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Metals Concentrations in the Sediments of Richard Lake, Sudbury, Canada and Sediment Toxicity in an Amphipod *Hyalella azteca*

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Abstract: Surface sediment from 9 different water depths at 1 m depth intervals (1 to 9 m) in Richard Lake, Sudbury, Canada was sampled in August 1998 and analyzed for 10 metals including copper (Cu), zinc (Zn), cadmium (Cd), nickel (Ni), lead (Pb), cobalt (Co), molibidenum (Mo), vanadium (V), barium (Ba) and titanium (Ti). Metal analysis showed that surface sediment at the depth of 3 m depth has the highest concentrations of metals especially of Ni (4721.1±821.6 $\mu g\ g^{-1}$) and Cu (1011.0±46.4 $\mu g\ g^{-1}$). The results of a toxicity study in the laboratory which showed that surface sediment from a depth of 3 m was the most toxic to *H. azteca* (LT50 129.12 h) and had the highest metal concentrations (especially Ni and Cu) in overlying water and in amphipod tissues.

Key words: *Hyalella azteca*, Richard Lake, toxicity test, sediment, acute, bioaccumulation

INTRODUCTION

The Sudbury region of Ontario lies just North of Lake Huron (46°00'N-47°30'N; 79°39'N-81°30'W) and is noted as one of the world's largest sulphide ore deposits of nickel and copper. Sudbury has been the centre of nickel-copper smelting in North America for the past 100 years. Mining and smelting activity increased after the Coniston and Falconbridge smelters began operating in 1913 and 1920, respectively and a 155 m high stack was installed at Copper Cliff in the 1920s. Sulphur dioxide and trace metal emissions from the Sudbury smelters have contaminated local lakes, reducing water quality and affecting aquatic biota over the past century (Freedman and Hutchinson, 1980; Keller, 1992; Gauthier *et al*., 2006). There is a trend of declining metal concentration, especially for Cu, Ni and Co in water, sediment and biota (*Hyalella azteca*) with distance from the smelters (Shuhaimi-Othman *et al*., 2006). Richard Lake (RIC) (46.4378°N, 80.9167°W) is one of the lakes in Sudbury area located about 12 km from the smelter stacks at Copper Cliff in Sudbury.

Contaminants in sediments pose a treat to human health, aquatic life and the environment. Pollutants release to surface water from industrial and municipal discharges, atmospheric deposition and polluted runoff from agricultural, urban and mining areas can accumulate to environmentally harmful levels in sediments. Toxicity tests in the laboratory with sediment or ambient water from a suspected polluted area can be used to document or confirm toxic agents in that area. Concentration-response information generated under controlled laboratory conditions can be compared with predicted or measured concentrations in the environment and estimates of relative risk can be made (Graney *et al*., 1995). Using fathead minnows (*Pimephales promelas*), Gauthier *et al*. (2006) identified nickel and cadmium as the primary toxicant that increased mortality and hatching time to the fish in experiment conducted in metal contaminated lakes around Sudbury; Ingersoll *et al*. (1994) used sediment contaminated with As, Cd, Cu, Pb and Zn from Clark Fork River, Montana in laboratory toxicity tests with *H. azteca* and Borgmann and Norwood (1997) used sediment from Manitouwadge Lake to identify the toxic agent using toxicity-accumulation relationships in *H. azteca*.

In this study, sediments from 9 different water depths in Richard Lake, Ontario, Canada were sampled in August 1998. Sediments sampled were brought back to laboratory for metal analysis. Water quality parameters such as dissolved oxygen, pH, conductivity and water hardness were also recorded at different depth. Laboratory experiments (acute bioassay) were conducted with sediments from the lake using *H. azteca* cultured in this laboratory. Metal concentrations in the overlying water and in exposed animals were measured and compared with metal concentrations from the field.

