Willow-Leaf Analysis Determines Extent of Mine Contamination Plume on the Willow Creek Floodplain, Creede, Colorado

by
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HIGHLIGHTS

Ground- and surface water in and along the broad floodplain of Willow Creek below Creede, Colorado, are contaminated by various mine adits and waste rock piles above the town and from leachates of a gravel-capped tailings pile below. These waters have been sampled through a set of some 18 monitoring wells and found to be elevated in metals concentrations, especially zinc and cadmium.

Zinc is of most concern because of its known toxicity to freshwater fish. Moreover, the mouth of Willow Creek spills into the Rio Grande, a prime trout fishery. At issue, then, is the impact of the water quality of Willow Creek as it enters the Rio Grande.

In a feasibility study, leaf samples of sandbar willow *(Salix exigua)*, with but one exception (probably blue willow, *Salix drummondiana)*, were collected from 14 sites mostly on the Willow Creek floodplain below the town of Creede, Colorado. Willow, a phreatophyte or "well-plant," functions as a surrogate well and serves as a groundwater quality sampler. It has also been shown to accumulate cadmium far more than other shrubs and trees in mineralized areas. Because cadmium associates closely with zinc in plant tissue, and because willow is fairly common at the project site, this proved to be an ideal plant to sample.

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. A monitoring well was located close to the willow sample site at 5 of the 14 sites. 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 contaminated with zinc and cadmium, more than any other of the 37 elements analyzed. A few sites on the shoreline of the Rio Grande 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 taken from a previously determined anomalous seep seven miles below Willow Creek yielded elevated concentrations of both zinc and cadmium, 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 in the late 1800's and continued well into the 1900's. The narrow valley above the town is lined with abandoned mines. Part of the legacy of this historic silver mining district is serious water pollution from both zinc (Zn) and cadmium (Cd) in Willow Creek that flows into the Rio Grande. Cadmium occurs mainly in the zinc sulfides sphalerite and wurtzite, and is recovered with zinc usually from polymetallic ores containing lead and copper (Fleischer and others, 1974).

In the late 1990's, a small group of citizens in Creede fought to keep their town from being placed on the priority list for Superfund designation. This unique assortment of 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 downstream - a premier fly-fishing site.

In 1999, the project received its first grant to characterize the problem and identify the pollutant loadings to 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 make a significant improvement to the water quality of Willow Creek and, in so doing, protect the Rio Grande.

Rationale for the willow-leaf study -

The purpose of this study was to test the feasibility of using 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, just below what's 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, for example, Robinson, 1958, or Freeze and Cherry, 1979), it appears to have fallen out of favor by some botanists specializing in root-system ecology (Lisa Donovan, University of Utah, personal communication, May, 1992). In his monograph on phreatophytes, of more than 70 plant species then classified as such, Robinson (1958) lists willow as one of the eight most common phreatophytes in the western United States (the others are alfalfa, greasewood, pickleweed, rabbitbrush, saltcedar, saltgrass, and cottonwood - the last also in the willow family). Willow commonly grows along streams or on 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 zinc enters the plant passively, and that elevated zinc concentrations are typical of the leaf tissue. However, zinc, like copper, is stored mainly in the seeds. That leaf tissue takes up the most zinc is supported by a monograph by Antonovics, Bradshaw, and Turner (1971). Further, they say, "The quantity of zinc in plants is related to the amount of zinc in the soil often in a clearly linear pattern." More, "Zinc therefore is readily taken in by plants growing on zinc-contaminated soil."

Plants assimilate cadmium 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 cadmium had the most intense degree of accumulation, far greater than the four other elements in that intensity range, boron, bromine, cesium, and rubidium, in that order. Zinc was slightly below the lowest of the above five elements. Fleischer and others (1974) stated that plants exposed to concentrations of cadmium above those of normal background contain higher than normal concentrations of cadmium.

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.

