Distribution of heavy metals in vegetation surrounding the Blackstone River, USA: Considerations regarding sediment contamination and long term metals transport in freshwater riverine ecosystems

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Abstract: *The Blackstone River, a 74 km interstate stream located in South Central Massachusetts and Rhode Island (USA), has had a long history of problems due to high concentrations of metals such as copper and lead. The river has been subjected to metals load that include contributions from urban runoff, wastewater discharges, contaminated sediments, and also resuspension of contaminated sediments in the river-bed. All of these effects lead to elevated concentrations of metals such as lead, copper, zinc, chromium, cadmium and arsenic. Furthermore, the contaminated sediments located behind impoundments become especially important when higher flows cause resuspension of the previously deposited sediments and associated metals. While it is known that high metals concentrations in this river are found in the bottom sediments, the fate of the metals and impact on the ecosystem are not well known. This paper addresses the potential impacts that metals may have on vegetation and plant tissues in the vicinity of the river. Plant tissues (primarily mosses), were collected from a number of sampling sites along a 14 km stretch of this river. At each site, samples were collected from multiple distances from the riverbank. Laboratory analyses made use of both wet digestion and dry ashing digestion methods, followed by analysis using an atomic absorption spectrophotometer. The wet and dry ashing digestion methods yielded similar results, although the results afforded by the dry ashing methods were slightly lower than the results obtained from the wet method. The results showed that the metals concentrations in vegetation (as determined from plant tissue analyses) were generally inversely related to the distance between the vegetation and the riverbank, with higher metals concentrations existing in plant tissues located close to the riverbank. In addition, it was found that the transport of metals concentrations to the terrestrial vegetation adjacent to this section of the Blackstone River was affected by the river morphology and flow characteristics (including velocity, flow rate and depth of flow, which can govern the potential for plant submergence, as well as the dynamics of flow and transport in the soil near the river). The analyses help to provide an improved understanding of metals transport and potential significance of metals contamination in a terrestrial ecosystem that is located adjacent to a river.*

Key words: *Bioassays, Metal contamination, Copper, Lead, Zinc, Resuspension, Blackstone River, USA*

Introduction

Heavy metals such as lead, arsenic and cadmium can cause severe problems in aquatic environments due to their persistence, toxicity and tendency to accumulate in fish and shellfish tissues (Sawyer *et al.*, 2003). While these constituents have been studied extensively and standards have been identified, their chemical reactions in the environment and their overall effects on aquatic life are still complex and are poorly understood (Windom *et al.*, 1991). For this reason, the scientific community is continuing to conduct research to understand both processes that govern the fate and transport of these metals, alongwith the potential toxicological impact of these metals.

It is well known that the fate and transport of metals in the environment is governed by the metals' interactions and reactions with water, sediments and aquatic organisms (Holdway *et al.*, 2001; Ouyang *et al.*, 2002; Sawyer *et al.*, 2003) and these metals are also affected by environmental conditions such as streamflow (Smith, 2001). Contaminated sediments have been investigated by many researchers, such as Evans (1989);

McBride (1989) and Borovec (2000), who demonstrated the importance of grain size distribution in relation to transport of chromium, silver, lead, zinc, copper and other constituents. Since large portions of trace metal loadings are normally associated with the solid particles and thus transported *via* particulate matter in the aquatic environment, many researchers have addressed the role of grain size and organic matter of sediments (Borovec, 2000; Wen *et al.*, 2001; Lu and Allen, 2001; Vignati and Dominik, 2003). Moreover, concentrations may rely on other sources, such as loads in storm water runoff, remobilized metals that were bound on river sediments and even loadings from atmospheric deposition.

The toxicological impact of heavy metals on the environment have been investigated extensively. Toxicological evaluations often make use of aquatic bioassays, in which the effect of a contaminant on a receptor (*e.g.* aquatic organism or plant) is assessed. Still, complete toxicological testing procedures are relatively complex, often including the need to define a variety of physiological and chemical parameters (Metcalf and Eddy,

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2003; Windom *et al.*, 1991; Wolterbeek and Verburg, 2001; Yu *et al.*, 2001; Holdway *et al.*, 2001). For the purposes of this paper, the scope of the analysis concentrates on the metals accumulation in plant tissues. The quantification of the metals accumulation can also provide some insight into the nature of the fate, transport and accumulation of metals in aquatic environments.

One river where metals have been a persistent concern is the Blackstone River, a 74 km long river in the USA that flows from Massachusetts to Rhode Island (Shanahan, 1994). This river has a mean flow of 6 m^{3}s^{-1} and peak flow exceeding 75 m^3 s^{-1}(Socolow *et al.*, 2001). The high metals concentrations in this river represent potential threats to both the aquatic organisms and the surrounding terrestrial ecosystem. However, it is also known that sediments play a key role in the processes governing the distribution of the metals in this system. Several researchers have addressed the resuspension of metals in the Blackstone River such as Chaudhury *et al.* (1998), who noted a significant increase in total suspended solids in the river under wet weather conditions, and Ji *et al.* (2002). With the increasing suspended solids, metal concentrations in the water column were also found to be elevated due to both contaminated runoff and heavy metal resuspension from the contaminated streambed sediments. In the Blackstone River, some of these sediments (and associated metals) result from urban runoff, which has high sediment loads and metals that partition into the finer portion of the grain sizes (Ozdilek and Mathisen, 2003). It is well known that high concentrations of copper and lead in stream sediments are often remobilized into the water column. With these and other metals being remobilized into the water column, it is likely that they are making their way into the aquatic life and biota along the shores of the river. Thus, it is also possible that these metals can enter the terrestrial ecosystem adjacent to the river.