MATERIALS AND METHODS

Sediment Sampling

Transect surface sediment samples were taken from shallow to deep water at 1 m depth intervals using a Mini Ponar (Wildco-Petite) sampler (9 different depths). Surface sediment samples were stored in polypropylene cups (100 mL × 3 replicates) and kept in the dark at 4°C. *In situ* water quality parameters (temperature, pH, conductivity and dissolved oxygen) were also taken at each depth using Hydrolab® profiling system (Data Sonde 4, Hach Environmental). Dried sediment samples (50 mg) were digested in 2 mL Aristar® (Merck) nitric acid (70%) in a block thermostat (80°C) for 3 to 4 h until the solutions were clear. The solutions were then made up to 25 mL with double distilled water in 25 mL volumetric flasks. Metal analyses in all samples were done by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, model Perkin-Elmer Elan 5000A) or for nickel by flame or furnace Atomic Absorption Spectrophotometry (AAS-Perkin-Elmer 4100ZL) because of restriction of the ICP-MS (Perkin-Elmer Elan 5000A) to detect nickel. Standard and blank samples were analysed every 20 samples. The sediments were analysed for ten metals i.e., Cu, Zn, Cd, Ni, Pb, Co, Mo, V, Ba and Ti. Metal concentrations in reference soil material (SRM 2711, National Institute of Standard and Technology, USA) were determined using the same analytical procedures and values obtained were within 10% range of the reference values.

Studies on Bioaccumulation and Acute Toxicity of Sediments from Richard Lake to Adult *H. azteca*

Fourteen days acute sediment toxicity tests were performed using adult *H. azteca* obtained from laboratory cultures (Shuhaimi-Othman and Pascoe, 2001). One milliliter of sediments from depths of 1, 3, 5, 7 and 9 m was carefully injected to the bottom of a glass vial (10 replicates) containing 15 mL of declorinated mains tap water (conductivity 230±1.2 μS cm^{-1}, dissolved oxygen exceeding 60% of air saturation value, pH 7.6±0.1, Ca 123.8±2.8 mg L^{-1}, Mg 30.3±0.8 mg L^{-1}) using a syringe (i.e., 1 part sediment : 15 part water). A leaf disc (0.6 cm^{2}) (conditioned alder leaf *Alnus glutinosa* (L.), Bird and Kaushik, 1985) was used as substrate for a control with the same size of vial and water volume. Test vials with sediment were allowed to settle for 3 days before 2 animals (1 male and 1 female) were added in each vial. Ten replicates each containing 2 adults of *Hyalella* (approximately 4-5 mm body length) in a 20 mL glass vial (2×5 cm) containing 1 mL of the appropriate sediment and 15 mL of declorinated water. A total of 20 animals per treatment were used in the experiment and a total of 120 animals, were employed in the investigation (5 treatments and 1 control). Animals were fed *ad libitum* twice a week (approximately 0.2 g) with ground Tetramin® (Tetrawerke, Germany). Fifty percent of the test water in each vial was changed every week. Pooled water samples (5 mL of solution removed from each exposure vial) were acidified to 1% with Aristar® nitric acid (70%) before metal analysis by Atomic Absorption Spectrophotometry and Inductively Coupled Plasma-Mass Spectrometry. Mortality was recorded every 24 h. Criteria used to determine mortality were failure to respond to gentle physical stimulation and the absence of any beating pleopods. Observations were made under a light microscope. After experiments were terminated, surviving animals were prepared for metal analysis by transferring them to a plastic petri dish (50×10 mm) containing 20 mL of exposure solution with a piece of cotton gauze (1 cm^{2}) as substrate but without food for 24 h to purge their guts were empty. Animals were digested using the same procedure as described above. Data for Ni in *H. azteca* were not available because the volume of samples left was too small and after dilutions were made, they were all below the detection limits of the graphite furnace AAS (4 µg L^{-1}).

Statistical Data Analysis

Statistical analysis was conducted by oneway ANOVA and Tukey-Kramer multiple comparison tests using the statistical package Minitab (Vers. 12). Data were tested for normality (Shapiro-Wilkes test) and homogeneity (Barlett's χ^2) and to meet these requirements, data were log10 or square root transformed. After transformation data for dissolved oxygen at different depths in Richard Lake were still not homogenous and nonparametric tests (Kruskal-Wallis and Mood's Median Test) were used. Bioaccumulation of metals in *Hyalella* tissues was also subjected to linear regression analysis. Student's t-test was employed to test the significance of regression coefficients. Median lethal times (LT50) for animals exposed to sediment from different depths were calculated using FORTRAN programmers developed in this laboratory and based on the methods of Lichfield (1949) and Lichfield and Wilcoxon (1949).