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

On September 4, 2003, fourteen sites were sampled, with nine concentrated on the Willow Creek floodplain (Fig. 1). Five of those sampling sites were within about 30 meters of monitoring wells (MW). These included Site #1 at MW1, 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 upstream of Willow Creek: Site #10 near the Marshall Park Campground and Site #11 on a tributary stream, Miners Creek (Fig. 2). Sample sites #12, #13, and #14 are located on the southwest side of the Rio Grande between the La Garita Bridge and Wagon Wheel Gap approximately seven miles from Creede (Fig. 3).

The willow leaves were stripped from the current year's growth, usually composited from several shrubs at each site. The samples were then placed in cloth HUBCO (Hutchinson Bag Corp.) 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, then shipped to the sample preparation service described below.

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 reducing noise (also called, in part, procedural error). The result is a more pure bio-organic sample.

Quality assurance includes the use of 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 occurring 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 fitted with a 0.5-mm screen. Only particles that were less than 0.5 mm were taken as sample material.

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 %, ppm, or ppb.

RESULTS

Precision (Reproducibility) of Willow-Leaf Data –

The analytical results from the willow-leaf samples are presented in Table 1. 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.

Comparisons between both pairs of splits are given in Table 1, in which the zinc and cadmium are bolded and enlarged because of their importance. The analytical precision is excellent for both elements, as it is for nearly all others, arsenic and lead excepted. That the two splits represent extremes in zinc and cadmium concentrations lends even more credence to the data. This method improves confidence in any spatial patterns of the concentration distribution of an element.

Areal Patterns of Zinc and Cadmium in Willow-Leaf Samples -

Zinc - Unlike cadmium, no information was available on the levels of zinc in plant tissue from mineralized areas. Extreme differences in concentrations of zinc are clear, ranging from background levels of ~100 ppm at Site #s 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 Site #s 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)*.

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

Cadmium - Fleischer and others (1974) report that in environments presumably having normal cadmium levels, leaves of deciduous trees were 0.1 - 2.4 parts per million in dry material, whereas in environments having greater than normal cadmium levels the leaf concentrations ranged from 4 - 17 ppm. Shacklette (1972) compared the cadmium 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 cadmium, typically ~1 ppm, dry-weight basis. More recently, an article by a staff writer for the Denver Rocky Mountain News reported that cadmium 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 stand out as anomalous far beyond those reported above. Background concentrations in this study were around 0.41-0.79 ppm and occurred in samples from Site #s 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 anomaly was found in the leaf sample from Site #9, one of the background sites for zinc and cadmium. It was the only sample that had gold (0.6 ppb) detectible above the 0.2 ppb lower limit of determination. However, because there is no good measure of precision for gold from the two pairs of splits, that value may simply be spurious.

Results from 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. Erdman, a plant ecologist, spent only one day, September 4, 2003, to locate the 14 sites and sample willow leaves. Labor was provided on a volunteer basis, although $153.08 was paid for associated costs like mileage. 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 is required, as it is with the drilling of monitoring wells or for some geophysical methods.

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 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 highly anomalous. The method of using plant-tissue analysis to assess the areal distribution of zinc and cadmium levels in a highly contaminated system seems well proven.

