UPPER ATHABASCA COMMUNITY BASED MONITORING REPORT

Assessment of Heavy Metal Toxicity in Sediment and Water

Zachary Mueller

December 2015

Introduction

The Athabasca River, with its head waters in the Columbia Icefields and mouth in Lake Athabasca, is an important waterway for many municipalities, industries, and native communities. The river and its watershed covers approximately 20% of the land mass of Alberta and is the drinking water source for approximately 80 000 residents (AEP 1997). The river is also an important water resource used for Oil and Gas industries in Northern Alberta. The Athabasca River is not only significant for its economic importance but also for its ecosystem services. The river and its watershed is considered one of the largest, longest, most diverse and productive in the Mixed Wood Boreal Forest ecosystems in Canada (AEP 1997). The river and surrounding foothills are home to grizzly bears, wolves, bald eagles as well as a diversity of other species (AEP 1997). Since humans are so dependent upon their environment, it is imperative that all stakeholders cooperate with one another to ensure the health of water resources.

While the Athabasca River is of crucial importance to the people and wildlife of Alberta, it is under serious threat from nearby industries. Industrial mining and oil processing operations near the oil sands have had a significant impact on the health of aquatic life in the river. Heavily developed areas around the Athabasca have seen a marked increase in heavy metals concentrations in their sediments and water (Kelly, et al 2010; Dube et al, 2006; Gueguen, et al 2011). Heavy metal contamination has been shown to be more extensive at or downstream of developed area in the lower Athabasca (Kelly, et al 2010). Many people live adjacent to these industrial-developed areas and, thus, stakeholders have expressed a desire to conduct environmental monitoring programs (Wrona, et al 1996; Walsh 2012). Given the complex relation between abiotic and biotic factors, these programs focus on assessing the whole ecosystem to ensure the safety of the public as well as wildlife (Wrona, et al 1996; Dube et al, 2006; Gueguen, et al 2011). While much monitoring has been conducted downstream of Fort McMurray, very little focus has been given to areas of the Athabasca upstream of Fort McMurray where the majority of industrial activities and infrastructure are located.

Many environmental monitoring programs have been conducted in the Athabasca region. The Northern River Basin study (NRBS) investigated how new and old development projects impacted the ecology in the Peace, Athabasca, and Slave rivers. This study used a cumulative effects assessment (CEA) approach in their environmental assessment. The NRBS determined that pulp and paper mills, municipal waste plants, and the W.A.C Bennett Dam were having adverse impacts on local wildlife and First Nations communities (Wrona, et al 1996). Nutrient loading from pulp paper mills and sewage treatment plants cause eutrophication in the Athabasca River. Excess phosphorus and nitrogen were resulting in mass algal blooms of periphyton which outstripped their predators' ability to control their population and changed the riverbed environment (Chambers, et al 2000). Eutrophication is detrimental because it can alter the biotic and abiotic makeup of a landscape. Also, dioxin/furan congeners released from several pulp and paper mills were causing acute toxicity in some important fish species (Wrona, et al 1996). Lastly, the combination of industrial activity with other natural perturbation compromised drinking water for some communities (Wrona, et al 1996). Afterwards, stakeholders came together to change policies. The NRBS was a successful example of how environmental monitoring can be advantageous to stakeholders.

Another monitoring program in the lower basin was the Regional Aquatics Monitoring Program (RAMP). It was responsible for assessing the environmental impacts associated with the oil industry in the Athabasca River. Walsh (2012) and others were concerned that RAMP monitoring efforts rarely extended west of Athabasca and only occasionally investigation near Hinton. Since CEA are designed to assess the whole ecosystem it possible there are gaps in RAMP assessments. Mining, agriculture, and oil and gas exploration are present in the middle and upper Athabasca watershed, making the exclusion of these areas problematic. On October 31, 2013, a coal slurry spill occurred northeast of Hinton. The tailings pond released approximately 650 million litres of slurry into the Apetowan and Plante Creeks. The Upper Athabasca Community Based Monitoring Project partners have begun their own monitoring program in the hope of raising awareness and stemming the adverse effects of development on aquatic and human life.

