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Extent of a Mine Contamination Plume on the Willow Creek Floodplain, Creede, Colorado, as Determined by Willow Leaf Analysis

Open-File Report 2005-1267

U.S. Department of the Interior
U.S. Geological Survey

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P. Patrick Leahy, Acting Director

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This report has not been reviewed for geologic or stratigraphic nomenclature.

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
mile, nautical (nmi)	1.852	kilometer (km)
yard (yd)	0.9144	meter (m)
Area		
acre	4,047	square meter (m^2)
acre	0.4047	hectare (ha)
acre	0.4047	square hectometer (hm^2)
acre	0.004047	square kilometer (km^2)
square foot (ft^2)	929.0	square centimeter (cm^2)
square foot (ft^2)	0.09290	square meter (m^2)
square inch (in^2)	6.452	square centimeter (cm^2)
section (640 acres or 1 square mile)	259.0	square hectometer (hm^2)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
Volume		
barrel (bbl), (petroleum, 1 barrel=42 gal)	0.1590	cubic meter (m^3)
ounce, fluid (fl. oz)	0.02957	liter (L)
pint (pt)	0.4732	liter (L)
quart (qt)	0.9464	liter (L)
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m^3)
gallon (gal)	3.785	cubic decimeter (dm^3)
million gallons (Mgal)	3,785	cubic meter (m^3)
cubic inch (in^3)	16.39	cubic centimeter (cm^3)
cubic inch (in^3)	0.01639	cubic decimeter (dm^3)
cubic inch (in^3)	0.01639	liter (L)
cubic foot (ft^3)	28.32	cubic decimeter (dm^3)
cubic foot (ft^3)	0.02832	cubic meter (m^3)
cubic yard (yd^3)	0.7646	cubic meter (m^3)

cubic mile (mi^3)	4.168	cubic kilometer (km^3)
acre-foot (acre-ft)	1,233	cubic meter (m^3)
acre-foot (acre-ft)	0.001233	cubic hectometer (hm^3)
Flow rate		
acre-foot per day (acre-ft/d)	0.01427	cubic meter per second (m^3/s)
acre-foot per year (acre-ft/yr)	1,233	cubic meter per year (m^3/yr)
acre-foot per year (acre-ft/yr)	0.001233	cubic hectometer per year (hm^3/yr)
foot per second (ft/s)	0.3048	meter per second (m/s)
foot per minute (ft/min)	0.3048	meter per minute (m/min)
foot per hour (ft/hr)	0.3048	meter per hour (m/hr)
foot per day (ft/d)	0.3048	meter per day (m/d)
foot per year (ft/yr)	0.3048	meter per year (m/yr)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic foot per second per square mile [(ft^3/s)/mi^2]	0.01093	cubic meter per second per square kilometer [(m^3/s)/km^2]
cubic foot per day (ft^3/d)	0.02832	cubic meter per day (m^3/d)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
gallon per day (gal/d)	0.003785	cubic meter per day (m^3/d)
gallon per day per square mile [(gal/d)/mi^2]	0.001461	cubic meter per day per square kilometer [(m^3/d)/km^2]
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
million gallons per day per square mile [(Mgal/d)/mi^2]	1,461	cubic meter per day per square kilometer [(m^3/d)/km^2]
inch per hour (in/h)	0 .0254	meter per hour (m/h)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
mile per hour (mi/h)	1.609	kilometer per hour (km/h)
Mass		
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	megagram (Mg)
ton, long (2,240 lb)	1.016	megagram (Mg)
ton per day (ton/d)	0.9072	metric ton per day
ton per day (ton/d)	0.9072	megagram per day (Mg/d)
ton per day per square mile [(ton/d)/mi^2]	0.3503	megagram per day per square kilometer [(Mg/d)/km^2]
ton per year (ton/yr)	0.9072	megagram per year (Mg/yr)
ton per year (ton/yr)	0.9072	metric ton per year
Pressure		

atmosphere, standard (atm)	101.3	kilopascal (kPa)
bar	100	kilopascal (kPa)
inch of mercury at 60ºF (in Hg)	3.377	kilopascal (kPa)
pound-force per square inch (lbf/in^2)	6.895	kilopascal (kPa)
pound per square foot (lb/ft^2)	0.04788	kilopascal (kPa)
pound per square inch (lb/in^2)	6.895	kilopascal (kPa)
Density		
pound per cubic foot (lb/ft^3)	16.02	kilogram per cubic meter (kg/m^3)
pound per cubic foot (lb/ft^3)	0.01602	gram per cubic centimeter (g/cm^3)
Energy		
kilowatthour (kWh)	3,600,000	joule (J)
Radioactivity		
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)
Specific capacity		
gallon per minute per foot [(gal/min)/ft)]	0.2070	liter per second per meter [(L/s)/m]
Hydraulic conductivity		
foot per day (ft/d)	0.3048	meter per day (m/d)
Hydraulic gradient		
foot per mile (ft/mi)	0.1894	meter per kilometer (m/km)
Transmissivity*		
foot squared per day (ft^2/d)	0.09290	meter squared per day (m^2/d)
Application rate		
pounds per acre per year [(lb/acre)/yr]	1.121	kilograms per hectare per year [(kg/ha)/yr]
Leakance		
foot per day per foot [(ft/d)/ft]	1	meter per day per meter
inch per year per foot [(in/yr)/ft]	83.33	millimeter per year per meter [(mm/yr)/m]

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
°F=(1.8×°C)+32
Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:
°C=(°F-32)/1.8
Vertical coordinate information is referenced to the insert datum name (and abbreviation) here for instance, “North American Vertical Datum of 1988 (NAVD 88).”
Horizontal coordinate information is referenced to the insert datum name (and abbreviation) here for instance, “North American Datum of 1983 (NAD 83).”
Altitude, as used in this report, refers to distance above the vertical datum.

