Representative Plant and Algal Uptake of Metals near Globe, Arizona

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ABSTRACT

Past acid-mining activities in the Globe-Miami, Arizona area have resulted in the release of metal contaminants into the perennial reach of Pinal Creek. Dissolved manganese (Mn(II)) is the dominant metal with lower concentrations of dissolved zinc (Zn(II)), nickel (Ni(II)), copper (Cu(II)), iron (Fe(II,III)), and cobalt (Co(II)). In this study, uptake of metals by plants along the perennial reach of Pinal Creek was measured. Specifically, water speedwell (Veronica anagallis-aquatica), rabbitfoot grass (Polypogon monspeliensis (L.) Desf.), duckweed (Lemna minor), and algae (Microcystis, Vaucheria, and Oocystis) and moss were collected, digested, and analyzed for total Mn, Zn, Ni, Cu, Fe, and Co to determine the extent of bioaccumulation. Results indicate that bioaccumulation of these metals is occurring along the perennial reach of Pinal Creek with bioconcentration factors of 100 to over 10,000 depending upon the plant and the location along the reach. Comparisons with data from Pinto Creek, a nearby perennial creek with significantly lower metal concentrations, indicate that the bioconcentration factors are similar, but the mass of metals present in the aquatic plants at Pinal Creek is significantly higher.

INTRODUCTION

Dissolved Mn is an essential element for higher plant systems and is involved in photosynthesis (the Hill reaction) and activation of different enzyme systems (e.g., superoxide dismutase production) (Mukhopadhyay and Sharma, 1991). Critical deficiency levels of Mn(II) range between 0.01-0.02 microgram Mn per gram (μg Mn(II) g^{-1}) dry weight in dry mature leaves but vary tremendously between plants (Mukhopadhyay and Sharma, 1991). Vascular plants and algae also require certain amounts of other trace metals for normal plant growth (Zn, Ni, Cu, Fe, Co, Ca, and Mg).

Although Mn(II) supplements can increase growth yields of plants, large amounts of Mn(II) can interfere with the uptake of other trace metals (Mukhopadhyay and Sharma, 1991). In addition, excess concentrations of Zn, Ni, Cu, Fe, and Co can trigger an inherent defense mechanism that plants have developed that involves production of phytochelatins—polypeptides that bind metals (Ahner and others, 1995). Phytochelatin production in response to high metal levels has been identified in land plants, vascular aquatic plants, fungi, and marine and freshwater algae. This mechanism results in an accumulation of the excess metals within the plants with the final metal concentration often being significantly higher than found in water supplied to the plants.

The work reported in this paper focuses on bioaccumulation of metals by aquatic plants, algae, and moss in Pinal Creek, an Arizona State Superfund site, near Globe, Arizona, that has been contaminated by acid-mining activities in the area. The primary purposes of this study were to determine the extent to which metals were taken up by the diverse plant community at Pinal Creek and to determine which plants were particularly effective at bioaccumulation of metals. To further aid in our assessment of the potential role of plants as a sink for metal contaminants in Pinal Creek, comparisons of metals uptake were made with other measurements reported for similar plants in Pinto Creek, also near Globe, Arizona.

SITE DESCRIPTIONS

Pinal Creek

The Pinal Creek Basin is a 504 km^2 drainage area with general surface flow direction to the north from the Pinal Mountains towards the Salt River (Figure 1) (Neaville and Brown, 1993).

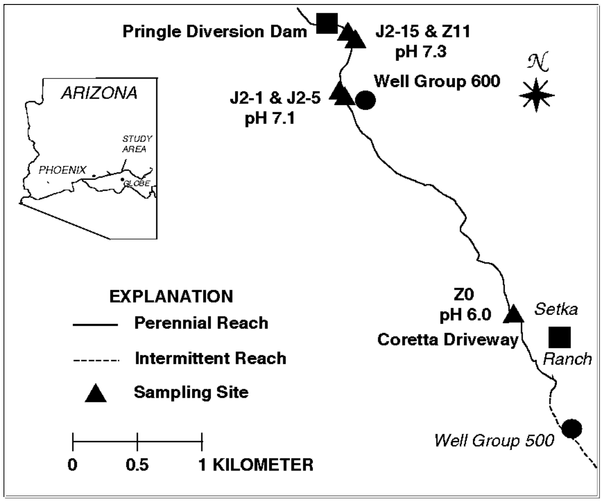

Figure 1. Study reach and sampling sites at Pinal Creek. Median pH values are shown for the study period.

