	6.5	0.7	0.1	—	0.1	—	0.2	tr	0.1	—	—	—	1.7	—	tr	
Cottonwood water	S05CO-079-002C	0.20	6.6	0.7	0.1	—	0.1	—	0.2	tr	0.1	—	—	—	1.4	—	tr	
Creek water	S05CO-079-003A-1	0.14	7.1	0.7	0.1	—	tr	—	0.4	—	tr	—	—	—	0.9	—	—	
Creek water	S05CO-079-003A-2	0.14	7.2	0.7	0.1	—	tr	—	0.3	—	tr	—	—	—	0.9	—	—	
Creek water	S05CO-079-003A-3	0.15	7.3	0.7	0.1	—	—	—	0.3	—	tr	—	—	—	0.9	—	—	
Creek water	S05CO-079-003B-1	0.14	7.3	0.7	0.1	—	—	—	0.3	—	tr	—	—	—	0.9	—	—	
Creek water	S05CO-079-003B-2	0.16	6.6	0.7	0.1	—	—	—	0.2	—	tr	—	—	—	0.9	—	—	
Creek water	S05CO-079-003B-3	0.15	7.1	0.7	0.1	—	—	—	0.4	—	tr	—	—	—	0.9	—	—	
Spruce water	S05CO-079-004A	0.17	7.0	1.0	0.1	—	—	—	0.6	—	tr	—	—	—	0.9	—	—	
Spruce water	S05CO-079-004B	0.18	7.1	1.0	0.1	—	—	—	0.6	—	tr	—	—	—	0.9	—	—	
Spruce water	S05CO-079-004C	0.18	7.0	1.0	0.1	—	—	—	0.7	—	tr	—	—	—	1.0	—	—	
Channel water	S05CO-079-004D-1	0.14	7.3	0.7	0.1	—	—	—	0.3	—	tr	—	—	—	0.9	—	—	
Channel water	S05CO-079-004D-2	0.14	7.4	0.7	0.1	—	—	—	0.2	—	tr	—	—	—	0.9	—	—	
Channel water	S05CO-079-004D-3	0.14	7.5	0.7	0.1	—	—	—	0.3	—	tr	—	—	—	0.9	—	—	
Channel water	S05CO-079-004E-1	0.14	7.4	0.7	0.1	—	—	—	0.3	—	tr	—	—	—	0.9	—	—	
Channel water	S05CO-079-004E-2	0.14	7.4	0.7	0.1	—	—	—	0.3	—	tr	—	—	—	0.9	—	—	
Channel water	S05CO-079-004E-3	0.14	7.4	0.6	0.1	—	—	—	0.3	—	tr	—	—	—	0.9	—	—	
Channel water	S05CO-079-004F-1	0.14	7.4	0.7	0.1	—	—	—	0.4	—	—	—	—	0.7	—	tr	—	
Channel water	S05CO-079-004F-2	0.14	7.4	0.7	0.1	—	—	—	0.3	—	tr	—	—	—	0.9	—	—	
Channel water	S05CO-079-004F-3	0.14	7.4	0.7	0.1	—	—	—	0.4	—	tr	—	—	—	0.9	—	—	
Westfork water	S05CO-079-013	0.11	7.3	0.6	0.1	—	—	—	0.6	—	tr	—	—	—	0.3	—	—	
Eastfork water	S05CO-079-014	0.06	7.5	0.2	tr	—	tr	—	0.4	—	tr	—	—	—	0.1	—	—	

<sup>a</sup> — = concentration below detection limits.<sup>b</sup> tr = trace.

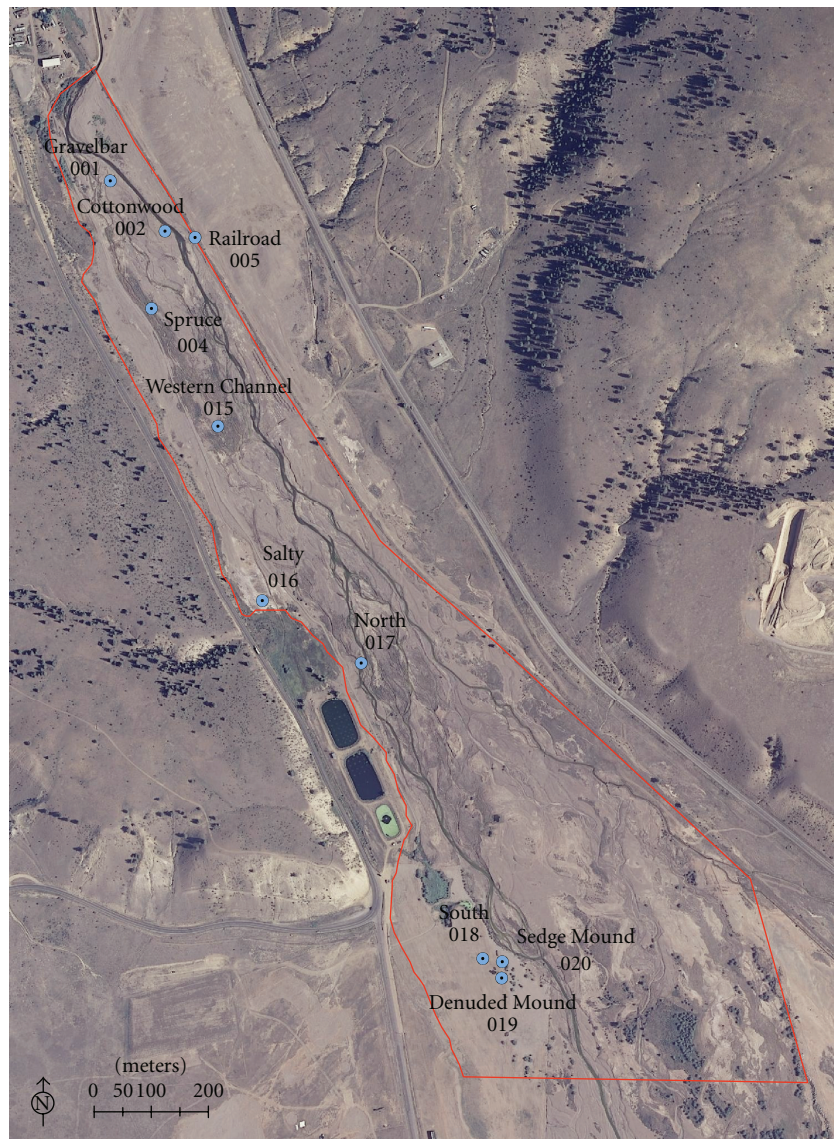


FIGURE 2: Willow Creek floodplain showing soil sample sites.

TABLE 2: Soil names, soil survey numbers, depth, and location (latitude and longitude).

Soil	Soil survey no.	Latitude	Longitude
Gravelbar	S05CO-079-001	37.84070384540	-106.92336102900
Cottonwood	S05CO-079-002	37.83992953880	-106.92225084200
Spruce	S05CO-079-004	37.83870504580	-106.92249156600
Railroad	S05CO-079-005	37.83983640960	-106.92165148000
Western channel	S05CO-079-015	37.83686982850	-106.92112031400
Salty	S05CO-079-016	37.83413546890	-106.92016960300
North	S05CO-079-017	37.83318101160	-106.91817641500
South	S05CO-079-018	37.82851821110	-106.91525304600
Denuded mound	S05CO-079-019	37.82856331670	-106.91564346400
Sedge mound	S05CO-079-020	37.82826082210	-106.91525936500

[10] and Keller and Vedy [8]. Sequential fractionations were determined on separate samples (0.1 g) in 50 mL centrifuge tubes. Extracts were replicated, with mean values reported. Residues were separated from supernatants by 80-min centrifugation at 4000 rpm. Soils were extracted twice on fractions 3 and 4 with designated reagents (10 mL), and both extracts combined. Washing steps (10 mL H<sub>2</sub>O, shake 15 min) were performed between fractionations 2 through 5, with resulting supernatants separated from residues by 80-min centrifugation and solutions combined with initial extracts. Concentrated (16 M) HNO<sub>3</sub> was added to fractions 1 and 2 to acidify final extracts. Trace element concentrations in all extracts were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Percent recovery was determined by summing the trace elements from the sequential-extraction process (SUM<sub>SEQ</sub>), divided by the amount determined by the TE elemental analysis by microwave digestion (SUM<sub>TE</sub>), and multiplied by 100.