The objectives of this paper are to characterize the distribution of metals along a 14 km section of the Blackstone River, to quantify the extent to which metals are being transported from the Blackstone River to the terrestrial vegetation in the vicinity of the river and to identify the key processes that are governing these transport processes. To assess the metals transport to the vegetation, lab analyses were completed on samples of plant tissue (mostly terrestrial mosses) collected from a number of sampling locations adjacent to the river. For a number of different locations along the river, plant tissue samples were collected at varying distances from the stream bank. In addition, two approaches for analyzing metals (dry ashing method and wet digestion approach) were used for the study and their results were compared. Comparisons of metals concentrations in plant tissues, sediments and the water column provide an indication of the distribution and transport processes affecting metals transport.

As such, the study provides information on the long-term transport of metals to terrestrial vegetation near the banks of the river. It also provides an indication of the usefulness of various laboratory techniques for characterizing metals in plant tissue. By investigating the distribution of metals in plant tissues for a few selected species of vegetation at different locations adjacent to the river and comparing these results with characteristics of metals in the river's water and sediments, the results provide an assessment the extent to which metals are transported to the adjacent terrestrial ecosystem.

Materials and Methods

The overall approach involved the collection, analysis and comparisons of metals in plant tissues, river bottom sediments, and river water samples. The sampling plan included the collection of sets of vegetation from four sites along the upper Blackstone River in Massachusetts. Terrestrial mosses, specifically *Sphagnum fuscum* and *Polytrichum juniperinum*, were selected for metals analysis since mosses have also been used to assess metals accumulation in other studies, many of which focused on the effects of atmospheric deposition (Glooschenko and Arafat, 1988; Glooschenko, 1989; Wappelhorst *et al.*, 2000). These analyses were supplemented by analyses of metals in bracket mushrooms and earth mushrooms (which are *Piptoporus betulinus* and *Agaricus silvaticus*, respectively). Analysis of metals in additional samples of bottom sediment and river water provided a basis for comparison.

Basic descriptions for each sampling site are included in Table 1 and a schematic showing the Blackstone River and the four sampling sites is shown in Fig. 1. Sampling sites 1 and 2 were set along reaches of the river where velocities were relatively high. The ponds along the study area include three impoundments, namely Fisherville, Riverdale, and Rice City ponds. Sample sites 3 and 4 are locations adjacent to Riverdale and Rice City ponds, respectively, for which velocities were relatively low. Sample sites 1 to 3 each include one sampling location, where the last one (Rice City pond) included samples at three locations. For most of the sampling sites, samples were collected at a number of distances from riverbank. When possible, mushroom samples were also collected to assess the difference between heavy metal concentrations found in primary lower level plant tissues and those found in upper level plant tissues. In addition, samples from submerged sediments were also collected at each sampling location. This approach provided a basis for assessing the trends in constituents for varying distances from the riverbank, as well as the differences between the plant tissues and sediment samples.

The collection of plant tissue, sediment and water column samples was completed on December 11, 2001. For each location, moss samples were transferred into sterile 7 ounce clear nylon containers. Submerged sediment samples were transferred into wide lid amber glass containers. In addition, water column samples were collected and stored in amber glass bottles to evaluate the metals concentration in the water column. Following

Table - 1: Sample locations, elevations and notes for various sites

Sample ID	River km and (elevation)	Latitude/ Longitude	General description	Distance from water	Height above water	Notes
1	58.8 km (~85 m)	42°10'36"N 71°41'17" W	Route 122-A - bridge on Depot St.- just after Fisherville pond;	29 cm 144 cm	8 cm 26 cm	Adjacent to the canal. Moderate flow velocity. On upper bank.
2	56 (~80 m)	42°09'17"N 71°39'14" W	Sutton street – at bridge over river - river; relatively constant width and high flow conditions	130 cm 145 cm	14 cm 11 cm	Narrow canal, station with the highest flow velocity. Flat bank.
3	53 (77.7 m)	42°08'28" N 71°38'23" W	Riverdale pond (western side)	29 cm 346 cm 605 cm	3 cm 8 cm 6 cm	Organic soft matter on raised flat section shaped like an island. Soft Organic material, section same as above. Same as above.
4 - 1	46 (72.8 m)	42°06'00"N 71°37'17" W	Rice city pond western upstream side of the pond	87 cm 259 cm 461 cm 605 cm	4 cm 21 cm 28 cm 37 cm	Sudden increase in canal width clear contamination deposition relatively fast velocity. Middle bank sudden increase in channel area. Lower level of upper bank. Same as above.
4 – 2	45 (72.8 m)	42°05'58" N 71°37'28" W	Rice city pond western downstream bank of the pond	25 cm 289 cm 461 cm 720 cm 1297 cm	6 cm 29 cm 33 cm 41 cm 76 cm	Taken from soil deposited on rock high velocity. Flat bank at moderate height above water. Same as above. Moderate height on upper bank. Upper level of upper bank level far from the canal.
4 - 3	45 (72.8 m)	42°06'00" N 71°37'17" W	Rice city pond eastern downstream side of the pond	87 cm 158 cm 519 cm 749 cm	9 cm 17 cm 19 cm 51 cm	Deposition of organic materials on bank, relatively low velocity, shallow side pond. Moderate slope on medium bank. Moderate height on Upper bank. Moss sample on a tree root on surface.

collection, the samples were chilled and transported to the Environmental Engineering Lab at Worcester Polytechnic Institute.