Most of Pinal Creek is ephemeral during the year with flows occurring during snow runoff (December and January) or summer thunderstorms (June, July, and August) (Neaville and Brown, 1993). However, a northern portion of the Pinal Creek Basin is perennial and extends approximately 13 kilometers (km) from the head of flow to its confluence with the Salt River. The upper 3-km length of the reach from the Coretta Driveway to Pringle Diversion Dam is the section of the reach included in our studies (see Figure 1).

Past mining in the Globe-Miami area created large piles of tailings and waste rock that eventually formed a barrier across Webster Gulch. Webster Lake, which has been drained, was formed from the liquid waste from the mining operations (Brown and Favor, 1996). Contaminated, acidic water originating from several sources including the former Webster Lake now travels through the alluvial material into the perennial reach of Pinal Creek Basin. Dissolved Mn levels in Pinal Creek have reached as high as 100 milligram per liter (mg L^{-1}) near the head of flow, but during the period of this study Mn(II) concentrations in the surface water ranged from 70 to 40 mg L^{-1} over the length of the study reach. Table 1 lists water quality data at the beginning of our study reach, values which essentially remained constant over the course of the work (November, 1996 through June, 1997).

The spatial variation in Mn(II) along the study reach is a function of groundwater inflow and mixing with surface water in the hyporheic zone, of microbial removal processes occurring within the streambed sediments at local values of pH and dissolved oxygen (O_2) (Harvey and Fuller, 1998; Marble and others, 1999), and of plant uptake. Although natural attenuation of Mn(II) and other trace metals due to microbial processes has been the subject of other research, the role of plants in attenuation of metal contaminants in Pinal Creek has not been previously considered.

Table 1. Physical and Chemical Values for Pinal Creek (Z0 on January 25, 1995) and Pinto Creek (near Miami, Arizona, on June 18, 1997, USGS). (mg L^{-1} except for pH which is in standard pH units).

	Pinal	**Pinto**
Parameter	Value	Value
pH	6.4	7.8
Oxygen	6.9	9.0
Alkalinity[1]	51	180
TDS	2,640	531
Co(II)	0.410	0.003
Cu(II)	0.050	0.010
Fe(II)	<0.130	0.0053
Mn(II)	72.0	0.0038
Ni(II)	0.790	0.010
Zn(II)	0.500	0.0060

[1] As $CaCO_3$.

Pinto Creek

Pinto Creek is a northerly flowing stream starting in the Pinal Mountains and is dependent upon runoff from snow, rain, and small springs. It is a 48 to 56 km long stream and is made up of ephemeral, intermittent, and perennial stretches (Lewis and Burraychak, 1979). Pinto Creek has two stream gages maintained by the U. S. Geological Survey, one near Haunted Canyon and the other near Miami; flows at these two stations are typically different Pinto Creek was also contaminated by mining activities in the area (Lewis and Burraychak, 1979), but remediation efforts were successful and returned this system to its current state of low metals concentrations. Table 1 also lists chemical and physical parameters for a perennial section of Pinto Creek. As is apparent, the metals concentrations are significantly lower than those reported for Pinal Creek, but values of other physical and chemical parameters fall within the ranges reported for Pinal Creek. Pinto Creek also has a wide variety of aquatic vegetation including cattail, water speedwell, water cress, pondweed, rush, monkey flower, various algae (Microcystis, Vaucheria, and Oocystis)(Lewis and Burraychak, 1979), similar to plant types and algae found in Pinal Creek.

METHODOLOGY

Plant grab samples were collected from several locations and rinsed with creek water to remove insects and loosely attached sediment material. At Pinal Creek, plant samples were collected from sites Z0, J^2-1, J^2-5, J^2-15, and Z11 (Figure 1). At Pinto Creek, grab samples were collected from USGS stream gaging sites 09498501 (below Haunted Canyon near Miami, Arizona) and 09498502 (Pinto Creek near Miami, Arizona).