RESULTS AND DISCUSSION

Sediment Sampling

Metal analysis shows that surface sediment from 3 m depth in RIC Lake has the highest metal concentrations especially of Ni and Cu. Nickel concentration in the surface sediment in descending order is 3 m > 8 m > 6 m > 4 m > 7 m > 9 m > 5 m > 2 m > 1 m and for Cu is 3 m > 8 m > 4 m > 2 m > 6 m > 5 m > 7 m > 1 m > 9 m. Statistical analyses show significant differences (ANOVA, $p<0.05$) between depths for Cu, Ni, Co, Mo, V, Ba and Ti and no significant differences (ANOVA, $p>0.05$) for Zn, Cd and Pb. Analysis of metal concentrations in surface sediment from Richard Lake shows that sediment from depth of 3 m has the highest metal concentrations especially Ni and Cu (Table 1) and this was confirmed with laboratory toxicity studies (Table 2). Borgmann and Norwood (2002) found that metal concentration (Cd, Co, Cu and Ni) in core sediment from Richard Lake were lowest in the deepest part of the core, increased rapidly up to approximately 5 cm depth and then decreased slightly towards the surface. In a mine tailing impoundment area near Sudbury, McGregor *et al*. (1998) found dissolved concentrations in excess of 10 g L^{-1} for Fe and 2.2 g L^{-1} for Ni within the shallow pore water. With increasing depth, these concentrations decrease to or near analytical detection limits.

Table 1: Metals concentration in the sediment (µg g^{-1} dry weight±SE) at different depth from Richard Lake

Depth (m)	Cu	Zn	Cd	Ni	Pb	Co	Mo	V	Ba	Ti
1	279.5±43.2	199.0±14.1	2.20±0.4	1632.0±280.2	53.0±17.1	41.9±6.4	0.18±0.02	16.2±0.1	54.8±1.0	346.2±5.8
2	526.1±37.8	326.6±132.6	3.11±0.08	2368.2±120.8	42.6±4.9	64.9±0.8	0.19±0.01	15.2±0.8	75.2±6.9	307.8±15.9
3	1011.0±46.4	297.4±22.2	5.60±0.5	4721.1±821.6	71.0±3.6	129.7±19.4	0.60±0.2	20.9±1.4	85.8±5.1	361.7±29.1
4	724.7±80.9	169.2±20.2	5.70±2.7	2438.2±90.3	54.8±7.4	67.8±8.5	0.50±0.1	21.2±0.2	97.6±0.5	364.8±8.1
5	533.5±113.1	136.4±7.4	4.80±1.8	1972.6±293.1	42.1±6.6	61.8±11.9	0.49±0.01	21.6±0.5	90.8±5.4	369.2±11.1
6	828.6±221.2	173.8±23.4	3.20±1.0	2070.6±314.8	64.6±15.1	58.2±9.9	0.44±0.02	23.8±0.8	97.1±1.1	372.1±12.9
7	685.8±214.8	158.1±29.9	2.20±0.4	1891.0±248.7	54.8±14.9	49.2±10.6	0.50±0.04	23.9±0.9	99.2±1.7	380.2±6.2
8	999.6±142.6	186.6±24.1	3.20±0.3	2435.6±282.2	73.5±11.8	80.7±13.0	0.52±0.04	24.4±0.4	99.4±2.9	382.3±9.0
9	590.9±95.4	158.6±13.2	2.40±0.1	1571.8±52.8	53.1±5.9	45.2±3.2	0.42±0.02	22.8±0.6	90.6±2.8	343.9±13.5

Table 2: Median lethal time (LT_{50}) and slope function (s) for adult *H. azteca* exposed to surface sediments from different depths from Richard Lake

Sediment depth (m)	LT_{50} (h)	s
1	327.89	1.89
3	129.12	1.47
5	272.56	1.59
7	300.02	1.37
9	507.54	2.39

Table 3: Guideline standard for metals in sediment (USEPA and CCME)