The samples were placed in uncontaminated containers and stored in a laboratory refrigerator until sample preparation. Preparation of plant tissue samples, which was completed within 5 days of the sample collection, included both wet and dry ashing digestion techniques. To extract the metals to solution, the wet digestion method basically includes the addition of nitric acid (HNO_3) and subsequent heating, while the dry ashing digestion method involves initial high temperature heating (*i.e.* ashing), followed by nitric acid addition and additional heating. Both methods have advantages for certain conditions and matrices. An advantage of the dry digestion method is that it provides more consistency in analyses since all samples are dried and the effects of the water content (which might vary relying depending on the sample age, species and other environmental factors) are avoided. The method is relatively free from reagent contamination. An advantage of wet digestion method is commonly considered to be that the sampling preparation eliminates elemental loss by volatilization.

For the first set of collected plant tissue samples, the wet digestion technique was completed. First, each sample was weighed and an HNO_3 solution was added to each sample. For the wet digestion process, an 8 hr period of digestion was provided at room temperature. After the 8 hr cold digestion period, the glass beakers were placed on a hot plate and heated for 1.5 hr. Then, eight drops of hydrogen peroxide (H_2O_2) were added to each beaker and the beakers were heated again until the wet digestion process was completed and a small sample volume remained. Subsequent to cooling, the samples were filtered and diluted to a 50 ml volume. After filtration of samples, centrifuge tubes were transferred to the atomic absorption lab for analysis.

For the second set of the bioassay samples, the dry ashing technique was applied. First, each sample was weighed and then placed on a ceramic plate. Each sample was dried at 500°C for 8 hr. After each sample was cooled, the prepared

Table - 2: Total metal concentrations in collected moss samples prepared by both dry ashing and wet digestion methods

Sampling location and distance from water	Metal concentrations (mg kg⁻¹)											
	Pb_t		Cu_t		Zn_t		Cr_t		Cd_t		As_t	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
1 (29 cm)	183	211	92	110	124	171	44	50	4.61	4.68	0.149	0.155
1 (144 cm)	223	259	181	230	258	340	96	102	11.1	14.5	0.327	0.349
2 (130 cm)	117	123	72	93	95	98	42	54	3.01	3.02	0.130	0.132
2 (145 cm)	158	158	101	116	124	135	69	70	4.84	5.53	0.160	0.159
3 (29 cm)	59	66	83	89	99	162	56	59	4.87	5.31	0.098	0.113
3 (346 cm)	194	220	81	90	86	111	47	62	2.66	3.22	0.092	0.093
3 (605 cm)	286	300	87	102	97	169	89	100	3.33	3.46	0.090	0.131
4 – 1(87 cm)	184	205	170	179	169	178	104	108	6.46	6.75	0.206	0.207
4 – 1 (259 cm)	118	124	102	106	173	209	70	72	6.22	6.63	0.100	0.099
4 – 1 (461 cm)	66	79	21	32	211	226	24	27	5.17	5.67	0.015	0.014
4 – 1 (605 cm)	56	74	10	17	207	213	16	18	4.24	4.63	0.033	0.058
4 – 2 (25 cm)	187	198	94	103	87	124	101	108	2.43	2.84	0.124	0.125
4 – 2 (289 cm)	133	144	106	107	114	129	74	83	3.88	4.15	0.111	0.122
4 – 2 (461 cm)	248	260	140	144	82	89	99	102	3.55	3.76	0.122	0.145
4 – 2 (720 cm)	175	179	41	49	41	48	56	60	2.41	2.63	0.135	0.143
4 – 2 (1297 cm)	72	75	11	14	11	12	4.3	4.6	1.26	1.49	0.007	0.008
4 – 3 (87 cm)	99	101	106	107	106	161	61	63	7.38	8.19	0.115	0.121
4 – 3 (158 cm)	193	211	161	172	65	59	209	224	5.52	6.26	0.056	0.063
4 – 3 (519 cm)	49	55	11	23	25	24	21	22	2.45	2.69	0.213	0.246
4 – 3 (749 cm)	114	161	42	55	27	25	30	33	1.33	1.52	0.077	0.139
Arith. mean	146	160	86	97	110	134	66	71	4.34	4.85	0.118	0.131
Range	237	245	171	216	233	328	205	219	9.84	13.0	0.320	0.340

HNO_3 solution was added to each ceramic container while the containers were being heated on a hot plate. After 15 min., eight drops H_2O_2 were added to each container and a ten minute period was allowed for completion of full digestion. New 50 ml centrifuge tubes (containing no heavy metals) were prepared and equipped with plastic filter funnels and laboratory filters. The prepared samples were filtered and then diluted to volume of 50 ml each.

For the sediment samples, an amount weighing between 1 and 2 g was used for the analysis. The smaller sample amounts were placed in a glass beaker and then 5 ml HNO_3 and 50 ml e-pure water added to the samples. Samples were acid digested on the hot plate for a two hour period. Following this digestion, ten drops of H_2O_2 were added on each container. Following acid digestion and H_2O_2 addition, previously unused 50 ml centrifuge tubes were prepared. The acid digested sediment samples were then filtered and the tubes were capped.

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For each of the water column samples, 50 ml of sample was transferred to a 100 ml beaker and a 5 ml lab grade HNO_3 was added. Water column samples were then acid digested following procedures that were similar to the procedures described above for preparation of sediment samples. For dissolved metal fraction, 0.45 ìm filter papers were used to obtain dissolved metal concentrations. After all plant tissue, sediment and water column samples were digested and prepared, they could be analyzed for total metal concentrations.