In this report, I created a water quality index for heavy metals based on the Canadian Council of Ministers of the Environment (CCME) guidelines. I also examined reported heavy metal concentrations in sediment to determine areas that may exceed the CCME water quality guidelines for the protection of aquatic life. I tried to identify habitat sensitive to heavy metal influxes or sediment disturbances, and the seasonality of the heavy metal deposition. I examined data collected between Hinton and Athabasca in the hopes of filling important gaps in current monitoring regimes. A goal was to assess the risk of heavy metal contamination on areas of the Athabasca that other agencies do not adequately examine.

Methods

The Upper Athabasca Community based Monitoring Project has compiled data from May 2014 to October 2015 from 12 sites along the Athabasca located at 12 locations between Hinton and Athabasca using CCME and Environment Canada CABIN protocols (Figure 1). Sediment and water analysis was done by Maxxam (2014 data) and ALS environmental (2015 data). In this report I examined antimony, arsenic, barium, cadmium, cobalt, copper, chromium, iron, lead, mercury, molybdenum, nickel, selenium, and zinc in the sediment. One way analysis of variance (ANOVA) and Holm-Sidak post hoc tests were conducted to determine if sediment concentrations differed significantly between sampling site and sample dates ($\alpha \leq 0.05$)

I also examined total arsenic, beryllium, boron, cadmium, cobalt, copper, iron, lead, mercury, molybdenum, nickel, selenium, silver, thallium, uranium, vanadium, and zinc concentrations in water and compared them to their guidelines to determine a Water Quality Index (CWQI). CWQI was calculated according to CCME report (2001):

$$\text{CWQI} = 100 - \left(\frac{\sqrt{A^2+B^2+C^2}}{1.732}\right)$$

Where A represents scope of failed thresholds, B represents frequency of failed thresholds, and C represents amplitude of failed thresholds. Threshold values were based on CCME guidelines and SigmaPlot (Systat, CA) was used for graphing and data analysis.

Results

All measured concentrations of metal in sediment where below CCME guidelines except arsenic during October 2014 and 2015 at sampling site UATH02 (Figure 2). Metal concentrations also did not vary much between sites and time however there were some exceptions. cadmium concentrations were higher in May 2014 than October 2015 (Table 1, Figure 3). In May 2014, lead concentrations were half that of April 2015, October 2014 and

2015 (Table 1, Figure 3). Mercury concentrations were significantly higher in October 2015 than in May 2014 and April 2015 (Table 1 Figure 3). Sampling site UATH09 had four times higher concentrations of copper, lead, and zinc than UATH12 (Table 1, Figure 4). Molybdenum concentration were higher at UATH01 than UATH04 and October 2014 data was significantly higher than May 2014 data (Table 1, Figure 5).

Some sampling sites failed no water quality benchmarks. However, iron concentrations were above the benchmark at UATH00, UATH01, UATH02, UATH04, UATH05, UATH06, and UATH07. Copper concentrations were above the benchmark at UATH00, UATH01, and UATH02.

Table 1. Statistical summary of heavy metals in sediment throughout the Athabasca River.

periodic element	mean ± standard deviation (mg/kg)	CCME guideline (mg/kg)	comparison	ANOVA p value	Holm-Sidak post hoc test
As	4.12 ± 1.28	5.9	--	--	--
Ba	104 ± 46	--	location	0.013	p=0.001
Cd	0.19 ± 0.07	0.6	date	0.017	May 2014 vs. October 2015 p= 0.002
Co	5.77 ± 1.76	--	--	--	--
Cr	14.32 ± 5.26	37.3	location	0.329	--
Cu	8.88 ± 3.82	35.7	location	0.022	UATH09 vs. UATH12 p<0.001
Hg	0.028 ± 0.02	0.17	date	<0.001	May 2014 vs. October 2015 p< 0.001
					April 2015 vs. October 2015 p=0.016
Mo	0.54 ± 0.23	5	location	0.005	UATH00 vs. UATH04 p<0.001
			date	0.009	April 2015 vs. May 2014 p=0.002
Ni	12.98 ± 6.06	45	--	--	--
Pb	6.22 ± 2.55	35	location	0.007	UATH09 vs. UATH12 p<0.001
			date	<0.001	May 2014 vs. October 2014 p<0.001
			date	<0.001	May 2014 vs. October 2015 p<0.001
			date	<0.001	May 2014 vs. April 2014 p=0.011
Sb	0.69 ± 1.51	20	--	--	--
Se	0.13 ± 0.15	1	--	--	--
Zn	38.3 ± 11.08	123	location	0.018	UATH09 vs. UATH12 p<0.001