After rinsing with creek water, the plant samples were placed in plastic bags and put into a cooler. Upon arrival at the laboratory, samples were dried at 60°C for 24 hours. Dried samples were ground and sieved, then digested with nitric acid (HNO_3). Digested plant samples were analyzed by flame or graphite atomic absorption spectroscopy (FAAS or GFAAS) for different metal concentrations. Results are reported as concentration ratios and bioaccumulation. Plant bioaccumulation is reported as mg of metal per kg of dried plant material (mg kg^{-1}) and the concentration ratio is the ratio of metal found in the plant material (mg kg^{-1}) to the metal concentration found in the creek water (mg L^{-1}). The values reported represent the average of 2 subsamples with the maximum and minimum values measured being within ±2 percent of the average value.

RESULTS

The aquatic plant species found at Pinal Creek varied in type and density depending upon the time of year and the location. Before plant sampling started in 1996, water speedwell and rabbitfoot grass dominated the upstream portion of Pinal Creek (J^2-1) and algae dominated in the downstream section (J^2-15). However, over the study period (November, 1996 through June, 1997), water speedwell, rabbitfoot grass, and algae were found along the entire study reach. Duckweed was less widely distributed and was typically only found in slow moving or stagnant water near the banks of the creek.

Water speedwell from Pinal Creek was collected from several field locations (Z0, J^2-1, and J^2-15) over a period of 8 months and analyzed for Mn(II) (Table 2). Site J^2-1 consistently had lower bioaccumulation than the downstream site J^2-15; approximately 30 percent that of J^2-15 in November, 1997, and increasing to 63 percent that of J^2-15 in April, 1998. There is no obvious correlation between sampling date and bioaccumulation of Mn at either site.

Mn(II) concentrations in Pinal Creek were lower at the downstream site (Table 2) due to dilution and natural attenuation caused by biogeochemical reactions and plant uptake (an overall loss of 10-20 percent of the entering Mn(II) has been attributed to non-dilution processes, Harvey and Fuller, 1998). Bioaccumulation values for water speedwell were greater downstream compared to upstream sites (Table 2). Since tracer studies were not conducted when the plant samples were collected, nothing definitive can be said regarding the temporal changes in Mn(II) levels determined at both sites.

A subset of the water speedwell samples from sites J^2-1 and J^2-15 were analyzed for other trace metals (Table 3). No trend with location was observed for concentrations of Fe, but Zn and Ni were higher at J^2-15 than at J^2-1 and Cu was higher at J^2-1 than at J^2-15 . Bioaccumulation of Mn and Co exhibited consistently higher bioaccumulation at J^2-15 compared to J^2-1, about a factor of 2 difference.

Table 2. Bioaccumulation by water speedwell and surface water concentrations of Mn in Pinal Creek (units are mg kg^{-1} for plant uptake and mg L^{-1} for surface water).

	Plant Concentration			Surface Water	
Date	Z0	J^2-1	J^2-15	J^2-1	J^2-15
11/15/96	6380	6610	23000	50.3	40.5
12/13/96		6450	18600	52.7	45.0
1/31/97		7990	16400	49.1	42.3

3/14/97		4600	8570	55.5	49.9
4/25/97		6190	9760	50.8	45.1
6/25/97		3870		52.0	
Average	6380	5950	15300	51.7	44.6
Standard deviation		1490	6070	2.24	3.56

Table 3. Water speedwell bioaccumulation from Pinal Creek collected on December 1996 and January 1997 for Mn, Zn, Ni, Cu, Co, and Fe (units are mg kg^{-1}).