*Transmissivity: The standard unit for transmissivity is cubic foot per day per square foot times foot of aquifer thickness $[(ft^3/d)/ft^2]ft$. In this report, the mathematically reduced form, foot squared per day (ft^2/d), is used for convenience.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

NOTE TO USGS USERS: Use of hectare (ha) as an alternative name for square hectometer (hm^2) is restricted to the measurement of small land or water areas. Use of liter (L) as a special name for cubic decimeter (dm^3) is restricted to the measurement of liquids and gases. No prefix other than milli should be used with liter. Metric ton (t) as a name for megagram (Mg) should be restricted to commercial usage, and no prefixes should be used with it.

SI to Inch/Pound

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
kilometer (km)	0.5400	mile, nautical (nmi)
meter (m)	1.094	yard (yd)
Area		
square meter (m^2)	0.0002471	acre
hectare (ha)	2.471	acre
square hectometer (hm^2)	2.471	acre
square kilometer (km^2)	247.1	acre
square centimeter (cm^2)	0.001076	square foot (ft^2)
square meter (m^2)	10.76	square foot (ft^2)
square centimeter (cm^2)	0.1550	square inch (ft^2)
square hectometer (hm^2)	0.003861	section (640 acres or 1 square mile)
hectare (ha)	0.003861	square mile (mi^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
Volume		
cubic meter (m^3)	6.290	barrel (petroleum, 1 barrel = 42 gal)
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
cubic meter (m^3)	264.2	gallon (gal)
cubic decimeter (dm^3)	0.2642	gallon (gal)
cubic meter (m^3)	0.0002642	million gallons (Mgal)
cubic centimeter (cm^3)	0.06102	cubic inch (in^3)
cubic decimeter (dm^3)	61.02	cubic inch (in^3)
liter (L)	61.02	cubic inch (in^3)
cubic decimeter (dm^3)	0.03531	cubic foot (ft^3)
cubic meter (m^3)	35.31	cubic foot (ft^3)
cubic meter (m^3)	1.308	cubic yard (yd^3)
cubic kilometer (km^3)	0.2399	cubic mile (mi^3)

cubic meter (m^3)	0.0008107	acre-foot (acre-ft)
cubic hectometer (hm^3)	810.7	acre-foot (acre-ft)
Flow rate		
cubic meter per second (m^3/s)	70.07	acre-foot per day (acre-ft/d)
cubic meter per year (m^3/yr)	0.000811	acre-foot per year (acre-ft/yr)
cubic hectometer per year (hm^3/yr)	811.03	acre-foot per year (acre-ft/yr)
meter per second (m/s)	3.281	foot per second (ft/s)
meter per minute (m/min)	3.281	foot per minute (ft/min)
meter per hour (m/hr)	3.281	foot per hour (ft/hr)
meter per day (m/d)	3.281	foot per day (ft/d)
meter per year (m/yr)	3.281	foot per year ft/yr)
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
cubic meter per second per square kilometer [$(m^3/s)/km^2$]	91.49	cubic foot per second per square mile [$(ft^3/s)/mi^2$]
cubic meter per day (m^3/d)	35.31	cubic foot per day (ft^3/d)
liter per second (L/s)	15.85	gallon per minute (gal/min)
cubic meter per day (m^3/d)	264.2	gallon per day (gal/d)
cubic meter per day per square kilometer [$(m^3/d)/km^2$]	684.28	gallon per day per square mile [$(gal/d)/mi^2$]
cubic meter per second (m^3/s)	22.83	million gallons per day (Mgal/d)
cubic meter per day per square kilometer [$(m^3/d)/km^2$]	0.0006844	million gallons per day per square mile [$(Mgal/d)/mi^2$]
cubic meter per hour (m^3/h)	39.37	inch per hour (in/h)
millimeter per year (mm/yr)	0.03937	inch per year (in/yr)
kilometer per hour (km/h)	0.6214	mile per hour (mi/h)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
megagram (Mg)	1.102	ton, short (2,000 lb)
megagram (Mg)	0.9842	ton, long (2,240 lb)
metric ton per day	1.102	ton per day (ton/d)
megagram per day (Mg/d)	1.102	ton per day (ton/d)
megagram per day per square kilometer [$(Mg/d)/km^2$]	2.8547	ton per day per square mile [$(ton/d)/mi^2$]
megagram per year (Mg/yr)	1.102	ton per year (ton/yr)
metric ton per year	1.102	ton per year (ton/yr)
Pressure		
kilopascal (kPa)	0.009869	atmosphere, standard (atm)
kilopascal (kPa)	0.01	bar

kilopascal (kPa)	0.2961	inch of mercury at 60°F (in Hg)
kilopascal (kPa)	0.1450	pound-force per inch (lbf/in)
kilopascal (kPa)	20.88	pound per square foot (lb/ft^2)
kilopascal (kPa)	0.1450	pound per square inch (lb/ft^2)
Density		
kilogram per cubic meter (kg/m^3)	0.06242	pound per cubic foot (lb/ft^3)
gram per cubic centimeter (g/cm^3)	62.4220	pound per cubic foot (lb/ft^3)
Energy		
joule (J)	0.0000002	kilowatthour (kWh)
Radioactivity		
becquerel per liter (Bq/L)	27.027	picocurie per liter (pCi/L)
Specific capacity		
liter per second per meter [(L/s)/m]	4.831	gallon per minute per foot [(gal/min)/ft]
Hydraulic conductivity		
meter per day (m/d)	3.281	foot per day (ft/d)
Hydraulic gradient		
meter per kilometer (m/km)	5.27983	foot per mile (ft/mi)
Transmissivity*		
meter squared per day (m^2/d)	10.76	foot squared per day (ft^2/d)
Application rate		
kilograms per hectare per year [(kg/ha)/yr]	0.8921	pounds per acre per year [(lb/acre)/yr]
Leakance		
meter per day per meter [(m/d)/m]	1	foot per day per foot [(ft/d)/ft]
millimeter per year per meter [(mm/yr)/m]	0.012	inch per year per foot [(in/yr)/ft]

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Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:
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Extent of a Mine Contamination Plume on the Willow Creek Floodplain, Creede, Colorado, as Determined by Willow Leaf Analysis

By James A. Erdman, Leigh Ann Vradenburg, and Shea Clark Smith

Abstract

Ground and surface water in and along the broad floodplain of Willow Creek below Creede, Colorado, are contaminated by drainage from various mine adits and waste rock piles above the town and by leachates from a gravel-capped tailings pile below. These waters have been sampled through a set of 18 monitoring wells and found to have elevated in metal concentrations, especially of zinc (Zn) and cadmium (Cd). Zinc is of most concern because of its known toxicity to freshwater fish (e.g., Beregeri and Patil, 1986; Farag et. al., 1999; Hilmy et. al., 1987). Moreover, the mouth of Willow Creek spills into the Rio Grande River, a prime trout fishery. At issue, then, is the impact of the water quality of Willow Creek as it enters the Rio Grande River.