	[a]USEPA-Freshwater sediment			[a]CCME-Freshwater sediment	
Metals	Not polluted	Moderately polluted	Heavily polluted	ISQG[b]	PEL[c]
Pb	<40	40-60	>60	35.0	913.0
Ni	<20	20-50	>50	22.7[d]	48.6[d]
Cd	-	-	>6	0.6	3.5
Cr	<25	25-75	>75	37.0	90.0
Cu	<25	25-50	50	35.7	197.0
Mn	<300	300-500	>500	-	-
Zn	-	-	-	123.0	315.0

All concentrations as μg g^{-1}, dry weight, [a]: Source from USEPA and CCME, 1999. [b]: ISQG-Interim sediment quality guideline, [c]: PEL-Probable effect level, [d]: Source from MacDonald *et al.* (2000)

Table 4: *In situ* water quality parameter (mean±SE) at 9 different depths in Richard lake

Depth (m)	DO (mg L^{-1})	Conductivity (μS cm^{-1})	pH	Temperature (°C)
1	8.29±0.01	188.3±0.1	7.92±0.0	23.90±0.0
2	8.25±0.002	188.4±0.1	7.92±0.0	23.80±0.003
3	8.21±0.006	188.3±0.3	7.92±0.0	23.80±0.006
4	8.17±0.004	188.2±0.1	7.91±0.002	23.60±0.02
5	7.89±0.09	186.7±0.2	7.70±0.02	21.90±0.1
6	6.84±0.12	186.6±0.1	7.50±0.02	20.80±0.09
7	5.21±0.15	186.5±0.2	7.33±0.01	19.46±0.21
8	2.81±0.27	195.6±1.1	7.16±0.01	16.82±0.19
9	1.11±0.06	201.5±1.45	7.04±0.02	15.61±0.08

Results for the mean of 9 depths of metals in the surface sediment samples were: Cu 686.6 μg g^{-1}; Zn 200.6 μg g^{-1}; Cd 3.6 μg g^{-1}; Ni 2344.6 μg g^{-1}; Pb 53.6 μg g^{-1}; Co 66.6 μg g^{-1}; Mo 0.43 μg g^{-1}; V 21.1 μg g^{-1}; Ba 87.8 μg g^{-1}and Ti 358.7 μg g^{-} .^{1}The metal concentrations in the sediments were evaluated by comparison with the sediment quality guideline proposed by United States Environmental Protection Agency (USEPA) and Canadian Environmental Quality Guideline (CCME, 1999) for freshwater sediment (Table 3). Comparison with USEPA (www.epa.gov) standard showed that the sediments were ''heavily polluted with Cu and Ni, moderately polluted with Pb and moderate/not polluted with'' Cd. However, comparison with CCME standard showed that Cu, Ni and Cd concentrations were higher than the Probable Effect Level (PEL) and Pb and Zn concentrations were higher than Interim Sediment Quality Guideline (ISQG) standards. Therefore, Cu and Ni and to a lesser extent Cd, Pb and Zn concentrations in the surface sediments of RIC Lake were toxic and may pose a hazard to the aquatic biota.

Statistical analyses show significant differences (ANOVA, $p<0.05$) for dissolved oxygen, conductivity, pH, temperature and hardness between different depths in Richard Lake (Table 4). Results show that parameters such as dissolved oxygen, pH and temperature decrease with increasing depth while conductivity increase with depth. Comparison with the reference lakes 94-154 km from the smelters shows that Richard Lake had high conductivity and total hardness compared with these reference lakes (Shuhaimi-Othman *et al*., 2006). Water quality parameters were known to influence the availability and accumulation of metal by aquatic organisms. Other studies have shown that water quality factors such as water hardness, alkalinity, pH and Dissolved Organic Carbon (DOC) might influence metal bioavailability and bioaccumulation in the natural environment (Stephenson and Mackie, 1988; Iivonen *et al*., 1992; Reimer and Duthie, 1993).