A Perkin Elmer® Analyst 300 atomic absorption spectrometer (AAS) was used to quantify the total metal concentrations. The flame method was used for both plant tissue and sediment analyses, while the furnace method was used for analyses of water samples. Calibration curves, developed using standards, provided the basis for quantifying metals concentrations for analysis of water, sediments and plant tissues using both the dry and wet analysis techniques. For example, to develop standard calibration curves for bioassays and sediment samples, 50, 100 and 250 mg kg⁻¹ standards of Cu_t and Pb_t were used. Throughout the text, t means total and d means dissolved fractions of the heavy metals examined in this study. Correlation coefficients for Cu_t and Pb_t in plant tissues and sediments were found to be 99.595% and 99.535% respectively. For the water column samples, standards of 1, 3, 5 and 10 μg l⁻¹ were used, and the correlation coefficient was read as 99.590%.
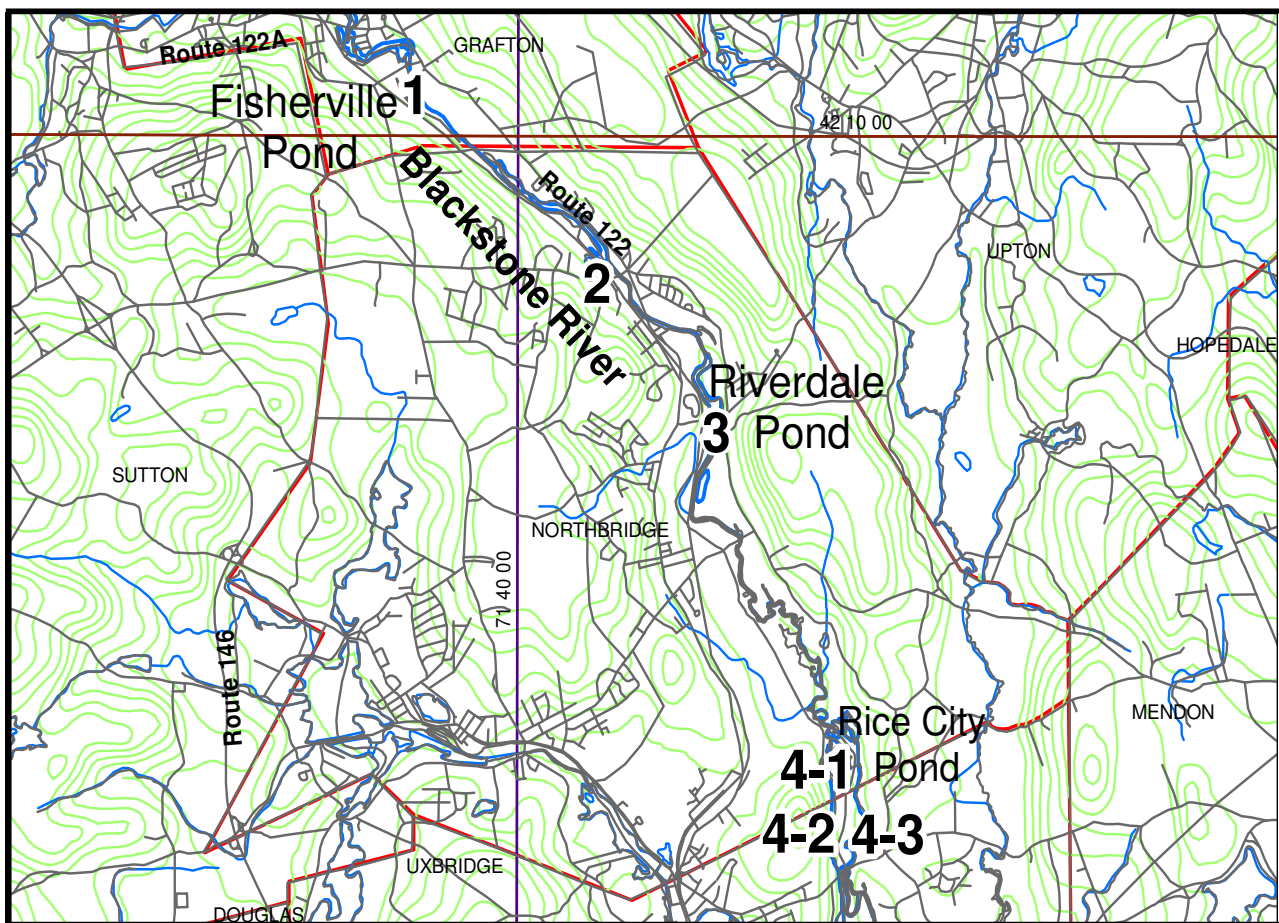
Fig. 1: Sampling sites in upper Blackstone River, Worcester County, Massachusetts (figure developed using data from Office of Geographic and Environmental Information (MassGIS), Commonwealth of Massachusetts Exec. Office of Environmental Affairs

Table - 3: Metals concentrations using the dry ashing and wet digestion methods in plant tissues in water column (site 4-3) and in additional plant tissues (including Pb_t, Cu_t, Zn_t, Cr_t, Cd_t and As_t)

Sample site and description	Distance from water	Metal concentrations, mg kg^{-1}											
		Pb_t		Cu_t		Zn_t		Cr_t		Cd_t		As_t (µg kg^{-1})	
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
1 Under-water moss	0 cm	13.1	15.9	42.2	46.5	124	99	11.8	14.0	2.66	2.74	6.16	6.30
3 Tree mushroom	1037 cm	38.6	42.9	9.99	13.8	246	245	3.1	3.3	1.85	2.02	1.79	BDL[1]
4-1 Underwater moss	0 cm	49.8	59.6	63.4	78.7	146	203	41.9	42.1	7.43	3.85	95.4	98.6
4-2 Earth mushroom	1445 cm	16.9	19.8	29.6	34.6	170	144	2.9	3.36	3.13	3.45	BDL	BDL
4–3 Water hyacinth	0 cm	11.3	12.6	16.5	22.9	43	50	6.9	7.12	3.06	3.14	20.1	22.3

[1] Number in parentheses indicates the distance from the stream for the sample collection point; "0 cm" indicates sample was collected from the stream, [2]BDL indicates "Below detection limit"