In an attempt to find a simple and cost-effective method to monitor contamination of surface and ground water in areas impacted by mining, we measured the content of 37 elements in willows (sandbar willow, *Salix exigua*, and one blue willow, *Salix drummondiana)*, which grow abundantly in this study area. We collected leaf samples at 14 sites, mostly on the Willow Creek floodplain below the town of Creede, Colorado. Willow functions as surrogate water well and a groundwater quality sampler because its roots usually extend into the ground water region (Robinson, 1956). Willows have also been shown to accumulate far more Cd than do other shrubs and trees in mineralized areas. Because Cd associates closely with Zn in plant tissue, and willow is fairly common at the project site, willow proved to be an ideal plant for our study.

The washed and dried leaf samples were macerated in a Wiley® mill and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) for 37 elements. Monitoring wells were located close to the willow sample sites at 5 of the 14 locations. However, groundwater samples were not collected simultaneously from these monitoring wells and thus no comparisons could be made between the two media.

Data from leaf analysis revealed clearly that the willows were highly enriched in Zn and Cd, more than any other of the 37 elements determined. A few sites on the shoreline of the Rio Grande River upstream from its confluence of Willow Creek provided values that can be considered background, which ran about two orders of magnitude less than the maximum concentrations found in samples at the base of the capped tailings. A few willow samples previously collected and analyzed from an anomalous seep seven miles below Willow Creek yielded elevated concentrations of both Zn and Cd, but not nearly to the extent as those sampled along the Willow Creek floodplain.

This phytogeochemical study provided a cost-effective method for assessing the extent of a leachate plume from generally non-point sources. Such a method may be useful as a preliminary sampling tool to guide the design of hydrogeochemical and geophysical studies.

Introduction

Historical background

Mining began in the mountains around Creede, Colorado, in the late 1800's and continued well into the 1980's. The narrow valley above the town is lined with abandoned mines. Part of the legacy of this historic silver (Ag) mining district is serious water pollution from both zinc (Zn) and cadmium (Cd) in Willow Creek that flows into the Rio Grande River. Cadmium occurs mainly in the Zn sulfides sphalerite and wurtzite, and is recovered with Zn usually from polymetallic ores containing lead (Pb) and copper (Cu) (Fleischer et al., 1974) and this ore type is common to the study area.

In the late 1990's, a small group of citizens in Creede, Colorado fought to keep their town from being placed on the priority list for the U.S. Environmental Protection Agency (USEPA) Superfund designation. This group of Creede residents, called the Willow Creek Reclamation Committee, joined forces to clean up the creek and preserve the mining heritage and quaint character of the town. The Willow Creek Reclamation Project was established to explore innovative, non-regulatory approaches to improving the water quality of Willow Creek and to protect the gold-medal fishery in the Rio Grande River downstream - a premier fly-fishing site. In 1999, the project received its first grant to characterize the problem and identify the pollutant loadings in the stream. Reclamation of an ecosystem that has been damaged by mine waste calls for an interdisciplinary approach. Success requires many disciplines: mining, aquatic biology, agriculture and riparian restoration, hydrology and hydrogeology, chemistry, soil science, public education, and outreach. According to Zeke Ward, the committee chairman, one of the four goals of the project has been to significantly improve the water quality of Willow Creek and, in so doing, protect the Rio Grande River.

Rationale for the Willow Leaf Study

The purpose of this study was to test the feasibility of using the chemical analysis of willow leaf samples as a low-cost, non-invasive surveying method to determine the extent of the contamination plume on the Willow Creek floodplain. An additional contaminated site, whose source is unknown, was sampled seven miles downstream on the Rio Grande River, just below what is locally known as the La Garita Bridge.

Meinzer (1923) defined a phreatophyte as "a plant that habitually obtains its water supply from the zone of saturation, either directly or through the capillary fringe." Although that term has continued in usage (see, e.g., Robinson, 1958; Freeze and Cherry, 1979), it appears to have fallen out of favor with some botanists specializing in root-system ecology (Lisa Donovan, University of Utah, personal communication, May, 1992). In his monograph on phreatophytes of >70 plant species then classified as such, Robinson (1958) lists willow (Salix spp.) as one of the eight most common phreatophytes in the western United States (the others are alfalfa [Medicago sativa], greasewood [Sarcobatus spp.], pickleweed [Salicornia europa; Allenrolfea occidentalis], rabbitbrush, [Chrysothamnus spp.] saltcedar [Tamarix spp.], saltgrass [Distichlis stricta], and cottonwood [Populus spp.] - the last also in the willow family). Willow commonly grows along streams or in river bottomlands where ground water is generally at shallow depth and readily available. Robinson (1958, p. 66) quoted a study that said: "Willows usually grow where the roots extend into the groundwater region."

Shkolnik (1984) reports that Zn enters the willow plant passively with willow leaf tissue typically elevated in Zn concentrations. However, Zn, like Cu, is stored mainly in the seeds. That leaf tissue takes up the most Zn is supported by a monograph by Antonovics and others (1971).

Further, they say, "The quantity of Zn in plants is related to the amount of Zn in the soil often in a clearly linear pattern. … Zinc therefore is readily taken in by plants growing on Zn-contaminated soil."

Plants assimilate Cd more readily than virtually any other element. Kabata-Pendias and Pendias (1984) plotted 33 elements using an index of bioaccumulation, and calculated the ratio of trace elements in plants to their concentrations in soils. They reported that Cd had the most intense degree of accumulation, far greater than boron, bromine, cesium, and rubidium (Rb), in that order. Zinc accumulation was slightly below Rb. Fleischer and others (1974) stated that plants exposed to concentrations of cadmium above those of normal background contain higher than normal concentrations of Cd.