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Water quality parameter (pH and hardness) for the overlying water measured in each exposure hambers are shown in Table 5. Data were analyzed using time/response (TR) methods by plotting cumulative percentage mortality against time on logarithmic-probit paper (Fig. 1). The median lethal

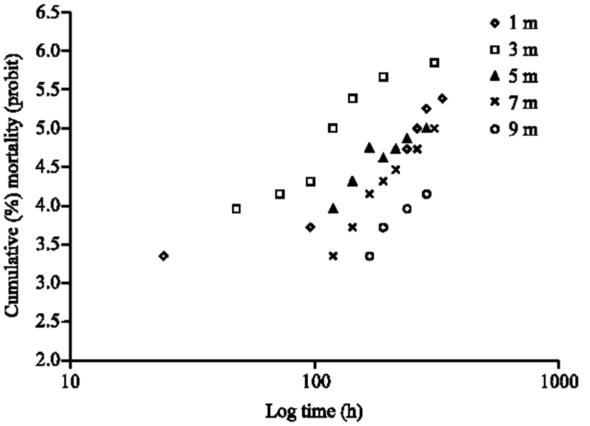

Fig. 1: The relationship between cumulative percent mortality of *H. azteca* and exposure time at different depths of sediment from Richard Lake

Table 5: Mean values (±SE) for pH and total hardness for each depth and control

		Depth (m)				
Variables	Control	1	3	5	7	9
pH	7.7±0.08	7.5±0.02	7.1±0.07	7.4±0.06	7.3±0.06	7.3±0.08
Hardness (mg L^{-1} as $CaCO_3$)	114.8±4.90	96.9±1.20	96.2±8.20	92.8±3.70	89.5±2.40	97.4±2.00

Table 6: Metal concentrations (mean (µg L^{-1}) ±SE) in the overlying water of control and sediment from different depths

Depth (m)	Cu	Zn	Cd	Ni	Pb	Co	Mo	V	Ba	Ti
Control	2.7±3.7	4.4±0.4	ND	<4.0	ND	0.11±0.01	0.14±0.05	ND	48.6±3.4	0.39±0.12
1	25.3±7.8	15.1±4.6	0.90±0.1	1181±206	0.82±0.39	7.15±2.37	0.41±0.06	1.70±0.10	57.0±2.3	7.20±3.60
3	36.0±10.5	172.0±6.8	4.45±1.28	7740±1920	0.37±0.04	10.00±4.60	0.59±0.05	0.64±0.08	65.7±3.8	1.71±0.20
5	14.6±3.8	23.8±5.6	0.76±0.11	1283±252	0.21±0.07	19.60±4.30	0.67±0.04	1.29±0.05	62.5±4.0	1.10±0.24
7	27.6±8.3	27.7±5.8	0.92±0.14	1540±407	0.83±0.26	28.50±5.90	0.66±0.08	1.94±0.07	59.0±3.5	3.34±1.24
9	13.6±4.6	10.8±2.3	0.36±0.03	548±141	0.38±0.19	7.11±1.98	0.69±0.09	2.68±0.21	54.8±2.2	2.16±0.89

ND: Not detected with ICP-MS

time (LT50) and the slope functions (s) of the time response line for each depth are given in Table 2. Figure 1 and Table 2 clearly show that surface sediment from depth of 3 m was the most toxic to *H. azteca* (LT50 129.12 h) of the 5 different depths with the order of toxicity 3 m>5 m>7 m>1 m> 9 m. Results were confirmed with metal analysis in the overlying water (Table 6) and *H. azteca* tissues (Table 7) and show that metal concentrations were highest at depth of 3 m especially with Ni, Cu and Zn. Results also show that Ni and to some extent Cu had the highest concentration in the overlying water (up to 7740 µg Ni L^{-1}) and was probably the most bioavailable to *H. azteca*. Shuhaimi-Othman *et al*. (2006) reported that metals in *H. azteca* are related more to metals in water than to metals in the solid phase sediment. Schubauer-Berigan *et al*. (1993) reported that the 96 h LC50 for Ni in *H. azteca* was 2000 µg L^{-1} at pH 6-6.5, in very hard water (300-320 mg L^{-1} $CaCO_3$). Kszos *et al*. (1992) showed that Ni at concentrations of 7.5 µg L^{-1} (water hardness 40 mg L^{-1} $CaCO_3$) was lethal to *Ceriodaphnia dubia* within 7 d. In stream water containing 49 µg Ni L^{-1} (hardness 656 mg L^{-1}) 100% mortality of *C. dubia* occurred in 7 d, but 70% of the *Daphnia magna* survived for 14 days. *C. dubia* was found to be much more sensitive to Ni than *D. magna*. With freshwater fish *Cyprinus carpio* L. Sreedevi *et al*. (1992) found that exposure to 40 mg L^{-1} of Ni resulted in a decrease in soluble, structural and total protein activities with an increase in the levels of free amino acids, protease, GDH activities and ammonia in the gill and kidney of the fish.