Total extractable (TE) and sequential fractions 1 through 6 are designated herein as water soluble (WS), exchangeable (EX), specifically sorbed/carbonate bound (SS/CAR), oxide bound (OX), organic/sulfide bound (OM/S), and residual (RES). The sums of total extractable and sequential fractions are designated herein as SUM<sub>TE</sub> and SUM<sub>SEQ</sub>, respectively (Table 3). This designated chemical partitioning of trace elements is based on the evaluations of the sequential fractionation method used herein as applied in various studies [6, 8–12, 59]. In this study, the CH<sub>3</sub>COONa/CH<sub>3</sub>COOH reagent is used for both calcareous and noncalcareous soils and is designated as SS/CAR. Tessier et al. [10] indicated that the pH 5.0 used in the SS/CAR fraction solubilizes not only the carbonate-bound fraction if present but also a large fraction of specifically adsorbed trace elements from various solid substrates. Similarly, the H<sub>2</sub>O<sub>2</sub> extraction (fraction 5) is designated as OM/S, recognizing that not only OM but also sulfide minerals may be extracted to a large extent [10].

**2.3.5. Water Analyses.** Water samples were analyzed for cations (Ca, Mg, Na, and K) by AAS and anions (F, Cl, PO<sub>4</sub>, Br, OAc, SO<sub>4</sub>, NO<sub>2</sub>, and NO<sub>3</sub>) by ion chromatography and carbonate and bicarbonate (CO<sub>3</sub> and HCO<sub>3</sub>) by acid titration. Electrical conductivity and pH were determined on water samples. Water samples were filtered (0.45 μm), acidified with HCl, and analyzed for major (Al, Ca, Fe, K, Mg, and Sr) and trace elements (Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Sb, Sn, Sr, V, W, and Zn) by ICP-AES. For purposes of this study, Sr is included as trace element.

**2.3.6. Quality Control.** Quality control (QC) included blanks, duplicates, certified reference material (CRM), and standards from the National Institute of Standards and Technology (NIST). Reference material for soil samples included CRM Loam Soil C, high-purity standards, Charleston, SC and NIST 2709a San Joaquin Soil. The high purity standard CRM-TMDW was used for water samples. Elemental recoveries and relative standard deviation (RSD) for soil and water QC standards ranged from 90% to 115% and ≤11%, respectively. Percent recovery for QC soil standards,

determined by dividing SUM<sub>SEQ</sub> by SUM<sub>TE</sub> and multiplying by 100, ranged from 124 to 130 percent.

### 3. Results and Discussion

**3.1. Water: Chemical Properties.** Water samples were less acidic than most of the sampled soils, with pH ranging from 6.5 to 7.5 (slightly acid to slightly alkaline) (Table 3). Of the sampled waters, the Channel and Creek water samples were generally less acidic than those waters sampled in conjunction with the soils (Gravelbar, Cottonwood, and Spruce). The relatively lower pH for the water associated with the sampled soils and for the water from the second day sampling of the Creek water may be due in part to the capturing of more sediment in the sample compared to the other samplings. In general, there are relatively small differences in water pH within sites, that is, same-day samples (concurrent) and different-day samples (sequential). For example, Channel water showed a mean and standard deviation of  $7.5 \pm 0.05$  over a three-day period. These data suggest minor daily fluctuations in the stream or channel pH may be anticipated under relatively similar environmental conditions. This lack of high daily variability within the time frame of sampling may also indicate that the water system has a reasonably good buffering system. Poorly buffered waters and high daily variability in pH are often attributed to biological processes that affect the carbonate buffering system.

The water pH for the two locations at the higher elevations designated as “reference” or “baseline” sites (Westfork and Eastfork) were 7.3 and 7.4, respectively. These data suggest the pH of the water at the upper elevations was not dramatically different from the water at the lower elevations (excluding those associated with sampled soils) during the time frame of sampling. As water moves through soils and rocks, the pH may increase or decrease as additional chemical reactions occur. The pH within streams can impact toxic materials, with high acidity or alkalinity tending to convert insoluble metal sulfides to soluble forms, thereby increasing the concentrations of toxic metals.

Other data [43] showed significant pH variability in groundwater across the Willow Creek floodplain, ranging from 2.6 to 7.0. Yochum et al. [43] suggests pH can be a good indicator for groundwater contamination, that is, the link between low pH and groundwater contamination can be used for early detection for ground water contamination plume movement, minimizing the expense of water quality analyses.

Electrical conductivity (EC) showed variability among sites, with the lowest EC values in the “reference” sites, with 0.06 and 0.11 dS/m in the Eastfork and Westfork waters, respectively (Table 3). Highest EC values were found in those waters sampled in conjunction with the soils, ranging from 0.16 to 0.22 dS/m. Data showed good agreement within sites, with the Channel and Creek waters showing the greatest consistency with means and standard deviations of  $0.15 \pm 0.008$  and  $0.14 \pm 0.000$  dS/m, respectively, over a three-day period. Similar to pH, these data suggest minor fluctuations in the EC of the stream or channels may be anticipated under relatively similar environmental conditions. Additionally,

TABLE 3: Designated partition and chemical reagents used for total extractable and sequential extractions<sup>a</sup>.

Partition	Reagents/procedure
Total extractable (TE)	9.0 mL 16 M HNO <sub>3</sub> + 3.0 mL 12 M HCl (concentrated); microwave digestion: 180 degrees C for 10 min; made to final 50-mL volume with distilled deionized (DDI) water
(1) Water soluble (WS)	10 mL distilled deionized water H <sub>2</sub> O; shake 1 h
(2) Exchangeable (EX)	10 mL 0.1 M NaNO <sub>3</sub> ; shake 1 h
(3) Specifically sorbed/carbonate bound (SS/CAR)	10 mL 1 M CH <sub>3</sub> COONa, adjusted to pH 5 with CH <sub>3</sub> COOH; shake 5 h
(4) Fe-Mn oxide bound (OX)	20 mL 1 M NH <sub>2</sub> OH·HCl in 25% v/v CH <sub>3</sub> COOH; shake 4 h
(5) Organic/sulfide-bound (OM/S)	2 mL 0.02 M HNO <sub>3</sub> + 5 mL 30% H <sub>2</sub> O <sub>2</sub> , adjusted to pH 2 with concentrated HNO <sub>3</sub> ; heat to 85 degrees C for 2 h with occasional agitation; add 3 mL H <sub>2</sub> O <sub>2</sub> ; heat to 85 degrees C for 2 h with occasional agitation; cool and wash with 5 mL 3.2 M NH <sub>4</sub> OAc in 20% v/v HNO <sub>3</sub> ; dilute to 20 mL; shake 30 min
(6) Residual (RES)	9.0 mL 16 M HNO <sub>3</sub> + 3.0 mL 12 M HCl (concentrated); microwave digestion: 180 degrees C

<sup>a</sup>After Tessier et al., 1979 and modified by Keller and Vedy, 1994.

these data may indicate that the salt load may increase in transport by stream waters from higher elevations to the valley floor and that these salts would be more significant in areas where water stagnates or pools with soils and sediments.

Predominant ions in water samples were SO<sub>4</sub> > Ca > HCO<sub>3</sub> (Table 3). Ion concentrations showed good agreement across all samples (among and within sites), with means and standard deviations of 1.0 ± 0.23, 0.8 ± 0.11, and 0.4 ± 0.13 mmol/L for SO<sub>4</sub>, Ca, and HCO<sub>3</sub>, respectively. Sulfate is a product of pyrite oxidation as well as the oxidation and dissolution of other metal-bearing sulfide minerals. Carbonate buffering results from chemical equilibrium between calcium, carbonate, bicarbonate (HCO<sub>3</sub>), carbon dioxide, and hydrogen ions in the water and carbon dioxide in the atmosphere. Buffering causes waters to resist changes in pH [60]. The amount of buffering is primarily determined by carbonate and bicarbonate concentration which are introduced into the water from dissolved calcium carbonate (i.e., limestone) and similar minerals in the watershed [61]. Glucose is the primary product of photosynthesis, with acetate (OAc) forming from the glucose as plants decompose. In comparison, Kimball et al. [38] found the stream water at the injection point in West Willow Creek a CaHCO<sub>3</sub>-CaSO<sub>4</sub> type water, reflecting the chemical weathering of bedrock in the watershed [44]. Kimball et al. [38] further determined these ions and pH remained constant until the inflow of the Nelson Tunnel, at which point the chemical character of water changed to a CaSO<sub>4</sub> type, and pH was lower. The Nelson Tunnel discharge is located on West Willow Creek about 2.4 km upstream of Creede and is considered responsible for 75% of the total inorganics (heavy metals) contamination in Willow Creek [42]. With the inflow of East willow creek, pH became more basic again, Ca and SO<sub>4</sub> diluted, and alkalinity remained nearly constant [38]. For this study, soil and water samples were collected below Creede on the southern part of the Willow creek floodplain.

