DETERMINATION OF SELECTED HEAVY METAL CONCENTRATIONS AND DISTRIBUTION IN THE GALLINAS RIVER USING MACROPHYTES.

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Abstract

Recent studies (Tabe-Ebob et al. 2004; Duran et al. 2005) have reported elevated concentrations of arsenic (0.039mg/L) and other heavy metals during high flow events in the Gallinas River (GR). This is of particular concern as the GR meets 95% of the domestic water needs of the city of Las Vegas, New Mexico (population of 18,000 people). Previous research to assess water quality in the Gallinas River has been limited to conventional analytical methods (soil, sediment, and water sample analyses). The use of macrophytes to assess heavy metal contamination in this river has not been reported. We hypothesize that concentrations of heavy metals (As, Pb, Cd, Cu and Zn) within macrophyte tissues will correlate positively with concentrations of the same metals in sediments of the Gallinas River.

Introduction

Over the years the Gallinas River (GR) has become one of the most widely studied river systems in Northern New Mexico. It feeds the Peterson, Bradner, and Storrie lake reservoirs as well as lends itself to a number of acequia users. Supplying approximately 95% of the water needs for the city of Las Vegas, a large amount of attention has been brought to monitoring and protecting the watershed. This is due to the ever increasing potential for water shortages and risk of catastrophic forest-fires capable of destroying the watershed. In 2006, the USFS and the USDA developed the Environmental Assessment for the Gallinas Municipal Watershed Wildland-Urban Interface Project. The primary goal of this assessment was to investigate and minimize potential risk of catastrophic wildfires, which would undoubtedly decrease water quality and water yield. More recently a significant amount of work has been done monitoring elevated heavy metal and particularly arsenic concentrations within surface water (Evans et al. 2004), ground water (Johns-Kaysing et al. 2006), and sediment (Eyong et al. 2007).

Previous studies showed that the river contained elevated arsenic levels during periods of high discharge, sometimes exceeding EPA drinking water standard of 0.010mg/L by nearly 400% (Johns-Kaysing et al. 2006).

The purpose of this study is to determine concentrations of As, Pb, Cd, Cu, and Zn in macrophyte species from the Gallinas River, correlate metal concentrations in macrophyte tissues with metal concentrations in sediment samples, and identify specific macrophytes with the potential to serve as indicators of heavy metal contamination in the GR.

We hypothesize that concentrations of heavy metals (As, Pb, Cd, Cu, and Zn) within macrophyte tissue will correlate positively with concentrations of the same metals in sediments of the Gallinas River.

Plants as Bio-indicators

Exploring and developing new techniques for monitoring water quality is of the utmost importance. Current chemical analytical methods, which have already been conducted, are limited to providing point-in-time data about soil and water pollution loads. The use of aquatic macrophytes as biological indicators is proving to be an effective tool in the detection of low levels of foreign substances from industrial effluent such as heavy metals, PCBs, and numerous other organic and inorganic compounds (Chandra et al. 2000).

Macrophytes are particularly useful as they have the potential to provide current environmental data as well as the ability to bio-accumulate and provide a range of information about past or seasonal environmental conditions and organism environment interactions. *Potamogeton* is among the species that has been employed to monitor pollution within aquatic systems. Wild species of *potamogeton* have been used to monitor copper, lead, and zinc levels in lakes and streams of the United Kingdom and Canada (Chandra et al. 2000).

Figure 1. *Elodea canadensis* separated into roots and shoots.

Geology and Geography

Las Vegas lies on the forefront of a range bounding fault, the Montezuma Fault, which was activated as early as the Ancestral Rocky Mountain Uplift and remains active to this day as the leading edge of the Modern Rocky Mountain's Southern Santa Fe Range east of the Sangre de Cristos.