Table 2. Summary of Canadian council of Ministers of the Environment Water Quality Index (CCMEWQI) for total heavy metals in water along the Athabasca River. Categories for CCMEWQI are Excellent 100-95, Good 94-80, Fair 79-65, Marginal 64-45, and Poor 44-0.

sampling site	CCMEWQI	failed parameter (mg/l)
UATH00	93.8	Cu 0.0042 Fe 0.551
UATH01	94.3	Cu 0.0042
UATH02	84.8	Fe 0.63 & 0.66 Cu 0.0047
UATH03	100	--
UATH04	91.7	Fe 0.884
UATH05	94.2	Fe 0.539
UATH06	94.3	Fe 0.421
UATH07	94.4	Fe 0.503
UATH08	100	--
UATH09	100	--
UATH11	100	--
UATH12	100	--

Discussion

Environmental monitoring of heavy metals in aquatic ecosystems is an important pursuit for industry and governments due to their shared stakes in public and ecosystem health. The first objective of this study was to determine if toxic levels of heavy metals existed in our study sites. I found two instances of toxic levels of Arsenic in sediment along the Freeman River, a tributary of the Athabasca River (Figure 1 and 2). The finding of elevated arsenic concentrations is consistent with other studies of acid sulfate soils in Alberta (5 mg/kg) (Wang and Mulligan 2006). In the water however arsenic concentrations were well below the toxic threshold (0.00099 mg/l and 0.00093 mg/l). However, given that the sampling sites are in close proximity to the Swan Hills waste treatment plant, nonpoint source contamination is possible. This sampling site is also downstream of logging and oil and gas activities. Further sediment and biotic monitoring is required to assess the specific threat of Arsenic in soil to wildlife in the Freeman River Watershed.

Unlike other toxins, heavy metals do not degrade and often accumulate in sediment and soil. Metals may be liberated from sediment and greatly increase wildlife exposure to heavy metals (Eggleton and Thomas 2004). Abiotic factors, such as remobilisation of heavy metals can occur during floods or human activities such as dredging (Eggleton and Thomas 2004). The Bioavailability and mobility of heavy metals in water is dependent on a number of factors such as partitioning behaviour, temperature, pH, salinity, conductivity, and dissolved organic matter (Gueguen, et al 2011). These toxic exposures are often brief and undetectable by monitoring efforts (Gueguen, et al 2011; Kim, et al 2015).

In this report I hoped to identify sites and time periods which were sensitive to heavy metal accumulation and resuspension and identify seasonal trends in these processes. Unfortunately, due to the limited sample size and non-normal distribution of the data, I could not statistically analyze some of the heavy metals concentrations. I found that cadmium, mercury, molybdenum, and lead varied through time but there were no discernible yearly or seasonal trends. The Klondike Ferry area could be susceptible to further adverse effects of development given its elevated concentrations of copper, lead, and zinc. Copper, lead, and zinc concentrations were 41$\pm$2%, 30$\pm$2%, and 46$\pm$1% of their toxic threshold respectively. Even small increases in the accumulation of heavy metals could alter the indigenous invertebrate community and could have a cascading effect up the food chain (Babich et al 1980). A possible source of contamination could be coming from extensive alluvial aquifer mining operations upstream of the Klondike Ferry site. Future monitoring analysis should utilize CEA with biotic and abiotic factors and assess whether mining operations are degrading the downstream environment.