Metal	Date	J^2-1	J^2-15
Mn	12/13/96	6450	18600
Mn	1/31/97	7990	16400
Fe	12/13/96	4400	1880
Fe	1/31/97	2520	2670
Ni	12/13/96	109	151
Ni	1/31/97	148	182
Cu	12/13/96	901	824
Cu	1/31/97	1750	1130
Co	12/13/96	80.5	158
Co	1/31/97	134	279
Zn	12/13/96	516	665
Zn	1/31/97	772	801

Rabbitfoot grass samples from J^2-1 and J^2-15 were also analyzed for Mn, Zn, Ni, Co, and Fe (Table 4). Both upstream and downstream sampling sites had similar bioaccumulation values for Zn and Ni, but Mn, Cu, Co, and Fe values were larger at site J^2-1 than J^2-15. A factor of about 2 between values at J^2-1 and J^2-15was observed for Mn, Co, and Cu, and a factor of about 10 for Fe. Bioaccumulation of Mn at both sites was also greater than the other metals.

Duckweed was found in Pinal Creek during the summer months and the early fall at sites with zones of slow moving or stagnant water. A sample was collected from site J^2-5 on June 25,

Table 4. Rabbitfoot grass bioaccumulation in samples from Pinal Creek collected on January 31, 1997 (units are mg kg^{-1}).

Metal	J^2-1	J^2-15
Mn	13600	5240
Fe	6890	691
Cu	1640	828
Ni	163	161
Co	237	130
Zn	581	534

1997 (surface water pH 7.1; Mn(II) concentration, 47.0 mg L^{-1}). The bioaccumulation value was 10760 mg kg^{-1} and the concentration ratio was 229 (mg kg^{-1})/(mg L^{-1}).

Algae is prolific at both Pinal Creek and Pinto Creek and grab samples included the species Microcystis, Vaucheria, and Oocystis. Samples were collected from both creeks to compare bioaccumulation and the concentration ratio for Mn (Table 5). Although Pinal Creek samples had more bioaccumulation, Pinto Creek samples had larger concentration ratios.

Table 5. Algae samples from Pinal Creek and Pinto Creek : bioaccumulation and concentration ratio for Mn (mg kg^{-1} for bioaccumulation and (mg kg^{-1})/(mg L^{-1}) for concentration ratio).

Site	Date	Mn	Concentration ratio
Pinal, Z11	7/17/96	49700	996
Pinal, Z11	11/15/96	90200	1810
Pinal, J^2-15	12/12/96	5550	1110
Pinal, J^2-15	1/31/97	79300	1590
Pinto, Miami	6/18/97	240	29800
Pinto, Miami	6/18/97	1460	181000

Water speedwell collected from Pinto Creek also had larger concentration ratios for Mn than samples collected from Pinal Creek (Table 6). However, the bioaccumulation of Mn was again greater in Pinal Creek samples: 3870 mg kg^{-1} for the Pinal Creek sample; 47, 97, and 505 mg kg^{-1} for the Pinto Creek samples.

Table 6. Water speedwell concentration ratio ((mg kg^{-1})/(mg L^{-1})) comparison between Pinal Creek and Pinto Creek.

Site	Date	Concentration Ratio
Pinal, J^2-1	6/25/97	74.5
Pinto, Haunted	6/18/97	133000
Canyon	6/18/97	25400
Pinto, Miami	6/18/97	12400

DISCUSSION

All of the plants analyzed exhibited bioaccumulation of metals, whether the samples were collected from Pinal or Pinto Creek. Water speedwell from Pinal Creek and Pinto Creek had high levels of Mn, as well as significant concentrations of the other metals considered in this study. Mn bioaccumulation and Mn(II) stream concentrations were basically the same over the sampling period at both the upstream (J^2-1) and downstream (J^2-15) sites (Tables 2). These bioaccumulation levels for Mn are similar to those measured for another type of water speedwell (Veronica americana) (Muztar and others, 1978) and to measurements reported for other aquatic plants (Kadukin and others, 1982; Albers and Camardese, 1993). Bioaccumulation by water speedwell of the other metals also occurred but to a slightly lesser degree than for Mn (Table 3).

Rabbitfoot grass had similar bioaccumulation levels of metals as measured for water speedwell. Bioaccumulation of Mn by duckweed was of the same order-of-magnitude as observed for water speedwell and rabbitfoot grass, but bioaccumulation of Mn by algae was an order-of-magnitude greater than any of the plants analyzed. These differences in metals uptake may reflect different uptake mechanisms and/or be due to the age of a plant or algal community and the length of time it has been exposed to metals contaminated water.