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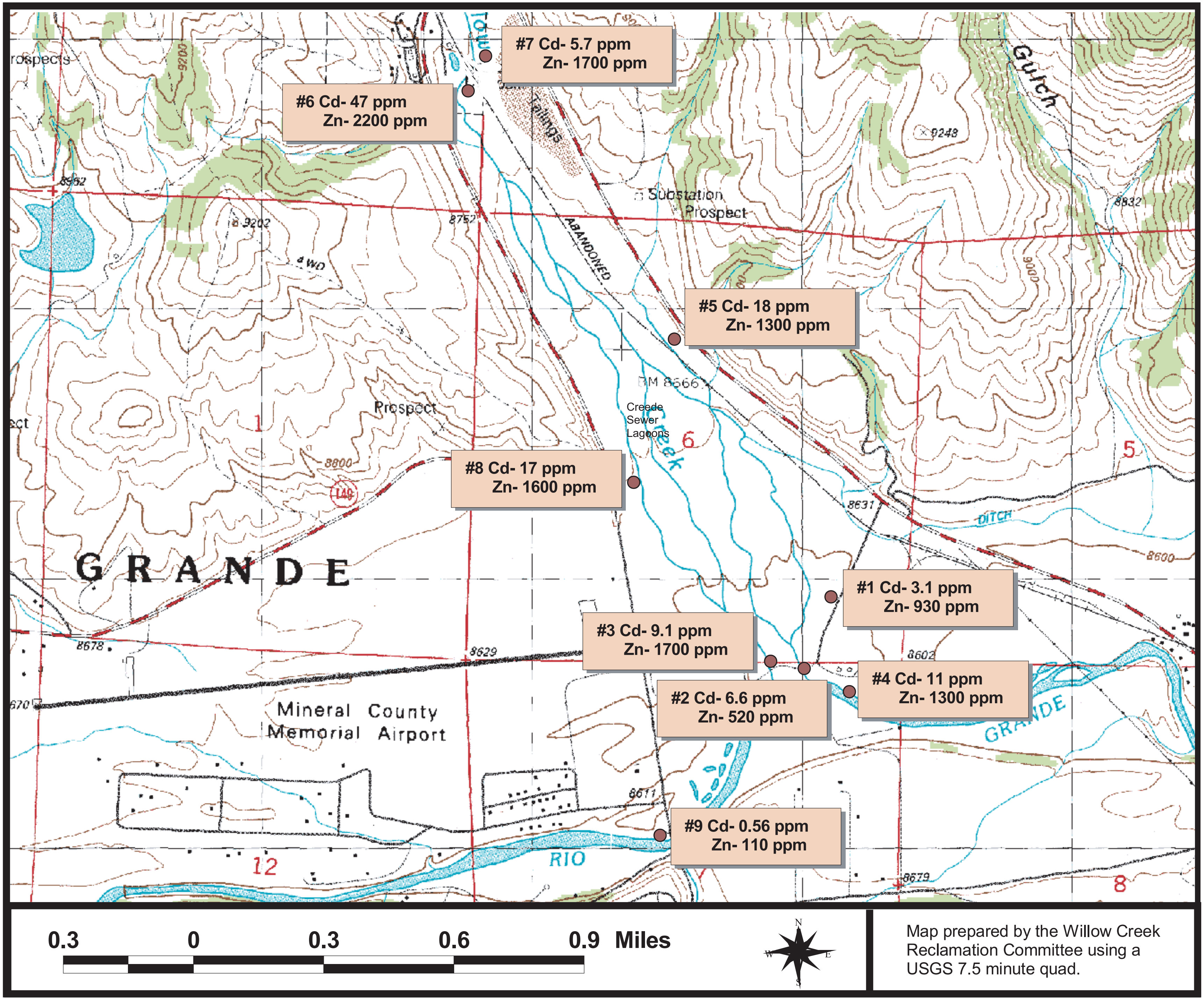
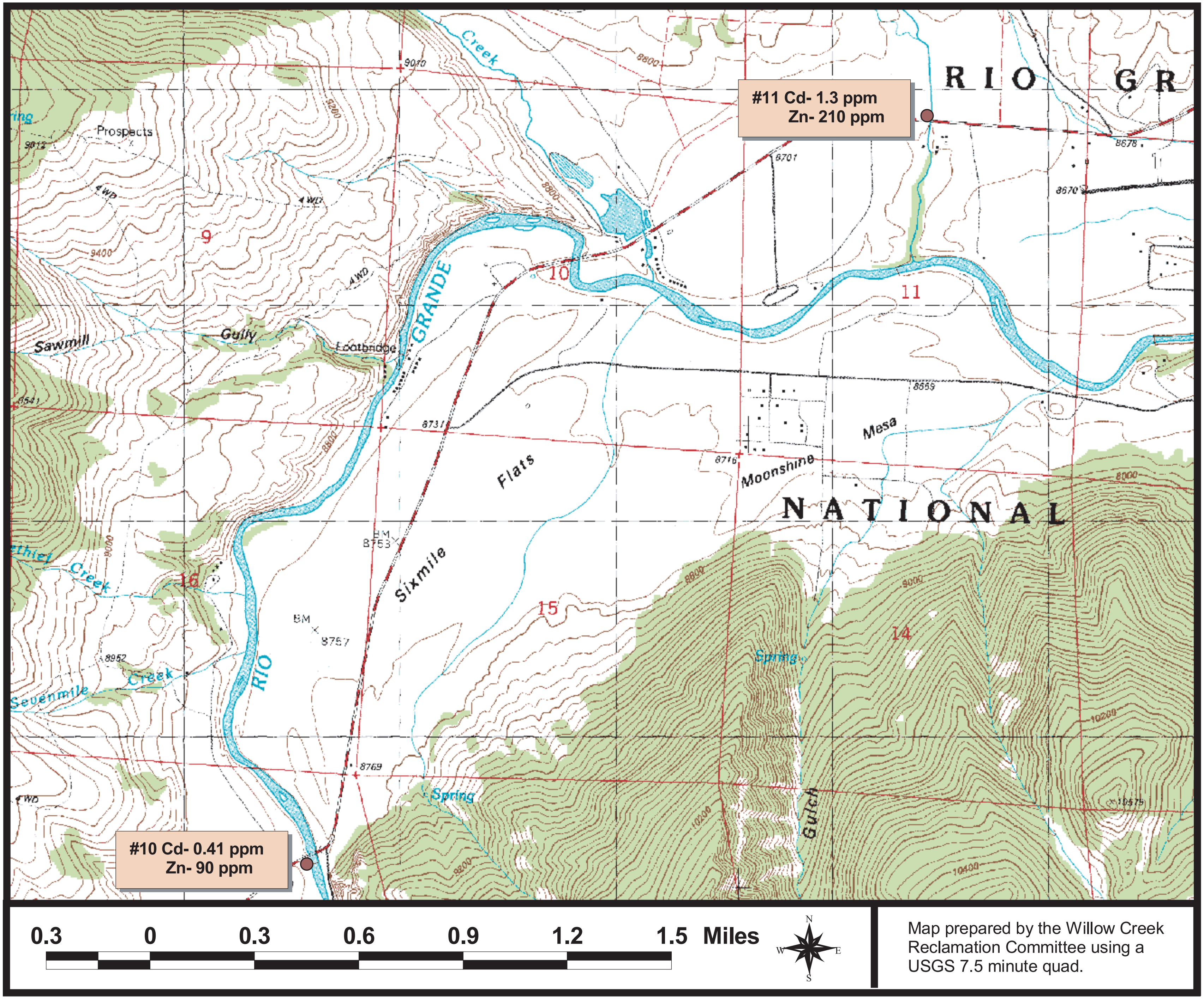
Table 1. Analytical data (dry-weight basis) for willow-leaf samples from the Willow Creek region below Creede, Colorado. Analyses by ICP-MS.