This report is the first I know of to examine water quality index in the areas east of Hinton and west of Athabasca. Our index values were identical to that of Alberta Environmental Monitoring, Evaluation and Reporting Information Service (AEMERA) monitoring program assessment of the river at Athabasca and Hinton (100 and 100 CCMEWQI; aemera.org). There appear to be some sources of iron and copper toxicity in the upper Athabasca River. This study is not the first to find elevated concentrations of copper in the Athabasca. Kelly et al (2010) found copper concentrations of 4.5$\pm$0.24 μg/L in the water next to Fort McMurray. Gueguen et al (2011) also found copper concentrations above guidelines around Whitecourt, Fort McMurray, and Fort Mackay during the mid summer months. Copper and iron are both essential nutrients but toxic to aquatic life in excess (Eisler, 1999; Vuori, 1995). Copper toxicity can act by altering chelating agents and membrane permeability (Eisler, 1999). As a result, copper often changes osmoregulation and causes gill damage in aquatic organisms (Eisler, 1999). The mechanism of action for iron toxicity is dubious and poorly understood (Vuori 1995). It is hypothesized that iron causes membrane damage in the gills and gastrointestinal tract through the generation of hydroxyl-free radicals (Vuori, 1995). Whether iron and copper is tied to fish deformities noted by Indigenous fisherman in the Athabasca River is unknown (Schindler 2013). Future research is needed to examine fish populations and investigate symptoms of copper and iron toxicity around the McLeod River, Freeman River, Plante Creek, and Athabasca River between Plante Creek and Whitecourt.

Oil sands development has been tied to many negative environmental impacts (Kelly 2010; Gueguen, et al 2011; Schindler 2013). What is concerning for the present study is that development may greatly increase the bioavailability of heavy metals (Gueguen, et al 2011). Although most heavy metals are currently considered within acceptable limits within the Athabasca River and tributaries, further monitoring efforts are needed to identify changes in toxic metal concentrations that may have adverse effects on wildlife and humans.