Duckweed collected from site J^2-5 at Pinal Creek had a significantly larger concentration ratio for Mn than reported by Frick (1985) for duckweed at a similar Mn(II) level (see Table 7). In addition, the bioaccumulation values measured by Frick were significantly lower than at Pinal Creek: 3.9, 129, 192, and 220 mg kg^{-1} for the lowest to highest Mn(II) values used by Frick versus 10760 mg kg^{-1} at Pinal Creek. The differences between the values for bioaccumulation and the concentration ratio at approximately the same concentration (47 mg L^{-1} in Pinal Creek versus 55 in Frick's work) suggests that concentration of Mn(II) is not the only variable that determines uptake by aquatic plants at Pinal Creek. Nutrients and other dissolved species (e.g., Mg^{+} and Ca^{2+}) present in Pinal Creek at different levels than in the laboratory experiments may explain part of this difference in bioaccumulation. However, a more likely explanation is that one, or more, of the other dissolved metals present in Pinal Creek (Zn(II), Ni(II), Cu(II), Co(II), and Fe(II,III)) has a synergistic effect that results in a greater bioaccumulation of Mn(II) by duckweed in the field situation than observed by Frick (1985).

Table 7. Comparison data for duckweed concentration ratios at Pinal Creek (mg L^{-1} for surface water and (mg kg^{-1})/(mg L^{-1}) for concentration ratio).

Source/Site	Mn(II))	Concentration Ratio
Frick, 1985	54.9	4.02
Frick, 1985	27.5	6.98
Frick, 1985	13.7	9.93
Frick, 1985	0.0560	69.6
J^2-5, 6/25/97	47.0	229

Mn uptake by water speedwell has been reported by Muztar and others (1978), although the species they used was Veronica americana and not Veronica anagallis-aquatica, the species identified in Pinal Creek. The concentration ratios for the Pinal Creek water speedwell samples were lower than determined by these researchers (Table 8), but the bioaccumulation was an order-of-magnitude greater in the Pinal Creek plants (3870 and 4040 mg kg^{-1} for Pinal Creek versus 315 to 370 mg kg^{-1}). Since the Mn(II) concentration in Muztar's studies was 3 orders-of-magnitude lower than the Mn(II) concentration in Pinal Creek (Table 8), the lower concentration ratio for Pinal Creek may be an indication of a capacity limitation and/or a toxic affect at the higher Mn(II) concentrations in Pinal Creek.

Table 8. Comparison data for water speedwell (Veronica anagallis-aquatica) from J^2-1 to Veronica americana concentration ratios (mg L^{-1} for surface water and (mg kg^{-1})/(mg L^{-1}) for concentration ratio).

Source	Mn(II)	Concentration Ratio
Muztar and others, 1978, washed	0.043	7330
Muztar and others, 1978, unwashed	0.043	8600
J^2-1, 6/25/97, rinsed	52.0	74.5
J^2-1, 6/25/97, not rinsed	52.0	77.7

Data from Pinto and Pinal Creek show that both sites have algal bioaccumulation of Mn. For algae, the concentration ratio at Pinal Creek is lower than Pinto Creek although Mn(II) creek concentrations are greater at Pinal Creek (Table 5). These differences in concentration ratios again suggest that at Pinal Creek the plant capacity for metal uptake may have been reached and/or that a toxicity effect is responsible for the differences between the algal samples from these two creeks. The same trend is also exhibited by water speedwell (Table 6).

CONCLUSIONS

These studies indicate that water speedwell, rabbitfoot grass, and algae bioaccumulate Mn. Zinc, Ni, Co, Cu, and Fe were shown to also bioaccumulate in water speedwell and rabbitfoot grass. Water speedwell and other aquatic plants are prolific in Pinal Creek and could play a significant role in determining the fate of metal contaminants entering the stream. Additional data concerning the total biomass in the system, and the potential release of metals as plants die and decay, are required to assess the potential and actual contribution of plants to total metals removal in this system.

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