Methods

Field Methods

This study of the phytogeochemistry of willow leaves was initiated to determine if their element concentrations could be used to determine the location of the leachate plume down gradient from the non-point sources. Usually a small feasibility survey is conducted first to determine whether a further in-depth study is warranted. No further study is planned because, unlike the project at the Norman landfill (Erdman and Christenson, 2000), the Willow Creek floodplain is very dusty and the surface has been unevenly contaminated by tailings.

On September 4, 2003, fourteen sites were sampled, with nine concentrated on the Willow Creek floodplain (Figures 1 and 2). Five of those sampling sites were within about 30 m of monitoring wells (MW). These included Site #1 at MW1,

Figure 5. Willow sampling site #7- Note the gravel-capped tailings pile from the former Emperious Mill in the mid-distance.

Site #5 at MW17, Site #6 at MW13, Site #7 at MW14, and Site #8 at MW3. Sites #6 and #7 occur at the base of the capped tailings. The willow leaf sample from Site #6 was most likely blue willow *(Salix drummondiana)* and not the more common sandbar willow, *S. exigua.* Two sampling sites are on or near the Rio Grande River upstream of Willow Creek: Site #10 near the Marshall Park Campground and Site #11 on a tributary stream, Miners Creek (Figures 1 and 3). Sample sites #12, #13, and #14 are located on the southwest side of the Rio Grande River between the La Garita Bridge and Wagon Wheel Gap approximately seven miles from Creede (Figures 1 and 4). Figures 5 and 6 are views from sampling sites #7 and #9, respectively.

Willow leaves were stripped from the current year's growth, and each sample usually was a composite of several shrubs at each site. The samples were then placed in cloth HUBCO® bags roughly 5 x 10 inches in size. The sampling locations were noted on the Creede quadrangle, the 7.5-minute series (topographic). The sample bags were later air-dried in the sun to prevent molding, and then shipped to the sample preparation service described below.

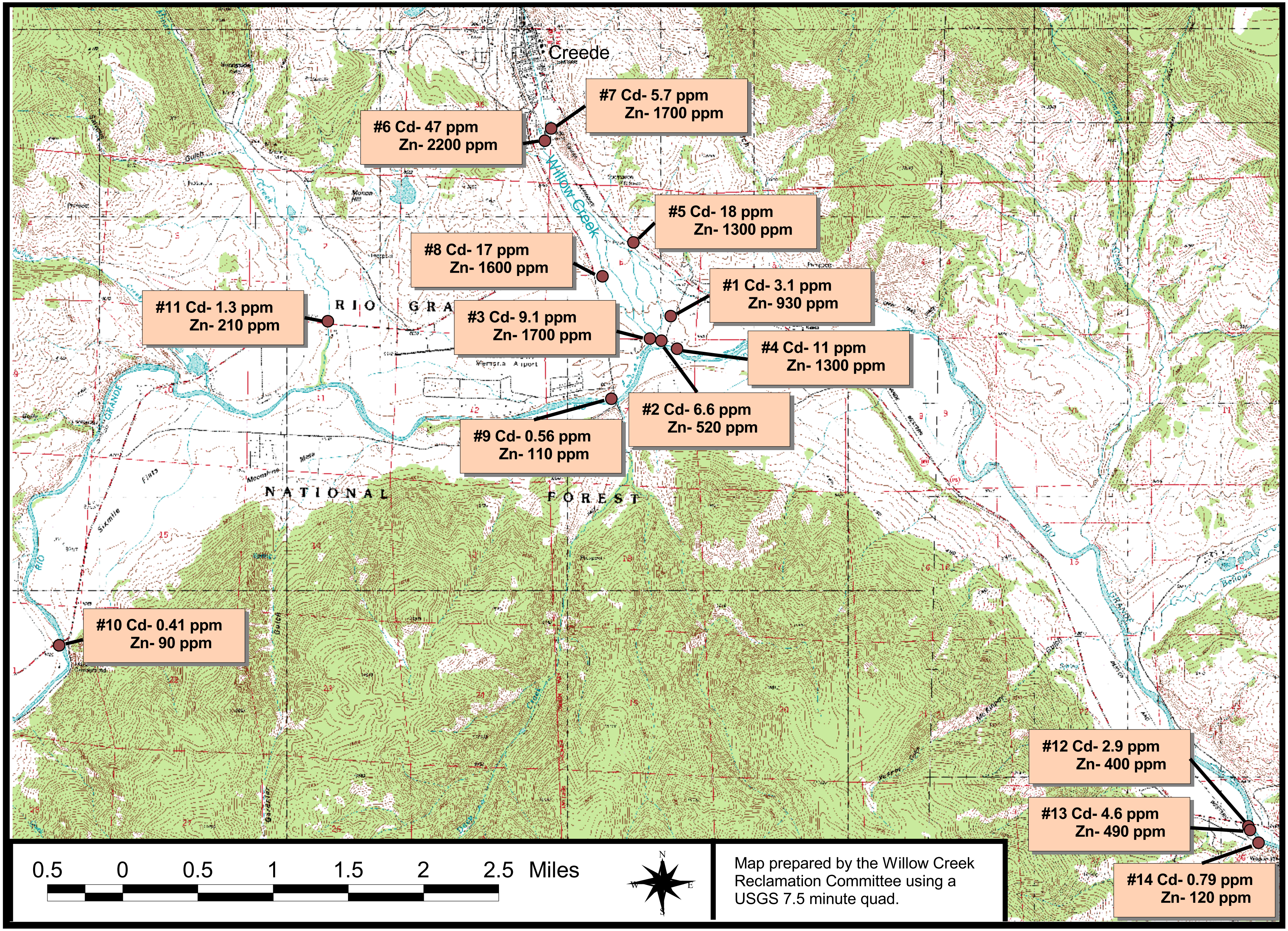

Figure 1. Willow leaf sample sites along Willow Creek and the Rio Grande. Corresponding cadmium (Cd) and zinc (Zn) tissue concentrations are shown in parts per million (ppm).