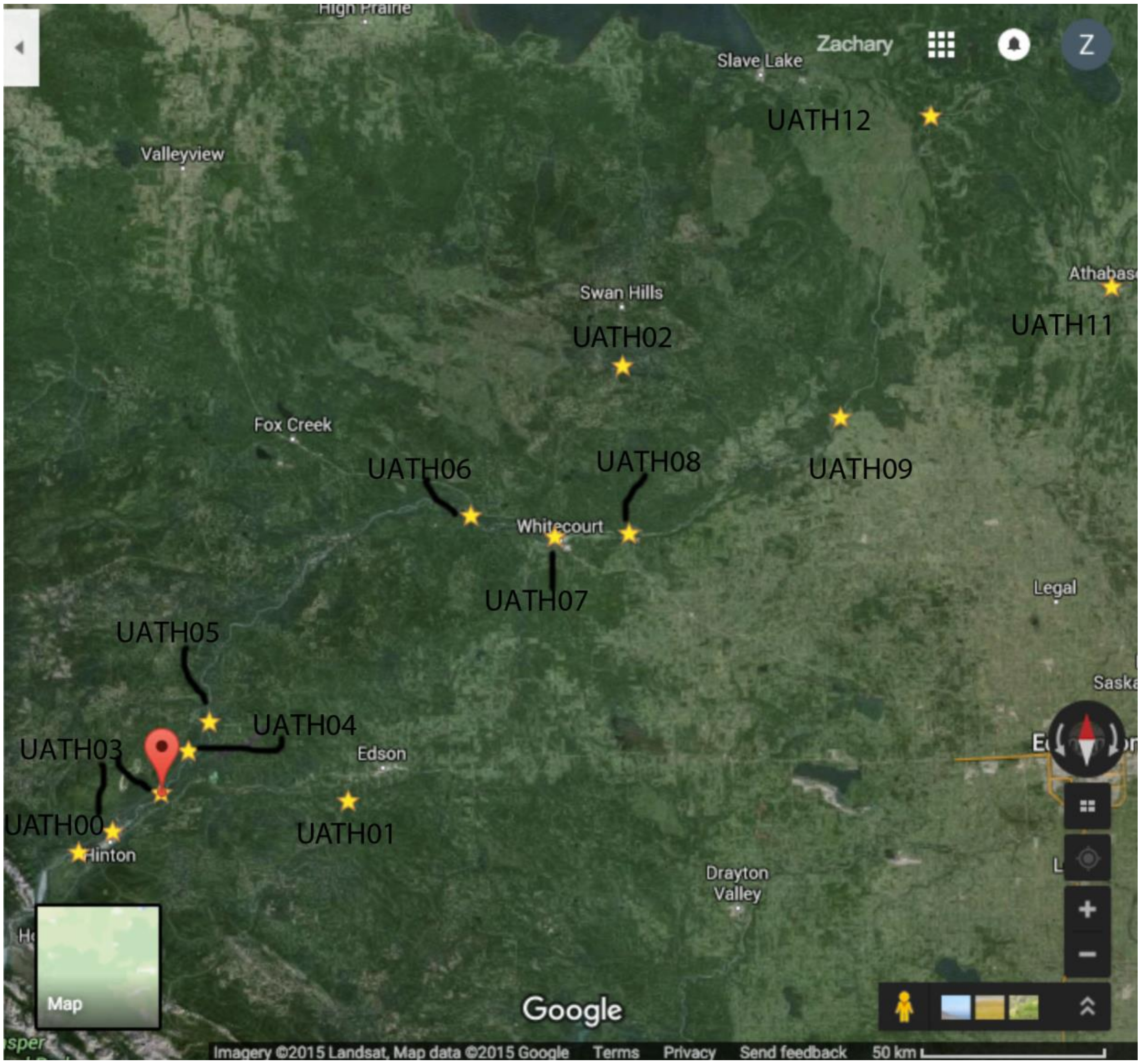

Figure 1. Sampling site map for Upper Athabasca Community Based Monitoring Project UATH00 (53.37608N,117.69993W), UATH01 (53.50478N,116.58469W), UATH02 (54.57385N, 115.40401W), UATH03 (53.42805N,117.56339W; 53.52717N, 117.36138W), UATH04 (53.62769N, 117.24683W), UATH05 (53.70028N, 117.16393W), UATH06 (54.20930N, 116.06324W), UATH07 (54.15216N, 115.70932W), UATH08 (54.15799N, 115.39059W), UATH09 (54.42876N, 114.47855W), UATH11 (55.16894N, 114.03520W), UATH12 (54.72449N, 113.28487W). Image taken from google maps.