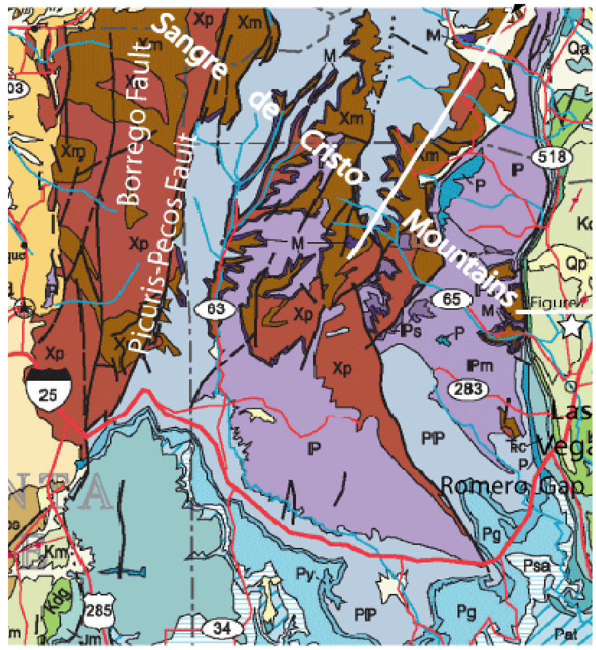

Figure 2. Geologic map of the Southern Sangre de Cristos. Xm= Precambrian Crystalline Rock Pm=Pennsylvanian Madera, Kc= Cretaceous Carlile Shale. (Modified from Wilks 2005)

The region has experienced a long-lived and complex tectonic history traced back as far as the Proterozoic related to the 1000 Ma Grenville Contraction and 750 Ma Rodinia Supercontinent Rifting (Erslev et al. 2004).

Along with the complex tectonic history, the region has been inundated numerous times by *paleoseaways*, depositing a vast amount of shallow marine and near shore sedimentary units. It is now known that the lithology of two particular sedimentary layers deposited during the Pennsylvanian and Cretaceous contain elevated arsenic levels.

Duran et al. 2005 observed that the shales of the Pennsylvanian Madera and Cretaceous Niobrara/Carlile formations contained relatively high arsenic concentrations (12 ppm) in the form of microcrystalline pyrite. This is important, as these units are exposed in over 60 % of the watershed and contribute large amounts of sediments, surface, and ground water.

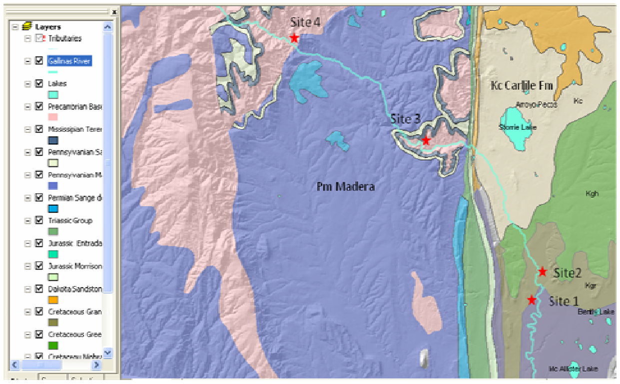

Figure 3. Simplified geological map of the study area with Sites 1-4. Pm= Pennsylvanian Madera, Kc= Cretaceous

The Gallinas River headwaters originate at the eastern flank of Elk Mountain, southern Sangre de Cristo Mountains within highly metamorphosed Precambrian crystalline basement rocks. These rocks like much of the crystalline basement rock underlying the Rocky Mountains, were formed by a series of orogenic events during the mid-Proterozoic, from approximately 1.0 to 1.8 billion years ago (NMBGMR).

Mid elevations of the watershed are dominated by Pennsylvanian limestones that lie unconformably on Precambrian basement rock. This is a local example of the "Great Unconformity", a well studied feature that can be seen throughout the Rocky Mountains where nearly 1.4 billion years of earth's history is missing. The Pennsylvanian Madera Limestone is of great importance as it is one of the arsenic bearing units within the watershed.

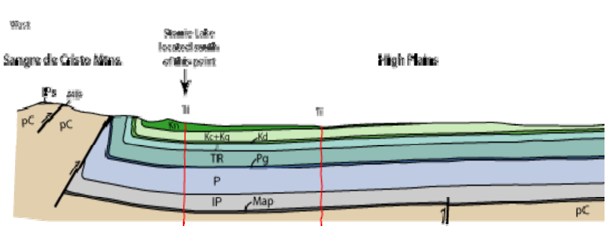

Figure 4. East –West geologic Cross Section from Fig 2, depicting the Montezuma Fault and transition from Rocky Mountain to High Plains physiographic provinces. (Modified from Lisenbee 2003)

Beyond the Montezuma Fault extending into the high plains are Cretaceous shale and Quaternary deposits overlaying Jurassic and Triassic strata. Cretaceous deposits were derived from the area's inundation by the Western Interior Seaway during the mid to late Cretaceous (NMBGR). At lower elevations, a majority of the GR courses through these Cretaceous sediments, including the Niobrara/Carlile formation which was shown by Duran et al. 2005 to contain elevated arsenic.