3.2. *Water: Major and Trace Elements.* Metals in natural waters undergo continual changes between dissolved, precipitated, and sorbed-to-sediment forms, with the rate of these

adsorption, desorption, and precipitation processes depending on pH, redox potential, water chemistry, and composition of bottom and suspended sediments [62]. These forms have traditionally been subdivided into two fractions, “dissolved” and “particulate”, according to an operationally defined limit (0.45 μm) and separated by filtration [63]. Using this partitioning, study waters were filtered with a 0.45-μm filter, with the filtrate analyzed for major and trace elements. In all samples, Fe and Al concentrations were below detection limits (Table 4). The pattern for Mn concentrations was not similar to any other trace element and showed spatial variability, ranging from below detection limits to 173.2 μg/L (Table 5). Other water pollution studies [37, 38, 63, 64] have examined additional fractions (dissolved, colloidal, and particulate), with the dissolved fraction generally characterized as the ultrafiltered (<10 kD). Using this partitioning, Kimball et al. [38] similarly found Al and Fe mostly near the limits of detection and Mn measurable in streams near Creede. Differences between concentrations of Fe and Al compared to Mn in study waters may due in part to the geochemical behavior of these solutes, that is, Fe and Al are among the most reactive constituents likely precipitating and forming colloidal materials, with Mn less reactive and more likely remaining in the aqueous phase.

Total concentrations of major elements showed slight variability among sites, ranging from 12 mg/L in Eastfork to 35 mg/L in Spruce (S05CO-079-004B). Overall, Eastfork had lower levels of all major elements compared to other sites. Total major element concentrations were in relatively good agreement across all samples (among and within sites), with mean and standard deviation of 28.3 ± 2.91 mg/L. The relative trend among major elements showed Ca > Na > Mg > K, with good agreement across all samples (among and within sites) showing means and standard deviations of 18.5 ± 2.1, 6.9 ± 1.5, 1.7 ± 0.1, and 1.1 ± 0.4 mg/L, respectively.

Total concentrations of trace elements showed significant variability among sites, ranging from 345 to 12108 μg/L, with much of this disparity explained by Zn levels (Table 5). Total trace element concentrations within sites were in relatively good agreement during the August sampling. It is expected that these concentrations may vary seasonally or

TABLE 4: Total major element concentrations for study waters.

Water site	Soil survey no.	Al	Ca	Fe	K	Mg	Na	SUM <sup>a</sup> (mg/L)
Gravelbar water	S05CO-079-001A	— <sup>b</sup>	18.5	—	1.2	1.6	5.9	27.2
Gravelbar water	S05CO-079-001B	—	19.2	—	1.1	1.6	6.4	28.4
Gravelbar water	S05CO-079-001C	—	19.3	—	1.2	1.6	6.2	28.2
Cottonwood water	S05CO-079-002A	—	17.7	—	1.9	1.9	11.4	32.9
Cottonwood water	S05CO-079-002B	—	18.1	—	2.1	2.0	10.9	33.1
Cottonwood water	S05CO-079-002C	—	18.4	—	2.1	1.9	9.5	31.9
Creek water	S05CO-079-003A-1	—	17.7	—	1.0	1.7	6.1	26.5
Creek water	S05CO-079-003A-2	—	17.5	—	1.0	1.7	6.0	26.2
Creek water	S05CO-079-003A-3	—	17.3	—	1.0	1.7	6.5	26.4
Creek water	S05CO-079-003B-1	—	17.6	—	0.9	1.7	6.6	26.9
Creek water	S05CO-079-003B-2	—	17.3	—	1.0	1.7	6.5	26.5
Creek water	S05CO-079-003B-3	—	17.4	—	0.9	1.7	6.4	26.4
Spruce water	S05CO-079-004A	—	22.9	—	1.3	1.9	6.1	32.1
Spruce water	S05CO-079-004B	—	23.7	—	1.2	2.0	6.8	33.7
Spruce water	S05CO-079-004C	—	24.6	—	1.3	2.1	6.7	34.6
Channel water	S05CO-079-004D-1	—	17.7	—	1.0	1.7	6.4	26.8
Channel water	S05CO-079-004D-2	—	17.9	—	1.0	1.7	6.4	26.9
Channel water	S05CO-079-004D-3	—	17.5	—	0.9	1.7	6.5	26.6
Channel water	S05CO-079-004E-1	—	17.6	—	1.0	1.7	6.3	26.5
Channel water	S05CO-079-004E-2	—	17.4	—	0.9	1.7	6.2	26.2
Channel water	S05CO-079-004E-3	—	17.1	—	0.8	1.6	6.4	26.0
Channel water	S05CO-079-004F-1	—	17.5	—	0.9	1.7	6.4	26.4
Channel water	S05CO-079-004F-2	—	17.3	—	0.9	1.7	6.2	26.1
Channel water	S05CO-079-004F-3	—	17.2	—	0.9	1.6	6.3	26.1
Westfork water	S05CO-079-013	—	15.0	—	0.7	1.6	5.0	22.2
Eastfork water	S05CO-079-014	—	7.1	—	0.6	0.6	3.7	12.0

<sup>a</sup>SUM = (Al + Ca + Fe + K + Mg + Na).

<sup>b</sup>— = concentration below detection limits.

year-round. In a study of the upper Animas River watershed in Colorado, affected by acid drainage, Besser et al. [35] found the annual stream discharge (with high runoff in spring and considerably lower discharge in winter) drives the trace element concentrations in the water column, resulting in aqueous concentrations of dissolved Zn and Cu typically near annual minima during summer and reaching annual maxima in late winter when these concentrations may be greater by a factor of three or more [65].

Water geochemistry showed a wide suite of trace elements present across the sampling area. The relative trend among trace elements showed (Zn > Sr > Ba) > (Mn > W > Cd) > (Sn > V ≈ Ni ≈ Cu > Co) > (Ag). Overall water composition, in terms of elements of potential concern, is in good agreement with the reports by the Willow Creek Reclamation Committee [39, 40].

Zinc concentrations ranged from 98.1 and 142.3 µg/L in Eastfork and Westfork waters, respectively, to 11088.3 µg/L in Cottonwood, S05CO-079-002B, suggesting significant metal loading downstream to Willow Creek. Zinc had the highest concentrations of all metals in study waters. Kimball et al. [38] similarly found East Willow Creek an insignificant

source of metal loads and Zn concentrations the highest of all metals in the Willow creek watershed, with its cumulative in stream load one of the highest of all the watersheds in the rocky mountains [66–71]. Zinc under oxidizing conditions and in the absence of other anions with which to react tends to remain as a dissolved cation, but in the presence of certain reactants, Zn can form sulfates, oxides/hydroxides, carbonates, and phosphates whose solubilities depend more on pH than on redox potential [62]. August sampling of Willow Creek showed SO<sub>4</sub> ranging from below detection limits to 1.7 mmol/L and the absence of Fe and Al. Study water pH ranged from 6.5 to 7.5, with those waters with pH < 7 (Gravelbar, S05CO-079-001A-C and Cottonwood, S05CO-079-002A-C) rendering the highest Zn values of 4027.9 and 11088.3 µg/kg, respectively. Total concentrations of colloidal Fe and Al in the Animas river near Silverton, Colorado, were considered limiting factors to Zn adsorption during the summer months, with Zn adsorption greater downstream in association with pH increases and during spring when Fe and Al concentrations were higher [37]. Studies that show significant Zn adsorption in the water column over a narrow



TABLE 5: Total trace element concentrations for study waters.