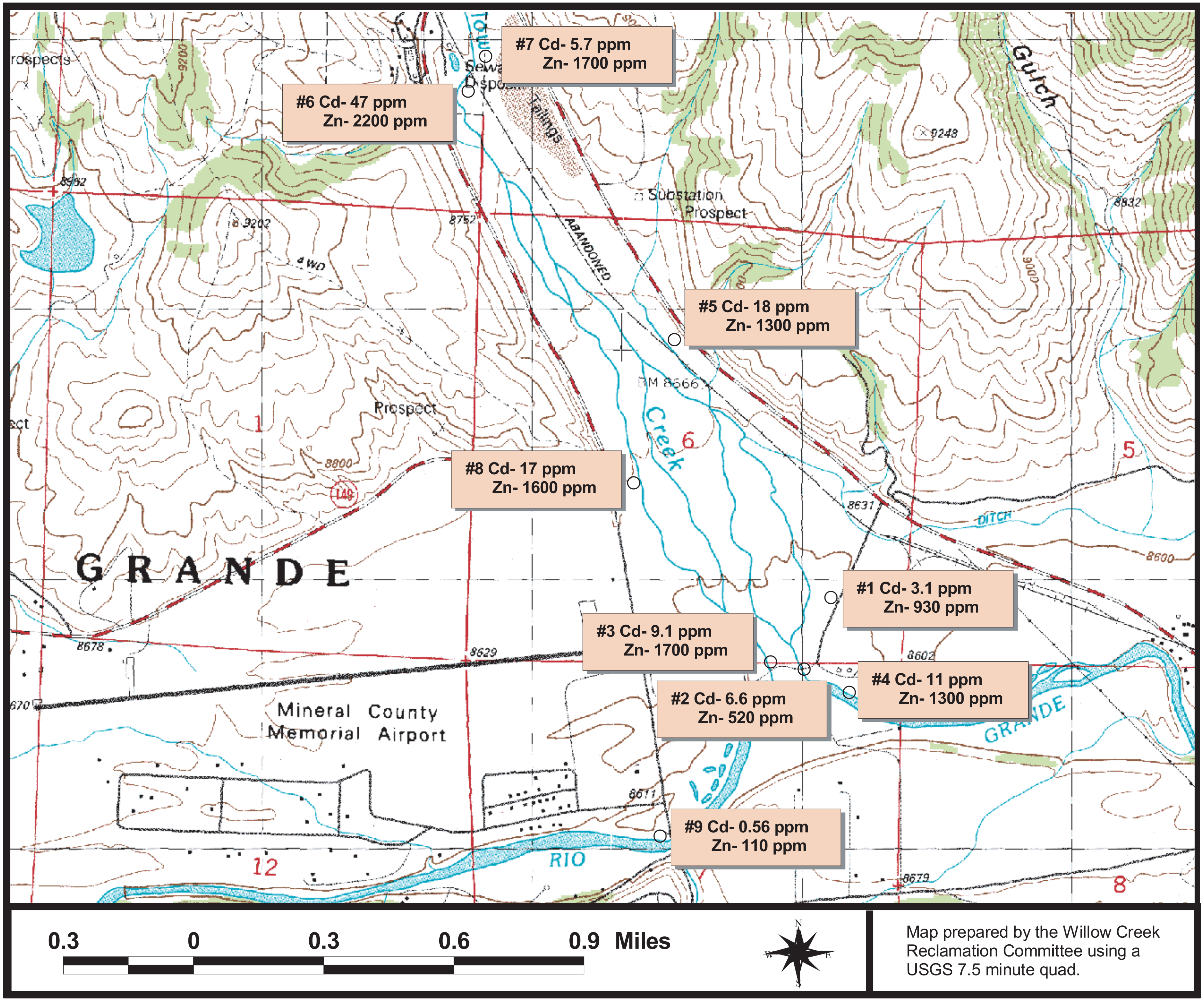

Figure 2- Willow leaf sample sites either on the Willow Creek floodplain or in proximity.