Field Procedure

Sampling was done on the same sites previous Gallinas River investigations have used (BWWTP, below the wastewater treatment plant; AWWTP, lower Gallinas, above wastewater treatment plant; MZ, USGS station, Montezuma; and HW, headwaters). This allowed for comparability between studies. Sampling was done in spring and summer, 2007. At least two macrophyte species were hand-picked at random from each sampling site (Table 1). In addition to collecting plants, stream discharge and physicochemical parameters were measured.

Figure 5. Research team collecting samples in the field.

Aquatic plant species were sparse, so it was necessary to take a specimen of each available species. In some cases two specimens were not possible. Samples were extracted in their entirety whenever possible and placed into sterile sample bags. Samples were then placed in a cooler for preservation until cleaning.

Stream discharge was determined following USGS protocol and measured using a Marsh McBriney Model 201d Water Current Meter with a Rickly Hydrological Co. pigmy attachment. Physicochemical data was also measured twice at each of the four sampling sites using portable meters. Salinity, conductivity, and temperature were measured using the YSI 30. The Oakton pH/CON 10 series was used to measure pH, and dissolved oxygen was determined on a YSI 55 meter.

Lab Procedure

Once specimens were collected they were removed from preservation for cleaning. This was done using sterile separating pans and distilled water. Whenever possible plant species were separated into roots and shoots and analyzed independently. Specimens were cleaned of all sediments and invertebrates before being put into sterile glass containers and placed in the drying oven. Dehydrated specimens were sent to Activation Laboratories of Canada, in sterile centrifuge tubes for metal analyses.

Activation laboratories digested 0.5 grams of the sample using a mixture of 3.5 ml HCL, 5.0 ml HNO_3, 3ml H_2O_2, and 0.1 ml HF. The digestion solution was diluted 1:10 with de-ionized water. The analysis was performed using HR-ICP-MS.

Mean values of heavy metal concentrations were calculated for plant roots and shoots and the Mann-Whitney test (non parametric) was used to identify significant differences in these metal concentrations in the different plant parts. Spearman's correlation coefficient analysis was conducted between average values of metal concentrations in sediments and plant tissue.

Concentration Factors (CF) were calculated by taking the ratio between the concentration of each metal in plant tissues and that of the same metal in the sediment.

Results

The mean concentration values of metals in the plant tissues decreased in the following order:

BWWTP: Zn > Cu > Pb > As > Cd

AWWTP: Zn > Cu > Pb > As > Cd

MZ: Zn > Cu > As > Pb > Cd

HW: Cu > Zn > Pb > As > Cd

Table 1: Macrophyte species from all four sampling sites and two sampling periods.

Sample Period	Sample site	Macrophyte Species
Spring	BWWTP	*Nasturium officinale*
		Potomageton sp
		Graminnae
	AWWTP	Periphyton
		Potomageton sp.
	MZ	*Ranunculus aquatilis*
		Elodea canadensis
		Fontinalis antipyretica
	HW	*Plagiomnium affine*
		Fontinalis antipyretica
		Liverwort
Fall	AWWTP	*Nasturium officinale*
		Graminnae
	BWWTP	*Fontinalis antipyretica*
		Periphyton
		Graminnae
		Moss
	MZ	*Ranunculus aquatilis*
		Elodea canadensis
		Fontinalis antipyretica
	HW	*Plagiomnium affine*
		Fontinalis antipyretica

Results of the Mann-Whitney test showed significant differences ($p < 0.05$) in concentrations of Cu, Pb, and As between plant roots and shoots. The difference in concentrations of As was highly significant ($p < 0.01$). No significant differences were found in concentrations of Cd and Zn between plant roots and shoots ($p > 0.05$). On average, heavy metal concentrations in roots were higher than in shoots.

Spearman's correlation analysis showed significant positive correlations between the following metal concentrations in plants and sediments: Cd ($p < 0.05$), Pb ($p < 0.05$), Zn ($p < 0.01$). No correlations ($p > 0.05$) were found between plant and sediment concentrations of Cu and As.