Results and Discussion

Results and basics statistics for total metals concentrations (including Pb_t, Cu_t, Zn_t, Cd_t, Cr_t, and As_t) are summarized in Table 2 for plant tissues (moss samples) for both the wet and dry preparation techniques. The ranges illustrate the variability of the data, with maximum values typically exceeding minimum values by factors of more than 10. The highest concentrations are generally found at sites 3 and 4, near the ponds. The maximum concentrations based on the dry analysis are 248 mg kg^{-1} for Pb_t, 181 mg kg^{-1} for Cu_t, 258 mg kg^{-1} for Zn_t, 209 mg kg^{-1} for Cr_t, and 6 mg kg^{-1} for Cd_t. These values are significantly higher than the background concentrations in samples located far from the riverbank, which were approximately 50 mg kg^{-1} for Pb_t, 11 mg kg^{-1} for Cu_t, 11 to 25 mg kg^{-1} for Zn_t, 5 mg kg^{-1} for Cr_t and 1.5 mg kg^{-1} for Cd_t. In reality, the significance and concern in regards to these concentrations will depend on the potential health impact and risk associated with each constituent. In this case, Cr_t and As_t concentrations would be of particular concern. Results for additional plant samples, including a water hyacinth, a land mushroom (*Agaricus silvaticus*), two bracket mushrooms (*Piptoporus betulinus*) and submerged mosses, are included in Table 3. The concentrations in the submerged samples generally tended to be lower than the samples in the terrestrial samples, and the concentrations in the mushroom samples were lower than the concentrations in the moss samples.

Total metals concentrations found in the riverine bottom sediments at the various sample sites are shown in Table 4. Review of the maximum concentrations for the various constituents confirms that sites 1 and 2 (which are along straight sections of the river) have lower metal concentrations, while sites 3 and 4 (Riverdale and Rice City ponds respectively) have the highest contamination levels. The highest metals concentrations were found in the sediments at the 4th sampling site and site 4-1 was found to have particularly high metals concentrations. Finally, the metals concentrations in the bottom sediments were higher and generally similar in magnitude to the metals concentrations in submerged plants summarized in Table 3.

Metals concentrations for the water column, determined at site 4 only, are included in Table 5. The total suspended solids (TSS) concentrations were moderate and varied between 45 to 55 mg l^{-1}. Pb_t and Cu_t concentrations are considered for the purposes of discussion. As expected, dissolved Pb concentrations were relatively low and most Pb was associated with the particles. On the other hand, the total Cu was generally equally split between the dissolved and particulate forms as similarly reported by Lu and Allen (2001). The use of the TSS and total and dissolved Cu concentrations to determine concentrations within the suspended solid material yielded values of 198 mg kg^{-1}, 164 mg kg^{-1}, and 121 mg kg^{-1} for sample sites 4-1, 4-2, and 4-3 respectively. These values differ from the metals concentrations in the bottom sediment concentrations for sites 4-1 and 4-2, but closely match the values at site 4-3, indicating that water column and bottom sediment may be in equilibrium at this location. Similar results were obtained for Pb, although the results are not presented since dissolved Pb concentrations were not above the detection limit of 2 to 3 µg l^{-1}. In general, the metals concentrations in the water column vary in time depending on ambient conditions, and therefore would not necessarily be expected to match the concentrations in bottom sediments or plants.

To gain more insight into the distribution of the metals in this area, some basic statistical analyses were completed. First, pair-wise correlations among all metals concentrations obtained from analysis of plant tissue. This analysis indicated slightly elevated correlations (e.g. greater than or equal to 0.6) between Pb_t and Cu_t, Pb_t and Cr_t, Cu_t and Cr_t, Cu_t and Cd_t, and Zn_t and Cd_t exist. Low correlations between other metal pairs may be attributed to the transport characteristics and chemical properties of the constituents. For example, some metals tend to be easily transported through the water column in rivers, while others tend to be associated with the sediments even if higher streamflow conditions exist. Furthermore, some metals may be affected by complexation reactions and some may have a low affinity for organic material (as was reported to be the case for Zn_t and Pb_t by Borovec (2000)). Next, a two-way ANOVA analysis was completed on samples that were prepared by the dry ashing method. This analysis showed that metals concentrations for each location could be considered to be statistically distinct since the F value of 28.818 exceeds the critical F of 2.603 for the 95% confidence level (with $P = 1.29 \times 10^{-9}$). Accordingly, additional analyses considered were completed to address the importance of sample location for the various metals of concern.