Water site	Soil survey no.	Ag	As	Ba	Be	Cd	Co	Cr	Cu	Mn	Ni	P	Pb	Sb	Sn	Sr	V	W	Zn	Total conc. by site (µg/L)
Gravelbar water	S05CO-079-001A	0.38	— <sup>a</sup>	133.8	—	18.7	1.5	—	10.3	—	6.0	—	—	—	9.5	242.7	6.0	45.1	4021.1	4495
Gravelbar water	S05CO-079-001B	0.40	—	207.5	—	19.1	1.5	—	8.7	—	5.8	—	—	—	9.7	247.4	6.0	45.1	4027.9	4579
Gravelbar water	S05CO-079-001C	tr <sup>b</sup>	—	169.2	—	18.1	1.4	—	6.4	—	5.8	—	—	—	9.8	248.6	5.9	44.6	4018.4	4528
Cottonwood water	S05CO-079-002A	0.36	—	414.0	0.01	70.3	2.2	—	5.8	141.3	7.1	—	—	tr	9.0	241.9	6.1	164.3	10405.6	11468
Cottonwood water	S05CO-079-002B	0.41	—	314.1	0.01	77.2	2.3	—	5.5	173.2	6.7	—	—	tr	9.4	243.4	6.0	181.9	11088.3	12108
Cottonwood water	S05CO-079-002C	0.36	—	202.6	0.01	62.1	1.9	—	4.5	101.7	6.2	—	—	tr	9.5	239.7	6.1	138.4	9521.3	10294
Creek water	S05CO-079-003A-1	0.42	—	138.8	—	19.4	1.6	—	5.6	76.3	5.7	—	6.7	—	9.3	221.9	6.2	31.1	2963.1	3486
Creek water	S05CO-079-003A-2	0.42	—	134.8	—	18.9	1.6	—	5.7	75.2	5.4	—	8.6	—	9.5	219.7	6.1	31.3	2961.2	3478
Creek water	S05CO-079-003A-3	0.35	—	136.5	—	19.1	1.6	—	5.6	75.4	5.5	—	9.3	—	9.6	217.8	6.0	30.9	2915.1	3433
Creek water	S05CO-079-003B-1	0.38	—	169.8	—	20.1	1.7	—	4.2	83.4	5.9	—	13.5	—	9.4	220.9	6.2	34.7	3198.1	3768
Creek water	S05CO-079-003B-2	0.43	—	175.3	—	24.2	1.6	—	5.8	81.8	5.3	—	149.6	—	9.4	220.0	6.1	41.7	3718.1	4439
Creek water	S05CO-079-003B-3	0.42	—	170.0	—	19.5	1.5	—	4.2	82.0	5.7	—	9.9	—	9.5	222.3	6.1	34.3	3235.4	3801
Spruce water	S05CO-079-004A	0.40	—	150.2	—	24.0	1.4	—	5.9	—	5.8	—	6.0	—	9.7	280.1	5.9	49.0	4335.8	4874
Spruce water	S05CO-079-004B	0.38	—	252.2	—	23.4	1.4	—	6.1	—	5.8	—	3.5	—	9.4	283.1	6.0	47.9	4256.8	4896
Spruce water	S05CO-079-004C	0.45	—	193.0	—	24.6	1.5	—	4.6	—	5.7	—	—	—	9.5	284.6	5.9	50.0	4359.5	4939
Channel water	S05CO-079-004D-1	tr	—	148.4	—	14.1	1.6	—	4.7	69.6	5.3	—	3.6	—	9.1	221.9	6.0	15.7	1650.5	2151
Channel water	S05CO-079-004D-2	tr	—	133.6	—	12.6	1.5	—	5.0	75.4	5.5	—	2.5	—	9.2	217.4	6.1	13.5	1425.5	1908
Channel water	S05CO-079-004D-3	0.41	—	209.0	—	12.3	1.6	—	5.1	67.3	5.4	—	4.0	—	9.3	219.2	6.0	13.6	1472.7	2026
Channel water	S05CO-079-004E-1	tr	—	152.2	—	17.3	1.6	—	4.9	74.8	5.6	—	7.3	—	9.3	221.9	6.1	26.6	2591.9	3119
Channel water	S05CO-079-004E-2	tr	—	148.3	—	17.3	1.6	—	5.3	79.5	5.4	—	6.9	tr	9.4	219.3	6.0	26.4	2570.5	3096
Channel water	S05CO-079-004E-3	tr	—	203.5	—	16.6	1.6	—	5.0	71.7	5.3	—	8.5	—	9.4	218.0	6.0	25.2	2464.2	3035
Channel water	S05CO-079-004F-1	tr	—	188.3	—	19.3	1.7	—	3.6	85.1	5.3	—	5.4	—	9.2	221.8	6.0	31.3	2949.6	3527
Channel water	S05CO-079-004F-2	0.40	—	166.1	—	19.8	1.6	—	3.6	90.6	5.4	—	9.3	—	9.7	220.7	6.0	32.4	3077.5	3643
Channel water	S05CO-079-004F-3	0.35	—	167.7	—	18.2	1.7	—	3.7	84.7	5.3	—	1.5	—	9.3	219.6	6.0	31.7	2941.5	3491
Westfork water	S05CO-079-013	0.38	—	218.3	0.01	2.6	1.4	—	4.8	—	4.5	—	—	tr	9.3	244.1	6.2	—	142.3	634
Eastfork water	S05CO-079-014	0.43	—	107.6	—	1.0	1.4	—	4.3	—	4.2	tr	—	tr	8.7	112.7	6.6	—	98.1	345

<sup>a</sup> — = concentration below detection limits.

<sup>b</sup> tr = trace.

range of about one pH unit near pH 7 have a large excess of absorbent, usually Fe or Al hydroxides, relative to the total Zn concentration [37, 72, 73].

Copper levels ranged from 3.6 to 10.3  $\mu\text{g/L}$ . Cadmium which most often exists in small quantities in Zn ores ranged from 1.0 to 77.2  $\mu\text{g/L}$ . Lead was detected in some samples, with the greatest amount (149.6  $\mu\text{g/L}$ ) in one replicate of the second-day sampling of the Creek water (S05CO-079-003B-2). This higher Pb value may be due in part to the capturing of more sediment in the sample compared to the other samplings and/or reflective of time or length scales of temporal or lateral variability in the stream. In a study of streams near Creede, Kimball et al. [38] found colloidal and dissolved Pb relatively high compared with many streams affected by mine drainage, with colloidal Pb > dissolved Pb and in higher concentrations downstream from Nelson Tunnel versus upstream despite no great variation in pH or major-ion concentrations. With observed pH range of study waters exhibiting mixed solid phases (organics and inorganics) [39, 40], preferential trace metal adsorption sequence in water system may be Pb > Cu > Cd > Zn [74], explaining in part the lack of Pb in some samples of stream waters compared to Zn.

Strontium and Ba levels showed relatively high levels, ranging from 112.7 to 283.1 and 107.6 to 414.0  $\mu\text{g/L}$ , respectively. Strontium sources are linked to nonore minerals with its loading profiles indicating sources upstream [38]. Study waters showed relatively low Ag levels, ranging from trace to 0.35  $\mu\text{g/L}$ . Arsenic, Be, Cr, P, and Sb were not detected in water samples.

Geochemistry of water samples associated with sampled soils showed higher levels of trace elements compared to stream samplings, for example, Cottonwood water (S05CO-079-002A) with Zn, Cd, and Mn levels of 11088.3, 77.2, and 173.2  $\mu\text{g/L}$ , respectively. Cottonwood had some of the lowest pH (6.5 to 6.6) and highest EC (0.20 to 0.2 dS/m) values compared to other sites. Under some circumstances, such as increases in salinity, decreases in redox potential (oxygen deficient), or decreases in pH, metals may be desorbed from sediments and solubilize in the water [75]. These circumstances may include when the water flow is physically obstructed causing water to pool and stagnate. The stream system may have a reasonably good buffering system, with low daily variability in pH and EC. The ability to resist abrupt changes in pH tends to prevent or slow metal conversion to soluble forms, which would increase the concentration of potentially toxic trace elements.

The "reference" or "baseline" sites of Westfork and Eastfork waters had relatively low levels of trace elements compared to other sites with Zn (98.1 and 142.3  $\mu\text{g/L}$ , resp.) and Cd (1.0 and 2.6  $\mu\text{g/L}$ , resp.). Overall, Eastfork showed lower levels of trace elements compared to Westfork. These data indicate trace element concentrations are significantly different at these higher elevations compared to the sampling sites at the lower elevations.