Element		**Prep Duplicate**	**Original Sample**	**Analytical Duplicate**	**Original Sample**	**Survey Samples**													
	Sequence:	16	5		11	10	9	13	6	11	8	14	12	7	5	4	15	3	2
	Sample ID:	**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	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
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	0.02	0.04	0.03	0.03	0.02	0.05	0.04	0.04	0.04	0.04	0.06	0.04	0.06	0.06
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**



Map prepared by the Willow Creek Reclamation Committee using a USGS 7.5 minute quad.

Figure 1. Willow leaf sample sites either on the Willow Creek floodplain or in close proximity.

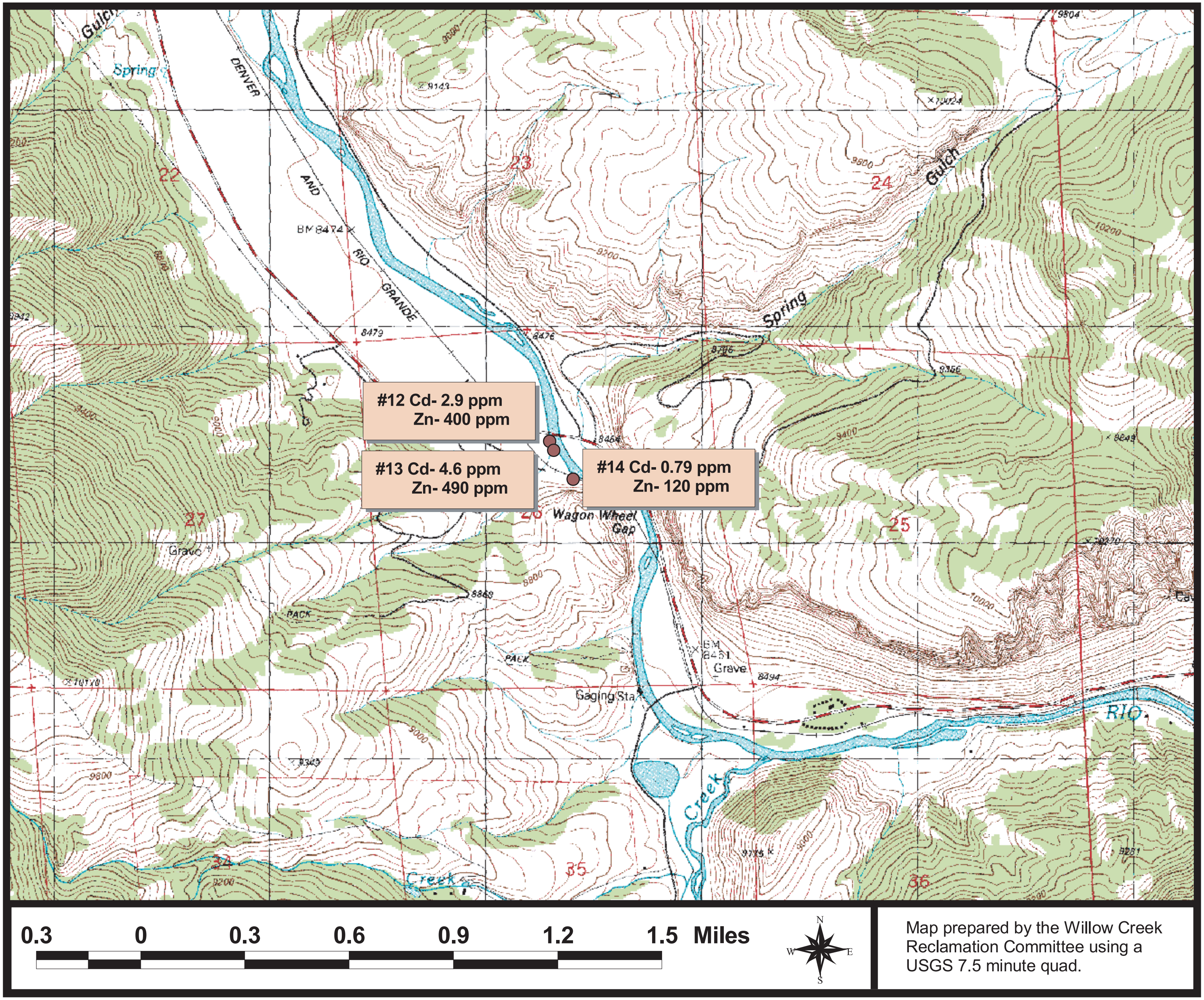


#11 Cd- 1.3 ppm
Zn- 210 ppm

#10 Cd- 0.41 ppm
Zn- 90 ppm

Map prepared by the Willow Creek Reclamation Committee using a USGS 7.5 minute quad.

Figure 2. Willow leaf sample sites above the confluence of Willow Creek with the Rio Grande.



Map prepared by the Willow Creek Reclamation Committee using a USGS 7.5 minute quad.

Figure 3. Willow leaf sample sites associated with a seep anomaly near the La Garita bridge.