For all metals, the results from the dry ashing analysis generally agree with those of the wet analysis. Concentrations determined by wet and dry analysis for Cu_t and Zn_t are within 20 to 25%, concentrations for As_t are within 15%, and concentrations determined by wet and dry analysis for Pb_t, Cr_t, and Cd_t are within approximately 10%. Nevertheless, the dry analysis method consistently yielded lower concentrations for all analyses. The concentrations determined by the wet analysis exceeded those of the dry analysis by 15 mg kg^{-1} for Pb_t, 11 mg kg^{-1} for Cu_t, 24 mg kg^{-1} for Zn_t, 5 mg kg^{-1} for Cr_t, 0.5 mg kg^{-1} for Cd_t, and 13 ig kg^{-1} for As_t. According to Perkin-Elmer Manual (1996), the dry ashing method is often recommended since this method is normally considered to be relatively free of reagent contamination. However, since the dry ashing digestion technique consistently yielded lower concentrations than the wet digestion technique, the possibility of volatilization of the metals during the heating phase of the dry ashing digestion process cannot be ruled out. Therefore, at the present time, use of the wet digestion technique is considered preferable for basic metals analysis and additional review of the use of these two techniques to analyze plant tissues in and adjacent to rivers.
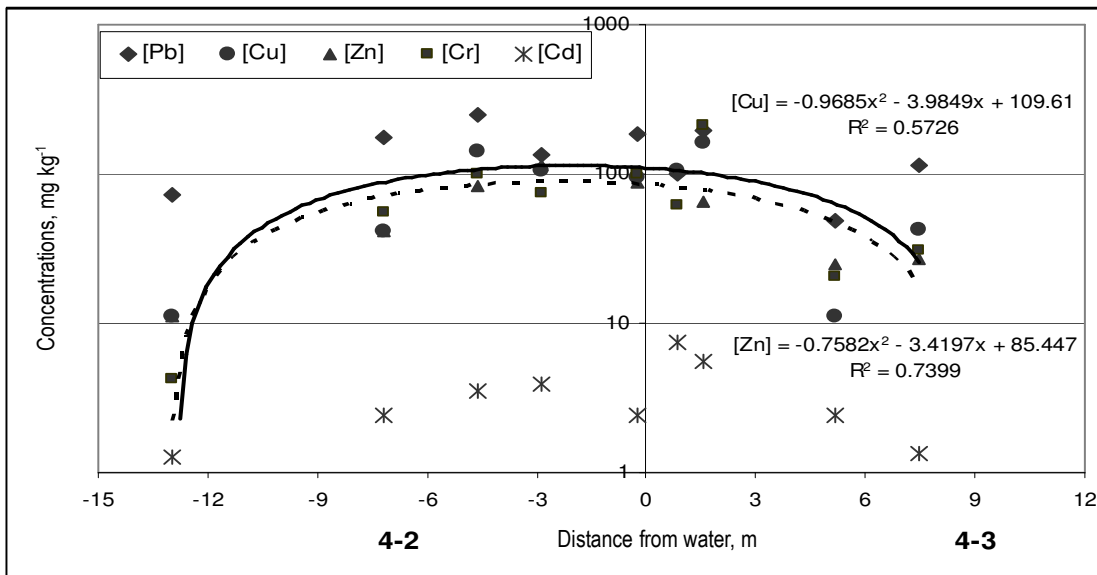
Fig. 2: Total metal concentrations (by dry ashing) with respect to distance from riverbank, with sample site 4-2 (shown in the "-x" direction), site 4-3) shown in the "+x" direction and the riverbank designated as "x=0'
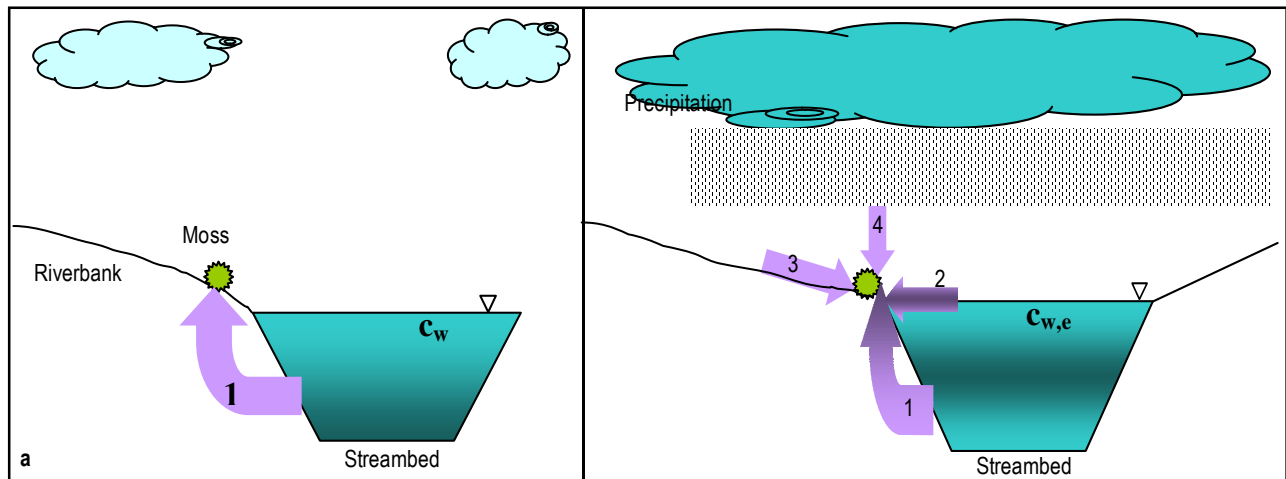

Fig. 3: Possible pathways of contaminants to bioassay located on a riverbank (a) under regular flow conditions (b) under elevated flow conditions; with contaminant availability *via* pathways designated as (1) groundwater and subsurface flow, (2) under higher flow conditions, direct contact with surface water and pore water, (3) under higher flow conditions, runoff from surrounding areas (4) direct atmospheric deposition *via* precipitation. Explanation: c_w: contaminant concentration in pore water, $c_{w,e}$: contaminant concentration in pore water under high flow conditions, due to either upstream wash off or contaminated sediment resuspension from streambed or both

Based on the results of individual sampling sites, the concentrations of the analyzed heavy metals in this case can be considered in relation to the distance from the stream bank. In general, with a few exceptions (*e.g.* sample site 3 in Riverdale pond), the results indicate that contaminant concentrations determined in bioassays decrease as distance from the riverbank increases. Thus, careful review of the results in Table 2 shows that an inverse relationship exists between the concentrations in plant tissues and distance from riverbank for this site. Trends for Cu_t and Zn_t at sample sites 4-1, 4-2, and 4-3 provide ideal examples of these trends.