**3.3. Soils: Physical, Mineralogical, and Chemical Properties.** Study soils were classified as Aquic Cryofluvents, showing redox depletions with low chroma within the upper 50 cm of

surface, and having aquic conditions for some time in normal years [54]. Soil textures were primarily coarse-textured (loam to coarse sand), with the >2-mm fraction ranging from 1 to 73% (Table 6). Soils had mixed mineralogy (kaolinite, smectite, and hydroxyl-interlayer smectite) (Table 6). Smectitic clays typically show the finest particle-size distribution of naturally occurring clay minerals (particles <0.05  $\mu\text{m}$ ) and have electrically charged surfaces that permit the adsorption and absorption of water and other substances, whereas the kaolin group of clays includes particles with relatively large size and neutral electrical charge resulting in less potential for persistent suspension and turbidity. Smectitic clays have been linked as a primary cause of persistent turbidity (fine inorganic and organic particles suspended within water column) in the Cascade Range, North Santiam River, Willamette National Forest [76]. For August and July surface and mine water sampling, total suspended solids (TSS) ranged upwards of 15.4, 18.1, and 12.8 mg/L in main channel sites in East Willow Creek, West Willow Creek, and Mainstream Willow Creek, respectively [39].

For sampled soils, the pH (1:1 water) for surface materials ranged from 5.4 to 6.8 (strongly acid to neutral), with the exception of the Denuded Mound soil with very strongly acidic pH of 4.6 (Table 6). The Sedge Mound soil which was in close proximity to the Denuded Mound soil had a pH of 5.6.

Acidic conditions and low fertility may explain in part the disparity of plant vegetation in the Sedge Mound (100% base saturation by CEC-7, pH 5.6) compared to the Denuded Mound (34% base saturation and 4.6 pH). Total C and N were also lower in the Denuded Mound (1.33 and 0.185%, resp.) compared to the Sedge Mound (2.43 and 0.246%, resp.) (Table 6). Additionally, the Sedge Mound compared to other soils showed the highest clay content (19.2%) and highest amount of available P (26.3 mg/kg) as measured by Bray P-1 (Table 6).

The Salty soil showed pH 5.7 with a relatively high saturated paste EC (8.00 dS/m) (Table 6), with the water soluble anion sulfate (168.1 mmol(-)/L) in greatest amount (data not shown). Typically, these water soluble cations and anions would show greater ion balance, suggesting some cations present in significant amounts were not measured by this method, with potential candidates of Fe, Cu, and Zn sulfates. Melanterite (hydrated Fe sulfate) is one of only a few water-soluble sulfate minerals, forming white to green encrustations and crystal aggregates. The primary source of Fe for melanterite is Fe sulfates such as pyrite, marcasite, and chalcopyrite. The chemical processes involved in mining that lead to widespread acidification of water bodies and deposition of heavy metals have been studied extensively, with some researchers [77] finding that microbes coat the pyrite surface with exudates that dramatically speed up oxidation and production of sulfuric acid instead of protecting the surfaces from oxidation as had been previously expected.

**3.4. Soils: Total Extractable Major and Trace Elements.** Total concentrations of major elements showed good agreement among soils. The relative trend among major elements showed Si > Al > K > Fe > Ca > Mg > Na > Ti > Sr >

TABLE 6: Selected chemical and physical properties of study soils.

Soil	Depth (cm)	EC <sup>a</sup> dS/m	pH	CEC-7 <sup>b</sup> (cmol/kg)	Base Sat. <sup>c</sup> (%)	Total C	Total N %	Total S	Bray P-1 mg/kg	Fe <sub>d</sub> <sup>d</sup> %	Al <sub>o</sub> <sup>e</sup> %	Mn <sub>d</sub>	Sand	Silt	Clay	>2-mm fraction (%)
Gravelbar	0–73	– <sup>f</sup>	6.8	6.9	86	0.47	0.060	0.04	22.5	1.1	0.04	0.2	91.9	5.0	3.1	65
Cottonwood	0–90	–	5.4	15.2	47	1.19	0.134	0.04	21.4	1.0	0.07	tr	69.0	18.3	12.7	19
Spruce	0–10	–	6.4	12.9	85	2.05	0.308	0.14	23.9	1.3	0.07	0.1	73.1	17.0	9.9	24
	10–40	–	6.7	6.8	97	0.43	0.708	0.10	30.8	1.3	0.04	0.1	88.7	6.4	4.9	63
Railroad	0–61	–	5.9	7.0	19	0.52	0.035	0.22	13.9	1.6	0.05	0.1	80.3	13.8	5.9	59
	61–120	–	4.9	5.3	42	0.23	0.040	0.13	21.0	1.4	0.03	0.2	89.6	6.8	3.6	66
Western Channel	0–40	–	6.4	6.2	84	0.41	0.139	0.17	23.9	0.9	0.03	0.1	89.5	5.9	4.6	70
Salty	0–20	8.00	5.7	22.4	29	2.76	0.229	0.28	–	1.3	0.09	0.1	51.4	32.5	16.1	1
North	0–40	–	6.2	7.1	100	0.50	0.063	0.19	10.1	1.3	0.07	0.2	87.0	7.8	5.2	73
South	0–40	–	6.1	6.0	57	0.27	0.034	0.08	9.6	1.4	0.03	0.1	93.4	3.6	3.0	47
Denuded Mound	0–40	–	4.6	16.1	34	1.33	0.185	0.23	17.0	1.2	0.08	tr	55.8	28.5	15.7	3
Sedge Mound	0–40	–	5.6	23.1	100	2.43	0.246	0.13	26.3	1.0	0.07	tr	50.8	30.0	19.2	4

EC<sup>a</sup> = electrical conductivity, saturated paste extract.

CEC-7<sup>b</sup> = cation exchange capacity by NH<sub>4</sub>OAc, pH 7.

Base Sat.<sup>c</sup> = base saturation by NH<sub>4</sub>OAc, pH 7.

Fe<sub>d</sub><sup>d</sup> = dithionite-citrate extractable iron.

Al<sub>o</sub><sup>e</sup> = ammonium oxalate extractable aluminum.

–<sup>f</sup> = concentration below detection limits.

Zr, with good agreement among soils (Table 7). This trend was also in relatively good agreement with a dataset of 486 pedons from across the US, inclusive of both anthropogenic and nonanthropogenic soils such as those affected by mining activities, with data showing Si > Al > Fe > K > Ca > Na ≈ Mg > Zr > Ti [6].

Relatively high amounts of K in these coarse-textured soils were related to naturally high levels of potassium feldspars. Optical analysis showed the same trend for predominant minerals among all soils as follows: Chert > Plagioclase Feldspar > Quartz > Potassium Feldspar.

Total Fe and Al ranged from 25 to 38 and 52 to 74 g/kg, respectively. These values exceed the geometric means for Fe and Al (22 ± 2 and 40 ± 2 g/kg, resp.) as determined by Burt [6]. Dithionite-citrate and ammonium oxalate extractions [78–82] showed “active” Fe, Al, and Mn components, with Fe<sub>d</sub> 1.0% to 1.6%, Al<sub>o</sub> 0.03% to 0.09%, and Mn<sub>d</sub> trace to 0.2% (Table 6). The Fe<sub>d</sub> and Al<sub>o</sub> are generally considered good measures of the total pedogenic Fe and Al in soils, respectively [79]. The Fe<sub>d</sub>/Fe<sub>t</sub> ratios in soils showed free Fe oxides comprise 38% to 46% of the total Fe pool. Data suggest study soils serve as seasonal sources of Fe- and Al-rich colloids to stream waters. The interface between soil surface horizons and streams becomes tightly linked during high-flow events, resulting in increases in stream concentrations and depletions of soil constituents [83].

Total concentrations of trace elements were significantly greater in soils than in water samples. Relatively low concentrations of metals in the Hei River, China despite the contamination to soils and sediments were related to water flow rates high enough to dilute releases from the stream bank soils and sediments [84]. Total trace element (TE) concentrations in study soils showed significant short-range spatial variability, ranging from 2819 in Sedge Mound to 19274 mg/kg in Salty,

and seeming to follow no directional pattern along the stream (Table 8). Most of this variability was explained by differences in Zn and Pb levels among soils, varying by factors of nearly 20 and 30, respectively.