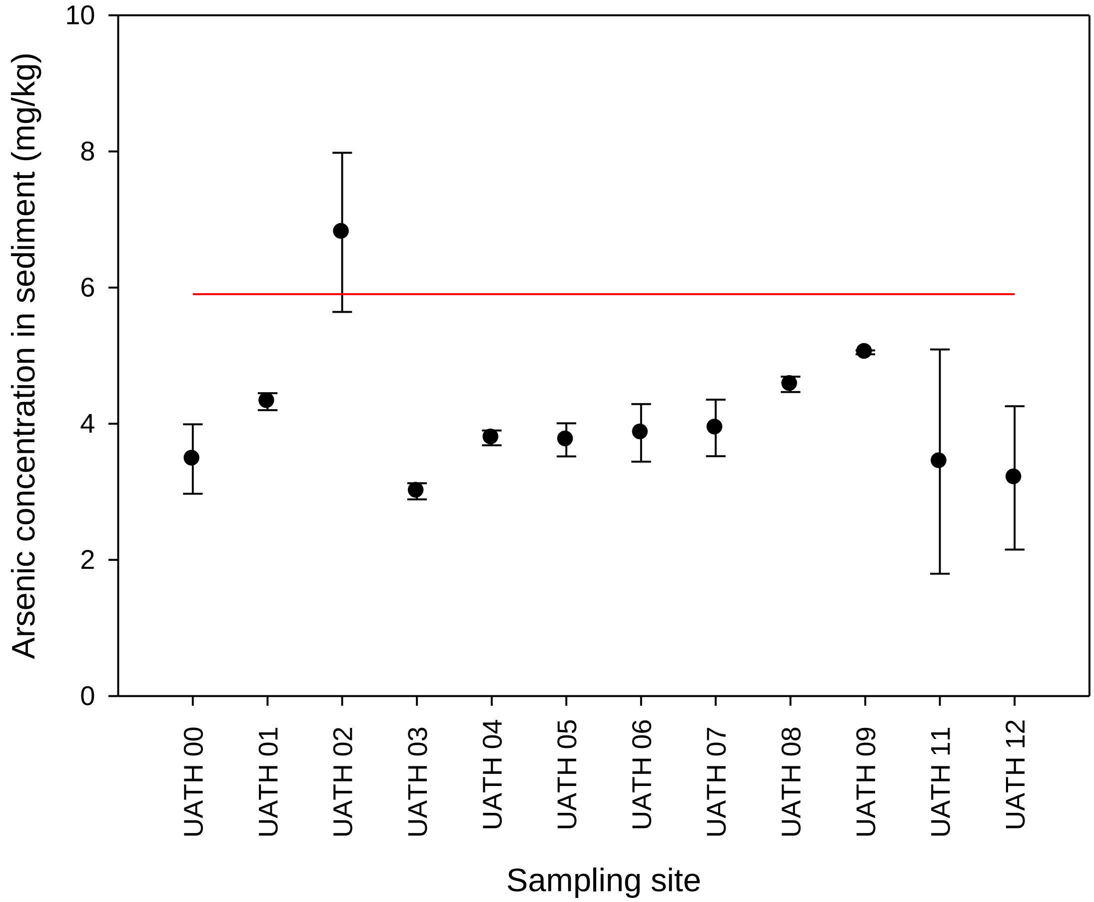

Figure 2. Mean arsenic concentration in sediment in mg/kg shown for Upper Athabasca Community Based Monitoring Project sampling sites along the Athabasca, McLeod and Freeman Rivers. Red line represents CCME water quality guideline for the protection of aquatic life and bars indicate standard error.

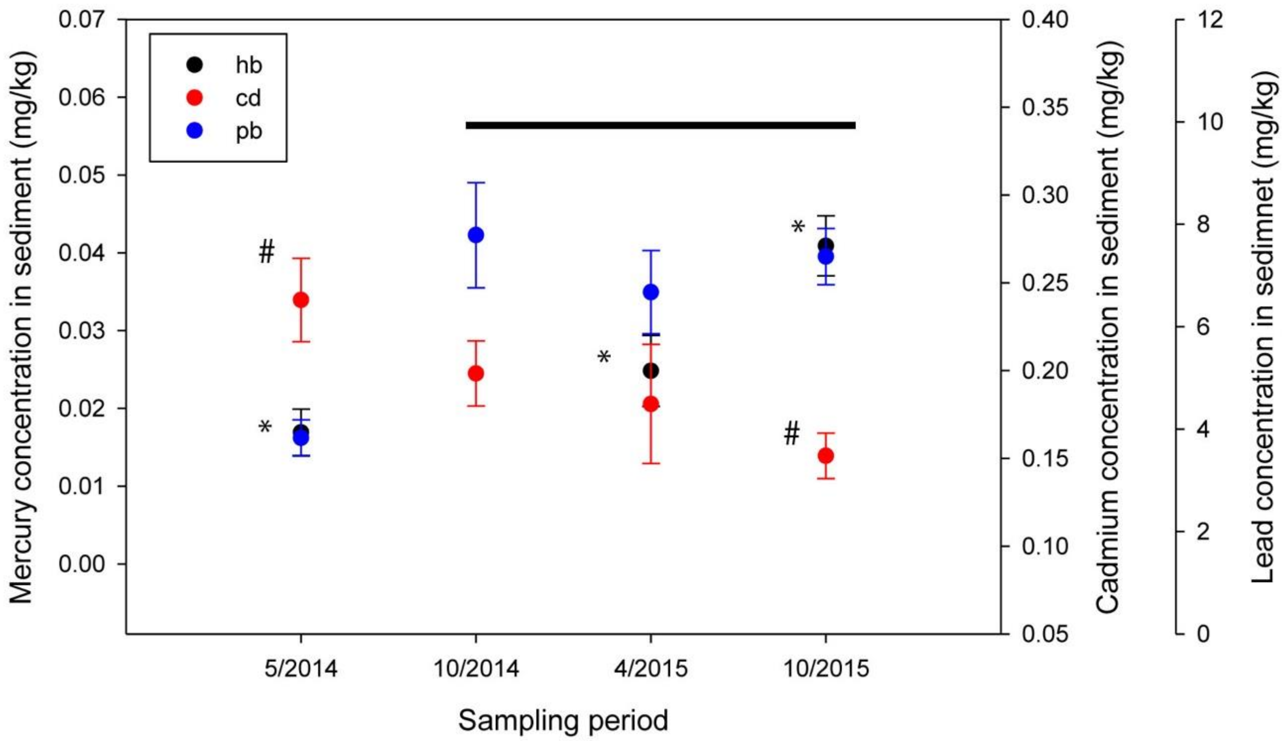

Figure 3. Mean mercury, cadmium, and lead concentrations in sediment over time. Where asterisks denote significances for mercury, hashtags significances for cadmium and the line denote significances difference from May 2014 for lead. Bars indicate standard error.