However, different constituents have different properties. For instance, at site 4-1, while Pb_t concentrations decrease with distance from the stream bank, Zn_t and Cd_t generally remain fairly uniform. Also, the region for which high Pb_t concentrations exist appears to extend to further distances from the stream bank than the regions for which Cu_t appears to remain elevated. At sampling site 3, a relatively homogeneous metal distribution is found, which may be attributed to the relatively flat topography of the riverbank in this location. Finally, it is noted that for a number of locations, the concentrations immediately adjacent to the stream bank are less than those located around 1 to 2 m from the stream bank.

Table - 4: Metals concentrations in bottom sediments (including total Pb_t, Cu_t, Zn_t, Cr_t and Cd_t)

Sample site	Pb_t, mg kg^{-1}	Cu_t, mg kg^{-1}	Zn_t, mg kg^{-1}	Cr_t, mg kg^{-1}	Cd_t, mg kg^{-1}
1	22.0	15.7	28.5	16.4	4.51
2	88.5	70.4	66.8	19.4	5.55
3	98.1	112.4	31.7	17.5	3.52
4 – 1	358.7	310.8	84.9	40.1	12.6
4 – 2	16.3	32.2	19.4	12.3	3.14
4 – 3	114.9	118.6	55.4	21.3	4.48

Table - 5: Water column total suspended solids (TSS), total and dissolved Pb and Cu concentrations under wet weather conditions (December 19, 2001)

Sample site	TSS, mg l^{-1}	Pb_t, µg l^{-1}	Pb_d, µg l^{-1}	Cu_t, µg l^{-1}	Cu_d, µg l^{-1}
4 – 1	55	4.1	BDL	17.1	8.2
4 – 2	56	8.5	BDL	14.3	6.9
4 – 3	45	3.7	BDL	11.1	5.6

BDL: Below detection limit

This could provide an illustration of the dynamic nature of the metal cycling. Typical conditions may exist in which concentrations in the stream (and associated transport to adjacent vegetation) are low or contaminant concentrations immediately adjacent to the stream are reduced. However, under different conditions (*e.g.* higher flows in wet weather or when the chemical conditions promote the release of metals to the water column), transport may be enhanced, resulting in higher concentrations in vegetation. In order to illustrate the relationship between the metal concentrations and distances from the stream bank, a set of polynomial expressions was developed. These expressions are included in Table 6. Given the wide range in concentrations and trends, the expressions were developed based on curve fits to the dry ashing and wet digestion results from Rice city pond (sampling locations 4-2 and 4-3). In addition, Fig. 2 shows the heavy metal concentrations obtained by dry ashing techniques, which were selected for graphical presentation since the dry ashing results, especially the results for Cu_t and Zn_t, appeared to yield relatively consistent trends. Due to the space limitations in Fig. 2, the polynomial curves for only Cu_t and Zn_t are shown. These curves illustrate the inverse relationship between metals concentration and distance from the riverbank.

The characteristics of the flow in the river can affect the transport of metals to the vegetation. To understand how these flow characteristics may impact the characteristics of metal transport to vegetation, it is helpful to consider the conceptual representation shown in Fig. 3, which illustrates the basic pathways that may be followed by a contaminant to a terrestrial plant tissue located near a riverbank. It is noted that this representation simplifies the dynamic processes involved and also does not necessarily include all minor pathways, but does provide some of the primary pathways of interest. For low water conditions, the primary pathway expected from the river to the vegetation would pass through the subsurface via groundwater. In this case, atmospheric deposition is considered to be negligible. For high flow conditions, metals could follow a number of pathways from the river to the vegetation. Potential pathways for high flow conditions include contaminant availability via (1) subsurface flow via groundwater, (2) pore water that becomes available to the vegetation through direct contact, (3) runoff from surrounding areas, and (4) direct atmospheric deposition via precipitation. For these locations, pathways 3 and 4 are likely to have relatively small effects for the sampled locations since the sample locations are in woodland areas (with reasonably good runoff quality for the local land use) and also because atmospheric inputs are relatively small as confirmed by metals concentrations at large distances from the river. Consequently, direct exchanges from the river (pathways 1 and 2) likely have an important effect on plant tissue concentrations adjacent to the bank.

River flow, morphology and channel shape can have an important effect on contamination levels in the plant tissues. First, it is helpful to consider the nature of the velocities in the various channel sections. In general, a listing of the sampling sites in order from highest to lowest velocities starts with site 2, followed by site 1, site 4-2, site 4-1, site 3, and finally site 4-3 (which had the lowest velocities). Since the highest metals concentrations were found at sites 3 and 4, it is evident that concentrations are higher in reaches with low velocities, as expected. Second, it is helpful to consider the variations in flow as they may relate to metals transport. Flow data compiled from United States Geological Survey, Northbridge gaging station (USGS 01110500) indicate that notable flow changes do occur in this reach of the river. Before 2001, mean flows were approximately 8 m^{3}s^{-1}, while high flows were 99 m^{3}s^{-1} in 1998, 49 m^{3}s^{-1} in 1999, 73 m^3 s^{-1} in 2000, and 80 m^3 s^{-1} in March of 2001 (Socolow *et al.*, 2001). Between March 2001 and the time of this investigation, flows were below the long term average flow estimated for over a 43 year period with no flow observations exceeding 13 m^3 s^{-1} (Socolow *et al.*, 2001). During the sampling period for this study, the recorded flow was between 1.8 m^3 s^{-1} and 1.9 m^3 s^{-1} (Socolow *et al.*, 2001).