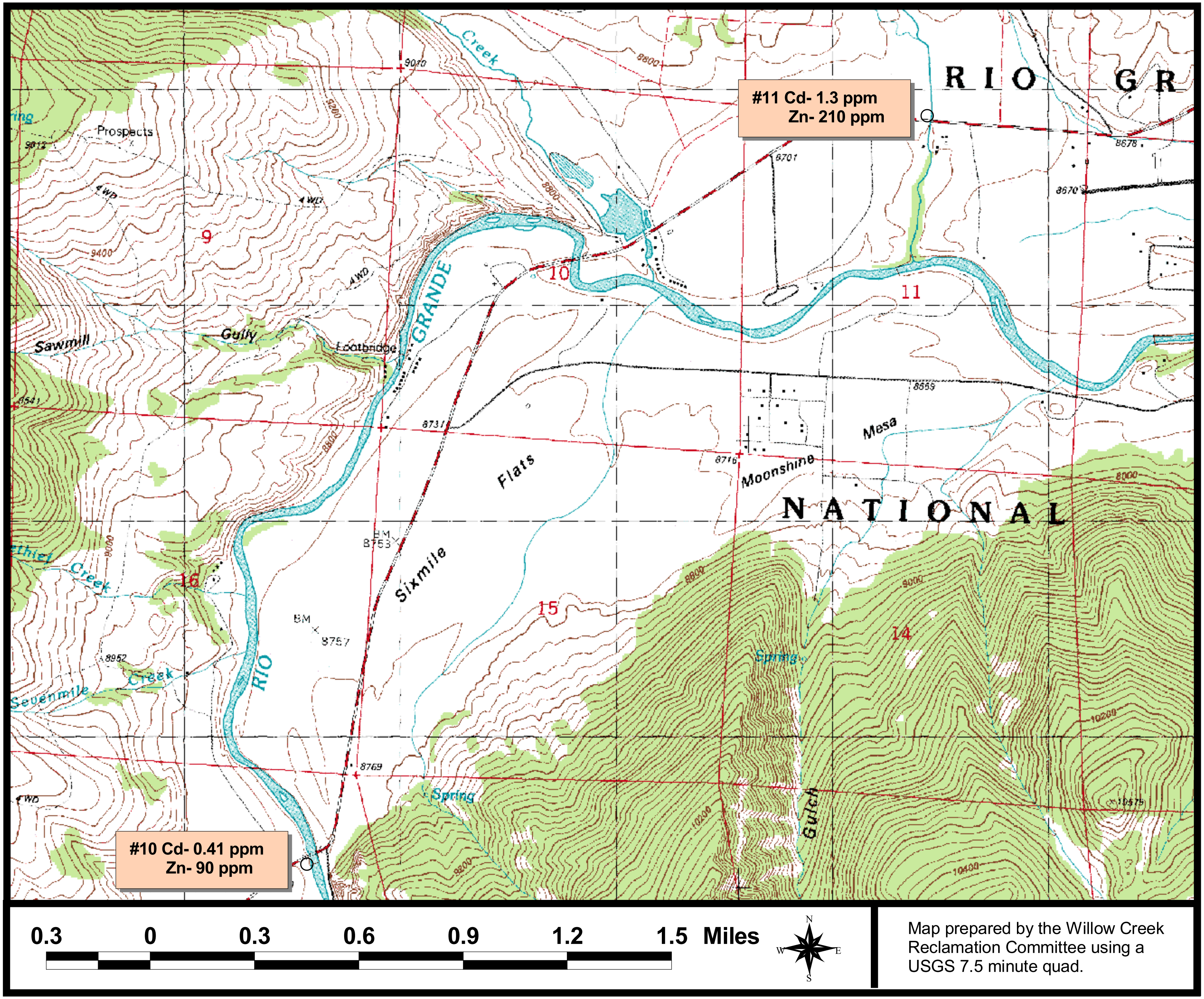

Figure 3. Willow leaf sample sites above the confluence of Willow Creek with the Rio Grande River.

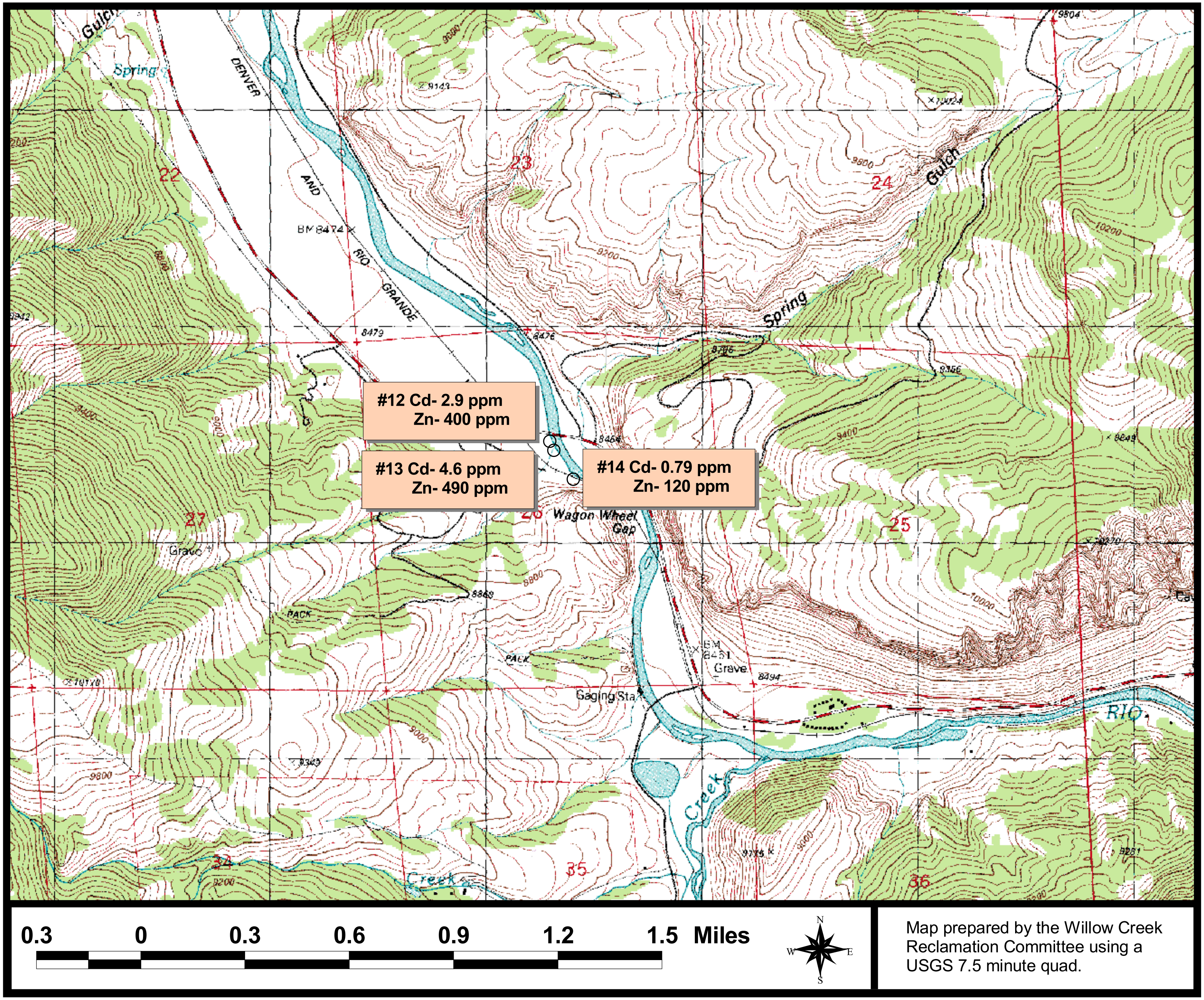

Figure 4. Willow leaf sample sites associated with a seep anomoly near the La Garita Bridge.