The Kruskal-Wallis Test showed significant differences in concentrations of Cd ($p < 0.01$), Pb ($p < 0.05$), Zn ($p < 0.01$) and As ($p < 0.05$) between all four sampling sites. There was no significant difference in the concentration of Cu ($p > 0.05$) between sites.

The mean CF for all metals calculated for moss (AWWTP), *Fontinalis sp.* (AWWTP) and *Nasturium sp.* (BWWTP) in the fall are high (5.06, 4.29, and 3.6 respectively). Meanwhile, CF values for *Plagiomnium sp*. and Liverwort (0.67 and 0.52 respectively) collected in the spring at the HW site are lower than for other plants. The mean CF values for the elements in the plants decreased in the order shown in Table 2.

Table 2: Trends in mean CF values for metals.

Site	Spring	Fall
BWWTP	Cu > Zn > Cd > As > Pb	Cu > Zn > Cd > Pb > As
AWWTP	As > Cd > Cu > Zn > Pb	Cd > Zn > Cu > Pb > As
MZ	Cu > Cd > As > Zn > Pb	As > Cu > Cd > Zn > Pb
HW	Cu > Cd > As > Zn > Pb	Cu > Cd > Zn > As > Pb.

Discussions and Conclusions

Mean concentrations of Zn in plant tissues were exceptionally high at all sites, with concentrations up to 2020 ppm found in moss collected from site AWWTP in the fall. These concentrations correlated highly ($r = 0.91$) with sediment concentrations. Further investigations are required to determine the sources of Zn within this watershed.

The significant differences in heavy metal concentrations between roots and shoots correspond with findings reported in other literature (St-Cyr et al. 1997). The nonsignificant difference in Cd concentrations between plant organs is most likely due to the fact that Cd is easily translocated from roots to shoot (Mayes *et al*. 1977).

Mean CF values reported for certain metals in the fall were by far greater than their corresponding spring values, with some values as high as 7.8. The highest mean CF value for the spring was 3.38. This suggests that some plants accumulated more heavy metals in the fall than in the spring. Plant organs attain maturity in the fall and begin to senesce; at this stage they are likely to have accumulated more heavy metals than in the spring, when growth and development are still taking place.

One characteristic of a good biomonitoring species is availability at all sites and seasons; no single macrophyte species met this criterion. However, some species were found at more than one site and some at the same site in both seasons (all species at MZ). Based on their presence and abundance at MZ, we recommend the use of *Ranunculus*, *Elodea* and *Fontinalis* as biomonitoring species. Of the three plants, *Elodea* is most suitable because it has the highest mean CF value for all metals (2.15). It has also been widely reported in other literature as a good biomonitoring species (Samecka et al. 2003). *Elodea* will be particularly useful for monitoring As at this site (its CF value for As is 7.67), while *Fontinalis* and *Ranunculus* are more suitable for monitoring Cu (CF values for Cu: 4.12 and 4.02 respectively). *Nasturium* and Gramminae are suitable monitoring species for site BWWTP (mean CF: 3.60 and 2.16 respectively). They are abundant and present on both seasons. The unidentified moss species at site AWWTP is suitable for use as biomonitor (mean CF: 5.06). It is especially so for Cd (its CF value for Cd is 12.03). CF values for plants at HW are low, compared to other sites, with most mean CF values below one. *Plagiomnium* could be used to monitor Cu at this site (CF value of 2.65 for Cu). The plants suggested as potential biomonitors also meet the tolerance criterion, as most of their tissue concentrations of the different metals exceed threshold toxicity levels as reported in the literature (Kabata-Pendias and Pendias 1992). This implies that some of the plants are highly tolerant to metal contamination.

Except for *Elodea* and *Fontinalis,* whose biomonitoring potentials have been widely reported, further research is required to validate the metal uptake and biomonitoring potential of the other suggested species.

It is obvious, from the high CF values and levels of metals detected in some plant tissues that heavy metals in sediments of the GR occur in bioavailable forms that are being taken up by macrophytes.

Significant positive correlations between sediment and plant concentrations of Cd, Pb, and Zn partly confirm our hypothesis. However, there were no correlations between plant and sediment Cu and As. One possible explanation is that plants may have accumulated these metals from the water column rather than the sediment. To confirm this, water samples need to be analyzed and their heavy metal contents correlated with those in plant tissue.

Acknowledgments

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