Trace elements from anthropogenic sources have been found to be more mobile than those of native origin [85–87]. A common method to quantify the release and transport of metals in surface-contaminated soils is the distribution of these contaminants within the soil profile [88]. Total concentrations were higher in surface layers of study soils compared to underlying materials, with Spruce showing 10991 versus 9925 mg/kg, respectively, and Railroad 11117 versus 7893 mg/kg, respectively. These data are in agreement with Burt [6] finding the median value of most trace elements (Cd, Cu, Ni, Pb, Zn, and Hg) significantly higher in surface horizons of anthropogenic soils ( $n = 392$ ) compared with those in surface horizons of nonanthropogenic soils.

Similar to the water data, there was a wide suite of trace elements present in the soils across the sampling area. The relative trend among trace elements showed (Pb ≈ Zn > Mn > Ba > P) > (As > Cu > Sr > V > Cd > Sb ≈ Ag) > (Co ≈ Cr > Mo ≈ Sn ≈ Ni) > (Be ≈ W > Se ≈ Hg), with good agreement among soils. Geochemistry of soils does not parallel the geochemistry of the stream waters. Relatively high Pb amounts in the soils compared to the water samples may be reflective of its relatively low solubility in water and low mobility in soils, accumulating primarily on the surface where its increasing presence can begin to affect soil microflora [89].

The Denuded Mound and Sedge Mound soils were demonstrative of the vegetative disparities along the stream bank. The Denuded Mound and Sedge Mound showed significant differences in total trace element concentrations

TABLE 7: Total major element concentrations for study soils.

Soil	Depth (cm)	Al	Ca	Fe	K	Mg g/kg	Na	Si	Ti	Zr	SUM <sup>a</sup> (g/kg)
Gravelbar	0–73	64	10	26	45	4	15	327	2	98	591
Cottonwood	0–90	74	14	26	33	6	18	314	3	100	588
Spruce	0–10	69	14	31	35	5	16	308	3	94	575
	10–40	62	14	38	37	4	17	324	3	88	587
Railroad	0–61	52	8	35	39	3	13	336	2	86	574
	61–120	55	9	32	41	3	15	339	3	88	585
Western Channel	0–40	63	12	34	38	4	16	336	3	92	598
Salty	0–20	66	12	30	28	6	14	312	3	108	579
North	0–40	66	11	30	40	4	16	332	2	93	594
South	0–40	62	12	35	37	4	17	338	3	84	592
Denuded Mound	0–40	66	13	30	28	6	16	332	3	92	586
Sedge Mound	0–40	72	17	25	29	7	17	306	3	96	572

SUM<sup>a</sup> = (Al + Ca + Fe + K + Mg + Na + Si + Ti + Zr).

(15317 versus 2819). Soil pH for the Denuded Mound and Sedge Mound was 4.6 versus 5.6, respectively. These results would tentatively suggest that a correlation may exist between metal levels and soil pH and vegetation or lack thereof along the stream. In a study of smelter-contaminated soils (Cu, Zn, Pb, and Cd) in Anaconda and Deer Lodge Valley, Montana, Burt et al. [49] found that low pH, alteration in species composition in plant communities, and reduction in plant growth and vigor often occur in conjunction with soil contamination, but that these easily measurable and observable properties alone could not be used as field indicators of total trace element concentrations. Observable differences in these Montana plant communities were determined to serve more appropriately as criteria to determine impact classes (e.g., severe, moderate, and slight) for soils affected by contamination but not correlated to total trace element content [49]. Soil pH is useful information in terms of bioavailability of trace elements [90–92].

**3.5. Soils: Chemical Fractionations.** Percent recovery ranged from 104 to 140%, indicating relatively good agreement between SUM<sub>SEQ</sub> and SUM<sub>TE</sub>. There was also good reproducibility between the two replications of the sequential fractionation (data not shown). Precision and accuracy of the sequential extraction procedure are generally considered inherently good, with the limiting factor the inherent heterogeneity of the specimen [10]. Study soils were located on the floodplain with colluvial and alluvial deposits which create a more heterogeneous medium for soil development (e.g., horizonation, morphology, and texture) [93]. For more details, see Table 9.

In general, study soils showed the OX (15 to 68%), SS/CAR (23 to 47%), and RES (7 to 25%) as the predominant fractions over the EX (3 to 22%), OM/S (5 to 14%), and WS (1 to 16%) fractions. Element-specific bioavailable fractions (WS and EX) showed Pb (0.29% to 4.60% and 0.94% to 24.27%, resp., see Table 10), Cd (0.99% to 23.37% and 5.28% to 40.18%, resp., see Table 11), Zn (0.77% to 24.39% and

4.14% to 32.67%, resp., see Table 12), and As (0.09% to 2.15% and 0.39% to 2.73%, resp., see Table 14). In contrast, the Montana smelter soils [11] had lower total metal concentrations (1836 to 3605 mg/kg), smaller WS (0.02% to 1.0%) and EX (0.2% to 9.3%) fractions, larger RES (14.3% to 70.1%) fraction, and smaller potentially bioavailable fractions (Pb, Cd, and Zn), exception being the greater EX Cu fraction in the Montana soils (4.67% to 30%) compared to Willow Creek (1.01% to 5.32%, Table 13). Similarly, the Montana smelter soils showed the OX fraction (29.7% to 39.8%) as the predominant fraction, with this fraction exceeding the RES fraction in surface layers in both studies. These data suggest that some anthropogenic inputs were added, as well as later transformed to, OX forms. Anthropogenic metals, initially present as poorly crystalline phases, may oxidize in surface soil horizons. Oxides have a scavenging action for trace elements disproportionate to their own concentrations, and as such constitute important sources of potentially bioavailable trace elements [10]. Overall, results suggest the Willow Creek soils are more contaminated than the Montana smelter soils, showing not only greater total metal levels but also an overall greater pool of potentially bioavailable trace elements, specifically those of concern (e.g., Cd, Pb, and Zn).

Soils in both studies have been affected by over 100 years of anthropogenic inputs, with the Willow Creek soils from mining and the Montana study soils from smelting of ores, primarily copper. While both sites have been inactive for a number of years, the geochemical processes are more active and impacts on-going in Willow Creek compared to the Montana study soils, related to site-specific differences, for example, topography, geology, climate, soil properties, and contaminant type. The Willow Creek soils are located on a floodplain whereas the Montana soils are on uplands with steep slopes (e.g., 30%), suggesting more active processes of metal transport to and potential accumulation in the Willow Creek soils. Smelter-derived particles have been shown to rapidly alter soon after deposition through weathering

TABLE 8: Total extractable trace elements (TE) of study soils.

Sample no.	Depth	Ag	As	Ba	Be	Cd	Co	Cu	Cr	Hg	Mn	Mo	Ni	P	Pb	Sb	Se	Sn	Sr	V	W	Zn	SUM <sub>TE</sub> <sup>a</sup> (mg/kg)
Gravelbar	0-73	8.5	98.4	522.8	0.8	15.2	6.5	85.2	4.5	0.10	1805.4	2.5	2.7	454.5	2622.8	7.9	0.37	2.1	39.6	37.6	0.69	2415.0	8133
Cottonwood	0-90	2.0	35.1	289.2	1.2	21.1	5.8	26.6	6.4	0.05	618.0	1.3	3.3	552.8	1154.4	3.2	0.50	1.3	57.8	44.0	0.17	2648.9	5473
Spruce	0-10	11.7	153.7	1138.4	1.3	25.6	7.5	112.7	5.9	0.17	1719.2	4.7	3.3	593.0	3776.6	11.6	0.51	3.3	59.0	45.0	1.03	3316.9	10991
	10-40	10.1	183.7	890.0	0.8	14.7	8.1	93.3	6.6	0.13	2130.0	5.3	3.6	561.5	3251.3	13.2	0.36	3.5	53.0	58.9	1.12	2635.9	9925
Railroad	0-61	30.0	559.6	817.2	0.9	17.0	5.5	125.3	5.5	0.30	1310.6	12.9	2.6	463.7	4977.2	46.2	0.31	5.2	36.8	41.1	2.40	2656.7	11117
	61-120	32.8	368.5	874.8	0.7	8.3	5.5	80.1	5.2	0.28	1528.9	6.6	2.5	476.9	3134.5	31.8	0.31	3.8	40.4	41.9	1.08	1248.4	7893
Western Channel	0-40	10.6	157.0	476.0	0.9	23.9	7.4	98.8	5.2	0.14	2113.0	3.5	2.8	523.1	3702.9	14.0	0.41	8.8	44.4	45.8	1.25	4043.4	11283
Salty	0-20	23.2	168.1	617.4	1.5	86.6	9.7	110.8	8.1	0.27	1675.1	4.3	4.4	695.1	4807.7	14.0	0.63	5.6	92.3	46.1	0.52	10903.0	19274
North	0-40	14.1	172.8	956.9	1.0	24.9	9.0	128.5	4.3	0.20	2786.6	3.3	3.0	448.7	4233.7	15.6	0.40	2.9	49.2	39.2	1.38	3767.0	12663
South	0-40	17.3	167.2	639.6	0.6	13.7	6.6	57.2	5.3	0.18	1324.1	5.0	2.6	509.7	2701.3	13.5	0.37	6.1	50.1	48.4	0.95	2093.9	7664
Denuded Mound	0-40	10.7	82.9	339.3	1.1	25.9	5.4	60.3	5.9	0.16	786.2	3.7	3.2	747.3	8748.5	7.1	0.71	1.6	73.1	40.0	1.46	4371.8	15317
Sedge Mound	0-40	0.9	25.2	343.7	1.4	4.5	6.1	17.2	8.1	0.04	627.4	0.7	4.4	733.0	306.6	1.7	0.69	1.2	100.5	45.8	0.06	589.8	2819