Sample Preparation and Analysis

Samples of willow leaves were received at the Minerals Exploration & Environmental Geochemistry (MEG) labs, Carson City, NV, in their cloth bags. These bags were tied and washed as a group in a washing machine through two wash-spin-rinse-spin cycles using unfiltered well water. This process has been proven to remove dust from the outer surfaces of plant tissue, thus decreasing surface contamination of the sample. The result is a more pure bio-organic sample.

Figure 6. Willow sampling site #9- The willow cluster on the right lies on the edge of the Rio Grande River, nearly a mile upriver from Willow Creek.

Quality assurance includes the use of internal standards and blind replicates. One of each was included in this run of 14 samples. In addition, the submittal was randomized to cope with possible systematic error or analytical drift (Miesch, 1976); although, given the relatively few samples, the likelihood of such an event was remote. The sample order was randomized after the washing process, and from that point the samples were handled in sequence order.

The samples were dried in microwave ovens, another proven method for rapidly removing moisture from the plant tissue. They were then milled in a Wiley® mill to pass a 0.5-mm screen

The macerated samples were sent to ACME Laboratories in Vancouver, BC, Canada, for analysis by inductively coupled plasma-mass spectrometry (ICP-MS) analysis after digestion of a 0.5-g aliquot with nitric acid. Thirty-seven elements were reported on a dry-weight basis either as percent (%), part per million (ppm), or part per billion (ppb).

Results

Precision (Reproducibility) of Willow Leaf Data

The analytical results from the willow leaf samples are presented in Table 1, including comparisons of both blind and non-blind duplicates. The analytical precision is excellent for both Cd and Zn, as it is for nearly all others, except for arsenic and Pb. That the two splits represent extremes in Zn and Cd concentrations lends even more credence to the data. This method improves confidence in any spatial patterns of the concentration distribution of an element. Two samples, those from Sites #5 and #10, were analyzed in duplicate to provide an estimate of precision or reproducibility, critical with any study (Miesch, 1971). The prep lab made a blind duplicate (QA 1) of #10 and placed it eleven positions away, at the end of the submittal. The analytical lab later made a split (RE #5) of sample #5 and analyzed it immediately after its parent sample. Unlike the duplicate of #5, the analytical lab did not know that #10 was being analyzed twice. The placement of these blind and non-blind duplicates, respectively, provided a long and short range measure of analytical drift, should it have occurred.

Table 1. Analytical data (dry-weight basis) for willow-leaf samples from the Willow Creek region below Creede, Colorado. Analyses by ICP-MS.

Element	Prep Duplicate	Original Sample	Analytical Duplicate	Original Sample	Survey Samples													
	QA1	#10	RE #5	#5	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14
Ag, ppb	4	4	65	62	10	24	9	52	62	30	15	11	5	4	8	5	10	10
Al, %	<.01	<.01	<.01	<.01	0.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
As, ppm	0.4	<.1	0.5	0.5	0.2	<.1	0.3	0.2	0.5	0.3	<.1	0.3	0.2	<.1	<.1	0.2	<.1	<.1
Au, ppb	<.2	<.2	<.2	<.2	0.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2	0.6	<.2	<.2	<.2	<.2	<.2
B, ppm	100	79	95	90	32	47	100	70	90	65	50	72	51	79	29	64	50	58
Ba, ppm	35	32	47	46	15	15	20	73	46	15	8.9	6.8	33	32	13	9.4	11	12
Bi, ppm	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02
Ca, %	1.4	1.3	2.7	2.9	2.3	1.5	1.9	2	2.9	1.2	0.76	1.2	1.8	1.3	1.1	1.3	0.77	0.67
Cd, ppm	**0.42**	**0.41**	**18**	**18**	**3.1**	**6.6**	**9.1**	**11**	**18**	**47**	**5.7**	**17**	**0.56**	**0.41**	**1.3**	**2.9**	**4.6**	**0.79**
Co, ppm	0.11	0.09	0.03	0.03	0.19	0.09	0.25	0.07	0.03	0.27	1.5	0.76	0.15	0.09	0.26	0.09	0.38	2.2
Cr, ppm	2.3	2.1	2.1	2.1	2.3	2	2.2	2.1	2.1	2.4	1.9	2.3	2	2.1	2.4	2.3	2.4	2.9
Cu, ppm	4.3	4	4.6	4.4	4.3	4.3	8.6	7.3	4.4	8.3	3.9	3.8	2.7	4	5.1	4.8	2.2	4.8
Fe, %	0.01	0.009	0.008	0.009	0.015	0.01	0.011	0.006	0.009	0.01	0.008	0.008	0.007	0.009	0.009	0.009	0.009	0.013
Ga, ppm	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Hg, ppb	9	10	16	7	5	9	7	7	7	7	11	11	7	10	15	5	10	9
K, %	0.54	0.53	0.48	0.48	0.39	0.71	0.36	0.48	0.48	0.61	0.75	0.49	0.66	0.53	0.54	0.85	0.4	0.37
La, ppm	0.05	0.05	0.08	0.07	0.12	0.07	0.04	0.13	0.07	0.03	0.34	0.05	0.05	0.05	0.07	0.05	0.02	0.09
Mg, %	0.28	0.27	0.36	0.36	0.39	0.18	0.17	0.24	0.36	0.22	0.24	0.22	0.27	0.27	0.22	0.21	0.19	0.23
Mn, ppm	47	41	62	64	280	72	38	110	64	83	500	190	120	41	240	35	63	290
Mo, ppm	0.57	0.53	2	2	0.23	0.32	0.32	0.42	2	1.1	0.35	0.48	0.49	0.53	1.1	0.38	0.59	0.51
Na, %	0.042	0.039	0.023	0.023	0.024	0.041	0.031	0.025	0.023	0.049	0.04	0.039	0.036	0.039	0.063	0.036	0.056	0.061
Ni, ppm	0.3	.0.2	<.1	0.2	0.7	0.2	0.2	0.5	0.2	0.1	2.6	0.4	0.2	0.2	0.5	0.2	0.2	3.1
P, %	0.35	0.31	0.29	0.27	0.23	0.22	0.35	0.25	0.27	0.22	0.33	0.3	0.23	0.31	0.22	0.3	0.25	0.26
Pb, ppm	0.28	0.1	3.3	3.1	5.9	3	1.2	3	3.1	19	0.88	4.5	0.18	0.1	0.11	0.19	0.06	0.2
S, %	0.57	0.53	0.79	0.74	1.4	0.67	0.64	0.73	0.74	0.42	0.28	0.29	0.51	0.53	0.25	0.65	0.23	0.23
Sb, ppm	<.02	<.02	0.02	0.02	<.02	0.02	<.02	<.02	0.02	0.03	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02
Sc, ppm	0.2	0.2	0.1	0.1	0.1	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.2
Se, ppm	0.1	0.1	0.3	0.3	0.1	<.1	<.1	0.2	0.3	<.1	0.1	<.1	<.1	0.1	0.1	<.1	0.1	0.4
Sr, ppm	120	110	150	150	110	78	110	130	150	85	40	54	130	110	58	54	35	35
Te, ppm	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	0.02	<.02	<.02	<.02	<.02	<.02
Th, ppm	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	0.01	<.01	<.01	<.01	<.01	<.01	0.01
Ti, ppm	10	9	8	8	7	7	10	8	8	6	10	9	7	9	7	9	8	8
Tl, ppm	<.02	<.02	<.02	<.02	<.02	<.02	<.02	0.05	<.02	0.1	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02
U, ppm	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	0.01
V, ppm	2	<2	<2	<2	2	<2	<2	<2	<2	2	<2	2	<2	<2	<2	2	<2	<2
W, ppm	1.2	1.1	0.4	0.4	0.9	0.6	0.7	0.5	0.4	0.8	0.7	0.6	0.7	1.1	0.9	0.7	1.1	1.2
Zn, ppm	**98**	**90**	**1300**	**1300**	**930**	**520**	**1700**	**1300**	**1300**	**2200**	**1700**	**1600**	**110**	**90**	**210**	**400**	**490**	**120**