Table 7: Metal concentrations (mean (µg g^{-1} dry weight)±SE) in adult *Hyalella* in control and sediment from different depths after 14 days exposure

Depth (m)	Cu	Zn	Cd	Ni	Pb	Co	Mo	V	Ba	Ti
Control	99.3±7.9	67.2±3.8	0.6±0.1	NA	0.86±0.2	0.57±0.04	ND	ND	87.0±3.0	1.1±0.4
1	115±2.2	82.2±5.8	8.35±1.65	NA	3.8±0.3	3.4±0.4	ND	0.78±0.28	167±31.7	12.4±2.2
3*	297	241	14.6	NA	11.0	17.3	ND	1.4	120	26.4
5	133±0.6	123±12.7	6.8±2.5	NA	4.49±0.82	7.11±0.27	ND	0.65±0.09	136±8.8	14.6±1.8
7	168±12.1	131±9.5	11.9±1.6	NA	6.20±0.12	6.53±1.01	ND	0.36±0.08	131±8.6	6.70±1.23
9	161±14.5	92.8±2.6	6.82±0.61	NA	2.71±0.13	4.24±0.17	0.42±0.04	0.62±0.19	106±15.5	10.3±3.5

ND: Not Detected with ICP-MS, NA: Not Available, *: Samples only available for one replicate

Table 8: Regression equations for effect of different metal concentrations in overlying water (X) on metal concentrations (Y) in *Hyalella* tissues^{+}

Metal	t-value	Regression equation (Y on X)
Cu	1.88	$Y = 1.85+0.282X$
Zn	9.04*	$Y = 1.58+0.359X$
Cd	0.46	$Y = 0.767+0.318X$
Pb	5.06	$Y = 3.53+3.02X$
Co	15.29***	$Y = 0.193+0.485X$
Ba	1.45	$Y = -0.10+1.24X$
Ti	1.47	$Y = 0.754+0.654X$
V	0.16	$Y = 0.58+0.04X$

$^{+}$: Regression for Ni and Mo were not available due to lack of data, *: Indicates a significant relationship ($p<0.05$), ***: Indicates a significant relationship ($p<0.001$)

Linear regression between metals concentration in *H. azteca* and in the overlying water (Table 8) shows that only Zn ($p<0.05$) and Co ($p<0.001$) has significant regression between Zn or Co concentrations in the *H. azteca* tissues and Zn or Co concentrations in the overlying waters and not for other essential metals such as Cu. This probably due to the ability of *H. azteca* to regulate Cu completely and Zn partially and did not regulate Hg, Cd and Pb (Borgmann *et al*., 1993). Borgmann and Norwood (2002) conducted toxicity with sediment core from Richard Lake to *H. azteca* and found that metal concentrations in *H. azteca* were correlated better with metals in water than with metals in sediment. The ability to regulate essential metals such as Mn and Cu has been shown for various species of mollusc, crustacean and fish, whereas the concentration of non-essential metals such as Hg and Pb in organisms depends on their concentrations in the environment (Kraak *et al*., 1992, 1994; Rainbow, 2007). A study by Vijayram and Geraldine (1996) with freshwater prawn *Macrobrachium malcolmsonii* showed that the prawn accumulated the non-essential metal (cadmium) at all exposure level (6.3-157 µg L^{-1}) without any regulation. However, the prawn regulates essential metal (zinc) until a threshold level (373 µg L^{-1}) when regulation collapses and net accumulation begins.

CONCLUSIONS

This study showed that Cu and Ni concentrations in the surface sediment of Richard Lake have the highest concentrations levels among the metals studied and can be classed as heavily polluted. Lead, Cd and Zn can be classed as moderately polluted. Among 9 different sediments depth in Richard Lake, sediment from 3 m depth has the highest metal concentrations especially of Ni and Cu and this was confirmed with laboratory acute toxicity and bioaccumulation studies.

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