<sup>a</sup>SUM<sub>TE</sub> = (AgTE + AsTE + BaTE + BeTE + CdTE + CrTE + CuTE + CoTE + HgTE + MnTE + MoTE + NiTE + PTE + SbTE + SeTE + SrTE + VTE + WTE + ZnTE)

TABLE 9: Sequential extraction as percent of total extractable trace elements (TE) in study soils.

Soil	Depth (cm)	Sequential fractionations <sup>a</sup>					Recovery <sup>b</sup> (%)	
		WS	EX	SS/CAR % of total	OX	OM/S		RES
Gravelbar	0–73	1	3	42	45	10	11	113
Cottonwood	0–90	1	21	40	36	9	12	119
Spruce	0–10	1	5	47	41	11	21	126
	10–40	1	3	41	68	9	19	140
Railroad	0–61	2	9	16	47	14	24	111
	61–120	1	11	23	48	6	25	113
Western Channel	0–40	1	4	41	42	14	10	112
Salty	0–20	16	16	43	28	5	7	115
North	0–40	1	4	37	47	14	10	113
South	0–40	4	10	31	38	10	15	108
Denuded Mound	0–40	8	22	42	15	9	7	104
Sedge Mound	0–40	2	6	28	54	12	22	124

<sup>a</sup>Sequential fractionations: WS, water soluble; EX, exchangeable; SS/CAR, specifically sorbed/carbonate bound; OX, oxide-bound; OM/S, organic /sulfide-bound; RES, residual.

<sup>b</sup>Recovery = (SUMSEQ/SUMTE) × 100.

TABLE 10: Sequential fractionation of Pb in study soils.

Soil	Depth (cm)	Pb <sub>WS</sub>	Pb <sub>EX</sub>	mg/kg			Pb <sub>RES</sub>	Pb <sub>SUMSEQ</sub> <sup>a</sup> (mg/kg)
				Pb <sub>SS/CAR</sub>	Pb <sub>OX</sub>	Pb <sub>OM/S</sub>		
Gravelbar	0–73	9.2	33.9	1756.2	773.3	13.6	157.8	2744
Cottonwood	0–90	4.1	11.9	903.5	287.0	10.3	58.6	1275
Spruce	0–10	11.9	39.9	2641.5	1194.3	24.2	228.6	4140
	10–40	12.6	34.7	2108.9	981.4	19.4	302.3	3459
Railroad	0–61	60.9	168.9	1097.5	2240.7	40.4	1351.5	4960
	61–120	24.6	175.2	1086.7	1056.9	19.1	865.4	3228
Western Channel	0–40	17.4	123.5	2529.5	1045.8	24.1	176.9	3917
Salty	0–20	22.1	50.2	3603.0	1267.1	16.1	223.9	5182
North	0–40	9.9	83.7	2625.0	1595.8	17.3	221.9	4554
South	0–40	126.9	148.7	1461.8	673.5	20.7	321.7	2753
Denuded Mound	0–40	284.2	2070.0	5628.9	402.5	13.7	130.3	8530
Sedge Mound	0–40	1.0	1.8	164.4	90.9	2.9	27.3	288

<sup>a</sup>Pb<sub>SUMSEQ</sub> = Pb sum(WS + EX + SS/CAR + OX + OM/S + RES).

processes, leading to a release of metals in soils [94]. The aquic conditions of the soils along Willow Creek provide for a more dynamic system of metal release and further transport into the soil–water environment compared to the aridic soils in Montana. The higher pH Montana soils (derived from calcareous alluvium) provide for a greater buffering against acidification, resulting in a less soluble and therefore less mobile trace element fraction compared to the strongly acid to neutral pH Willow Creek soils (derived from ashflow tuffs). Soil pH and redox conditions are considered important factors affecting the chemistry of metals in soils and their uptake by organisms, with alternating aerobic and anaerobic conditions leading to changes in both factors thereby affecting most of those processes regulating metal speciation in soils [95–99].

All study soils showed high levels of contamination, with the Salty and Denuded Mound soils being the most contaminated showing the greatest SUM<sub>TE</sub> (19274 and 15317 mg/kg, resp.) and some of the greatest WS (16 and 8%, resp.) and EX (16 and 22%, resp.) fractions. The Salty soil with pH 5.7 and EC 8.00 dS/m had the highest Cd levels of total, WS, and EX fractions, with 84, 19.4, and 21.1 mg/kg, respectively. In general, soluble Cd levels are greater in moderately acid, oxidizing conditions, increasing 10 fold under these conditions compared to reducing conditions at all pH levels [75]. Cadmium has also been shown to be affected by salinity, with increased salinity supporting increased Cd concentration in solution [75]. The Salty soil also had the highest levels of Zn with 12134, 2959.0, and 2850.1 mg/kg in the total, WS, and EX fractions, respectively.

TABLE 11: Sequential fractionation of Cd in study pedons.

Soil	Depth (cm)	Cd <sub>WS</sub>	Cd <sub>EX</sub>	Cd <sub>SS/CAR</sub>			Cd <sub>RES</sub>	Cd <sub>SUMSEQ</sub> <sup>a</sup> (mg/kg)
				mg/kg				
Gravelbar	0–73	0.21	1.4	6.9	1.5	3.8	0.4	14
Cottonwood	0–90	0.24	6.1	10.7	1.3	1.5	0.2	20
Spruce	0–10	0.54	3.5	14.5	1.7	4.7	0.5	25
	10–40	0.15	1.2	6.4	3.2	3.8	0.6	15
Railroad	0–61	0.63	4.7	1.7	1.3	8.2	0.7	17
	61–120	0.26	3.2	1.6	1.3	1.4	0.3	8
Western Channel	0–40	0.25	1.9	8.4	2.4	8.3	1.3	23
Salty	0–20	19.44	21.1	35.9	3.0	2.9	0.9	83
North	0–40	0.41	2.2	8.5	2.8	9.6	0.9	24
South	0–40	0.69	3.7	2.9	1.4	3.7	0.9	13
Denuded Mound	0–40	5.36	8.4	2.7	0.8	7.1	0.6	25
Sedge Mound	0–40	0.08	0.21	2.79	0.27	0.58	0.05	4

<sup>a</sup>Cd<sub>SUMSEQ</sub> = Cd sum(WS + EX + SS/CAR + OX + OM/S + RES).

TABLE 12: Sequential fractionation of Zn in study soils.