Table - 6: Mathematical expressions showing relation between the total metal concentrations and distance from water at two of the 4th sample sites (4-2 and 4-3) (n = 20)

Metal (mg kg^{-1}) and method	Polynomial expression (x = distance in m)	Regression coefficient %
Pb dry	$-0.9671 x^2 – 6.4354 x + 168.07$	42.68
Pb wet	$-0.8425 x^2 – 4.4802 x + 178.87$	28.43
Cu dry	$-0.9685 x^2 – 3.9849 x + 109.61$	57.26
Cu wet	$-0.9317 x^2 – 3.3368 x + 116.05$	56.38
Zn dry	$-0.7582 x^2 – 3.4197 x + 85.447$	73.99
Zn wet	$-0.9915 x^2 – 4.5238 x + 105.14$	62.24
Cr dry	$-0.8838 x^2 – 2.9799 x + 101.68$	40.54
Cr wet	$-0.9400 x^2 – 3.1636 x + 108.23$	40.31
Cd dry	$-0.0295 x^2 – 0.0925 x + 4.3273$	42.45
Cd wet	$-0.0318 x^2 – 0.0953 x + 4.7774$	40.74
As (µg kg^{-1}) dry	$-0.5143 x^2 – 1.3225 x + 127.69$	33.57
As (µg kg^{-1}) wet	$-0.2815 x^2 – 4.6135 x + 140.51$	38.66

After the samples were collected for this study, the flow increased on December 18-19, 2001, with a maximum flow of 6.46 m^3 s^{-1} (Socolow *et al.*, 2001). Moreover, a water level increase of 12.80 cm was recorded in the throughout the morning of December 19, 2001. Using flow variables and the gage height at the USGS gaging station, a gage height or stage flow relationship was developed. This analysis showed that a flow increase from 2 m^3 s^{-1} to 6 m^3 s^{-1} results in a 15 cm increase in water level at Rice City pond (*i.e.* Sample site 4-1). Thus, as a result of this flow condition on December 19th, it is likely that all of the samples that were collected from the sampling locations at the 4th sampling site would have been submerged a week after the collection of the samples.

Furthermore, by considering the depth changes expected for typical water level changes, it appears that the following sampling locations sites may potentially be submerged approximately once per year: site 1 (29 cm from the stream bank; 8 cm above the water surface), site 2 (130 and 145 cm from the stream bank; located 11 cm and 14 cm above the water surface respectively), site 3 (29, 346, 605 cm from the river shore, with respective elevations of 3, 8, and 6 cm above the river surface), site 4-1 (87 cm from the stream bank, with an elevation of 4 cm above the water surface), site 4-2 (25 cm from the stream bank and 6 cm above the water surface), and site 4-3 (87 cm from the stream bank and 9 cm above the water surface). For the other sample sites, it is possible that the vegetation could get submerged during high flow events, but these occurrences would be rare. Review of Table 2 confirms that the concentrations for metals are high for all of the sampling locations noted above (for which the likelihood of submergence in a given year is relatively high). For locations 1 and 4-3, the concentrations found in the samples that are likely submerged occasionally do not clearly exceed the concentrations of the sample that rarely gets submerged. However, for samples 4-1 and 4-2, the concentration of Pb$_t$ adjacent to the river clearly exceeds the concentrations of samples that rarely (if ever) get submerged. In addition, for essentially all sample locations, the two samples located nearest to the river clearly have the highest concentrations. Thus, it is likely that the concentrations are affected by the flow in the river, the amount of time(s) that the plant gets submerged, along with the nature of the material adjacent to the stream bank.

The results presented in this paper indicate that heavy metal concentrations in plant tissues generally decrease with increasing distance from the riverbank for most of the sampled locations along the Blackstone river. Terrestrial mosses, which are often used to assess the impacts of air pollution, also appear to yield useful information regarding water and sediment pollution. Analysis of metal concentrations using the dry ashing process yielded lower concentrations than those afforded by the wet digestion method, and the wet digestion process is the current recommendation since the approach avoids any effects of volatilization. In general, elevated heavy metal concentrations were detected in samples that were located close to the riverbank, while background concentrations in samples far from the river were low. Furthermore, the highest heavy metals concentrations for the plant tissues, sediments, and to some extent the water column are all found at the same sampling sites.

The high concentrations of metals adjacent to the river provide some confirmation that a transport or exchange process exists between the river and adjacent vegetation near the shore. As indicated in Fig. 3, transport pathways impacting the vegetation may include storm water runoff, flow from groundwater sources, possible direct input from the river via submergence and pore water, and input via groundwater. Here, the metals that originate in the river are likely transported to the vegetation via direct input through pore water, or via transport to groundwater and subsequent input to the vegetation from the subsurface. Additional research is recommended to characterize these transport processes.

Given the relationship between the plant tissue analyses and sediment analyses, as well as the consistent trends exhibited by the plant tissue results, one suggestion could be to consider

the use of terrestrial plant tissue analyses as a screening tool to identify the river reaches which have high heavy metals concentrations. In general, if sources other than the river (i.e. atmospheric deposition, storm water runoff, and even groundwater outflow from aquifers) are not significant sources of trace metal deposition, it is possible that riverbank bioassays could be used to identify or fingerprint heavy metals transported via stream flow and contaminated sediments. This possibility would require additional analyses on a number of river basins, which is suggested for additional research.

Finally, it is noted that review of channel characteristics and flow data in this investigation indicated that river channel geometry could have a significant effect on the metals concentrations in the adjacent plant tissues. In particular, the samples that were closest to the riverbank generally were found to have higher concentrations of heavy metals. For instance, the samples collected at the third sample site (at Riverdale pond, which had notably low metals concentrations in sediments), yielded remarkably higher heavy metals concentrations in vegetation. These trends, which were consistent for most sampling locations, illustrate the importance of the velocity and flow characteristics on heavy metals concentration in sediments and in adjacent plant tissue. It is clear that the processes in the vicinity of the streambed are dynamic and have an important impact on the exchanges of water and metals between the river, adjacent sediments, and adjacent vegetation. The results presented in this paper provide an indication of some of the considerations and potential implications of these processes.

Acknowledgments

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