Areal Patterns of Zinc and Cadmium in Willow Leaf Samples

Zinc - Unlike Cd, no information was available on the levels of Zn in plant tissue from mineralized areas. Extreme differences in concentrations of zinc are clear, ranging from background levels of ~100 ppm at Sites 9, 10, and 12 to highly anomalous levels in the thousands at many sites on the Willow Creek floodplain. The highest concentration occurred in the willow leaf sample from Site #6, which may reflect contamination from an alleged broken flume that crossed the creek from the former Emperious Mill to the west.

Zinc concentrations of 400 and 490 ppm from Sites 13 and 14 below the La Garita Bridge (Fig. 3) suggest subtle contamination from an unknown source. The willow sampled from Site #12 in that same area yielded a background value of 120 ppm; but that site was collected from a willow close to a volcanic cliff, well away from the seep area dominated by such wetland indicator plants as Baltic rush *(Juncus arcticus*; Weber and Wittman, 2001*)*, Rocky Mountain iris *(Iris missouriensis)* and shrubby cinquefoil *(Pentaphylloides floribunda)*.

Cadmium - Fleischer and others (1974) report that in environments presumably having normal Cd levels, leaves of deciduous trees contained 0.1 - 2.4 ppm Cd in dry material, whereas in environments having greater than normal Cd levels the leaf concentrations ranged from 4 - 17 ppm. Shacklette (1972) compared the Cd content of 14 plant species that were sampled from mineralized areas in Colorado. The plants included conifers and deciduous trees and shrubs, including willow. The leaf tissue of willow contained the highest levels of Cd, typically ~1 ppm, dry-weight basis. More recently, an article by a staff writer for the Denver Rocky Mountain News reported that Cd is absorbed by willows to a much greater degree below abandoned mines than those upstream from the mines (Morson, 2000).

Most willow leaf samples collected in this study contain anomalous levels of Cd far beyond those reported above. Background concentrations in this study were around 0.41-0.79 ppm and occurred in samples from Sites 9, 10, and 14. The maximum concentration reported (47 ppm) was two orders of magnitude greater than background and occurred at Site #6 at the base of the tailings. The next greatest concentration of cadmium occurred at Site #5, approximately one-half mile downstream from the tailings pile (Fig. 1).

A curious and unexplained gold (Au) anomaly was found in the leaf sample from Site #9, one of the background sites for Zn and Cd. It was the only sample that had Au (0.6 ppb) detectible above the 0.2 ppb lower limit of determination. However, because there is no good measure of precision for Au from the two pairs of splits, that value may simply be spurious.

Results from analysis of the other 34 elements seem to reveal no patterns that relate to the contamination plume in the Willow Creek floodplain.

Discussion and Conclusions

The main goal of this study was to test the feasibility of using plant leaf analysis as an alternative to groundwater sampling for site characterization. The method, as tested, has advantages and disadvantages. From a cost perspective, this method has great merit. Only one day, September 4, 2003, was needed to locate the 14 sites and sample willow leaves. Analytical costs for 14 samples plus 2 splits, which included sample preparation, totaled $312, or about $19.50 per sample. An analytical package that provided data on 37 elements with excellent precision adds to the value of phytogeochemistry. No clearing of vegetation or habitat destruction is required, as it is with the drilling of monitoring wells or for some geophysical methods, such as electromagnetic induction (Lucius and Bisdorf, 1995).

Disadvantages of leaf sampling include limitation of the method to areas where the water table lies relatively close to the land surface. The site also must have vegetation with roots reaching the water table. In addition, the sample is integrated over the volume of the aquifer included within the plant's root zone, as opposed to a sample from a monitoring well, which samples a more discrete zone. Despite these limitations, leaf sampling has merit as a reconnaissance technique. Phytogeochemistry can play a key role in helping guide the more labor intensive and costly efforts of hydrologic and geophysical studies.

Although only willows were used in this investigation, it is possible that other phreatophytes might be utilized in a similar manner. Also, it may be possible to delineate types of contaminants other than tailing leachates using phytogeochemistry.

In summary, the results far exceeded at least the senior author's expectations. Concentration spreads were well over an order of magnitude between what can be judged as background and what is highly anomalous. The use of plant-tissue analysis to assess the areal distribution of Zn and Cd levels in a highly contaminated system seems well proven.

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