Soil	Depth (cm)	Zn <sub>WS</sub>	Zn <sub>EX</sub>	Zn <sub>SS/CAR</sub>			Zn <sub>RES</sub>	Zn <sub>SUMSEQ</sub> <sup>a</sup> (mg/kg)
				mg/kg				
Gravelbar	0–73	22.0	113.3	1170.6	568.8	602.5	142.0	2619
Cottonwood	0–90	42.0	949.3	1051.4	496.1	273.7	93.3	2906
Spruce	0–10	66.0	304.8	1696.2	819.8	722.6	1129.4	4739
	10–40	20.3	111.4	1233.3	1169.0	586.7	747.5	2635
Railroad	0–61	89.6	534.4	237.1	551.4	1329.6	255.3	2997
	61–120	34.5	345.0	277.0	370.7	227.4	152.7	1407
Western Channel	0–40	22.9	183.1	1639.0	913.5	1364.0	300.1	4423
Salty	0–20	2959.0	2850.1	3932.7	1646.9	501.0	244.6	12134
North	0–40	32.4	173.0	1373.0	822.0	1515.3	228.6	4144
South	0–40	105.9	390.1	539.9	435.1	556.8	185.1	2213
Denuded Mound	0–40	855.0	1222.6	476.9	674.8	1190.2	225.9	4645
Sedge Mound	0–40	13.2	32.3	255.3	143.4	122.5	87.3	654

<sup>a</sup>Zn<sub>SUMSEQ</sub> = Zn sum(WS + EX + SS/CAR + OX + OM/S + RES).

TABLE 13: Sequential fractionation of Cu in study soils.

Soil	Depth (cm)	Cu <sub>WS</sub>	Cu <sub>EX</sub>	Cu <sub>SS/CAR</sub>			Cu <sub>RES</sub>	Cu <sub>SUMSEQ</sub> <sup>a</sup> (mg/kg)
				mg/kg				
Gravelbar	0–73	0.6	1.3	20.9	16.9	41.5	10.5	92
Cottonwood	0–90	0.6	0.4	3.6	9.1	7.7	9.1	31
Spruce	0–10	1.2	1.5	26.5	35.3	47.1	15.3	127
	10–40	0.7	1.1	22.1	30.7	44.9	11.3	111
Railroad	0–61	1.8	3.5	17.1	62.8	19.4	28.7	133
	61–120	0.8	4.4	15.9	31.4	10.9	19.6	83
Western Channel	0–40	0.6	2.9	27.5	22.6	46.6	8.6	109
Salty	0–20	1.0	1.3	38.2	38.0	24.0	15.7	118
North	0–40	0.4	2.4	31.9	45.3	40.6	15.0	135
South	0–40	2.5	2.5	12.1	14.5	15.1	9.4	56
Denuded Mound	0–40	0.6	1.0	12.1	20.3	13.0	11.1	58
Sedge Mound	0–40	0.4	0.6	0.5	4.0	4.2	8.6	18

<sup>a</sup>Cu<sub>SUMSEQ</sub> = Cu sum(WS + EX + SS/CAR + OX + OM/S + RES).

TABLE 14: Sequential fractionation of As in study soils.

Soil	Depth (cm)	As <sub>WS</sub>	As <sub>EX</sub>	As <sub>SS/CAR</sub>	As <sub>OX</sub>	As <sub>OM/S</sub>	As <sub>RES</sub>	As <sub>SUMSEQ</sub> <sup>a</sup> (mg/kg)
Gravelbar	0–73	0.6	1.8	15.4	70.5	4.6	53.2	146
Cottonwood	0–90	0.2	0.3	3.5	34.0	2.3	15.6	56
Spruce	0–10	0.7	2.2	25.7	143.7	8.7	70.7	252
	10–40	0.9	2.7	25.0	214.5	8.0	103.9	355
Railroad	0–61	5.7	7.6	18.6	520.5	10.3	294.5	857
	61–120	2.2	10.4	24.7	187.5	5.5	151.2	381
Western Channel	0–40	0.8	4.2	23.6	125.8	15.6	77.1	247
Salty	0–20	0.3	1.6	23.9	180.2	3.8	80.0	290
North	0–40	0.5	3.4	25.2	169.9	8.8	78.5	286
South	0–40	4.5	4.2	21.8	83.4	2.3	95.1	211
Denuded Mound	0–40	0.1	0.5	10.2	73.4	1.5	34.2	120
Sedge Mound	0–40	0.3	0.5	2.3	21.9	1.7	10.6	37

<sup>a</sup>As<sub>SUMSEQ</sub> = As sum(WS + EX + SS/CAR + OX + OM/S + RES).

Metal mobility was evaluated using the mobility factor (MF) [59, 100], representing the proportion of metals in the water soluble and exchangeable fractions and calculated as follows:

$$MF_x = \left( \frac{(WS_x + EX_x)}{WS_x + EX_x + OX_x + (SS/CAR_x) + RES_x} \right) \times 100, \quad (1)$$

where x = element.

The MF was assessed for the highly contaminated salty and denuded soils as follows: Cd  $\approx$  Zn > Pb > Cu > As. Values ranged as follows: 48.7 to 55.3% Cd; 44.7 to 47.9% Zn; 1.4 to 27.6% Pb; 1.9 to 2.8% Cu; and 0.5 to 0.6% As. These MFs are in relatively good agreement with other studies [101, 102], with Cd and Zn showing the highest mobility. Low CEC, sandy nature, and high permeability of study soils indicate inherently low sorption capacity for Cd and Zn, and as such high mobility. Generally, in all study soils, Cd appears mainly in the SS/CAR form, whereas Zn in the SS/CAR, OX, and OM/S forms. The relatively high MF<sub>Pb</sub> in the Denuded soil may be due in part to having the lowest OX fraction (15%) compared to other study soils, and similarly a low OM fraction (9%). Both of these fractions (Fe–Mn oxide and organic) have been shown to adsorb or complex Pb in less available forms in soils [103–105]. Generally, in all study soil, Pb appears mainly in the SS/CAR and OX forms. The low MF<sub>As</sub> for the salty and denuded soils may be due in part to its greater association with the OX and RES fractions over the more soluble fractions. These results show good agreement with other studies investigating As forms and distribution in soils [106–109].

#### 4. Conclusions

Historic mining activities and impacts from these activities have resulted in significant fluvial contamination of sampled soils and water in the Willow Creek floodplain. Thorough understanding of the factors affecting this contamination requires a good knowledge of the local geology, geomorphology, hydrology, climate, soil properties, and contaminant

amount, type, and form. There is a wide suite of trace elements present in both soils and waters. Trace element forms in water are strongly affected by site-specific water quality factors such as pH, EC, and other dissolved constituents. Total concentrations of trace elements in water showed significant variability among sites, with much of this disparity explained by Zn levels. Soil properties such as pH and redox conditions affect chemical forms and potential reactivity. Total trace element concentrations in study soils showed significant short-range spatial variability, and seemed to follow no directional pattern along the stream. In general, study soils showed the OX, SS/CAR, and RES as the predominant fractions over the EX, OM/S, and WS. The relative distribution of trace elements within the more soluble fraction (e.g., WS and EX) of soils is similar to their respective total concentrations, suggesting a relationship between total trace elements and the concentration of soluble, mobile fraction. Largest element-specific bioavailable fractions (WS and EX) were found in Cd, Zn, and Pb.

The expected outcome of the Willow Creek study and similar studies of anthropogenic soils conducted by USDA Soil Survey (e.g., [6, 7, 11, 49–51, 110]) is to better characterize important soils in specified-project areas, and more generally establish important relationships with other soil properties as well as with other soils both uncontaminated and contaminated. Our knowledge of the various soil processes affecting the elemental amounts and distribution in US soils and their relationships with other soil properties will enhance the understanding of the fate and transport of anthropogenic elements, thereby expanding the utility and application of soil survey knowledge in areas of environmental concern (e.g., urban, mine spoil reclamation, munitions disposal, smelter emissions, and agricultural waste applications).

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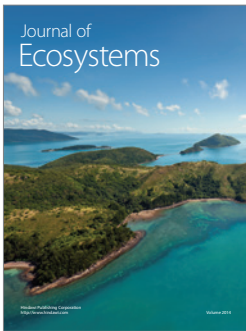
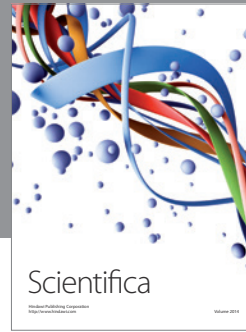
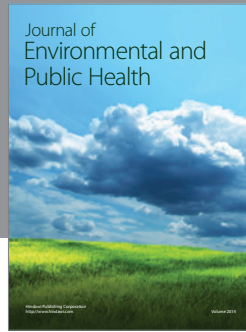


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