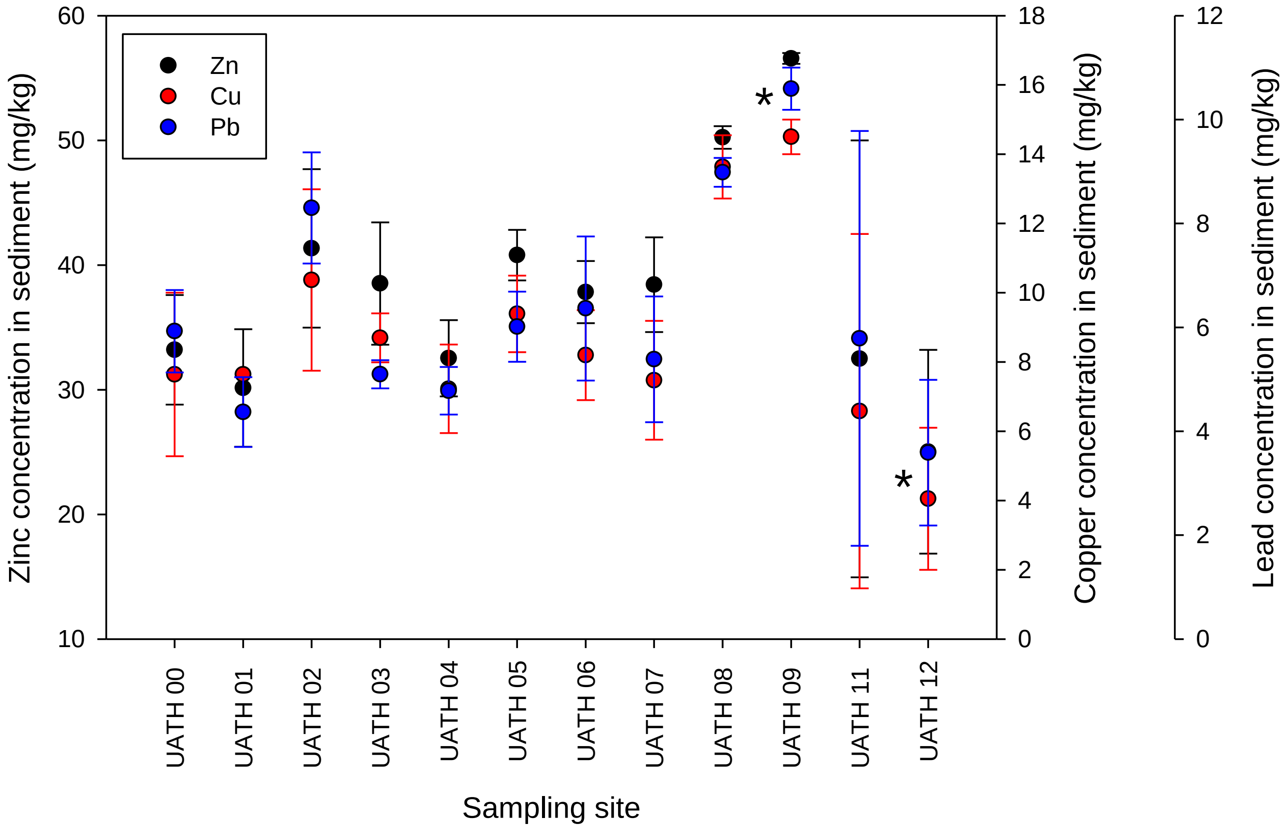

Figure 4. Mean copper, zinc, and lead concentration in sediment in mg/kg shown for Upper Athabasca Community Based Monitoring Project sampling sites along the Athabasca, McLeod and Freeman Rivers. Where asterisks denote Holm-Sidak post hoc significances and bars indicate standard error.

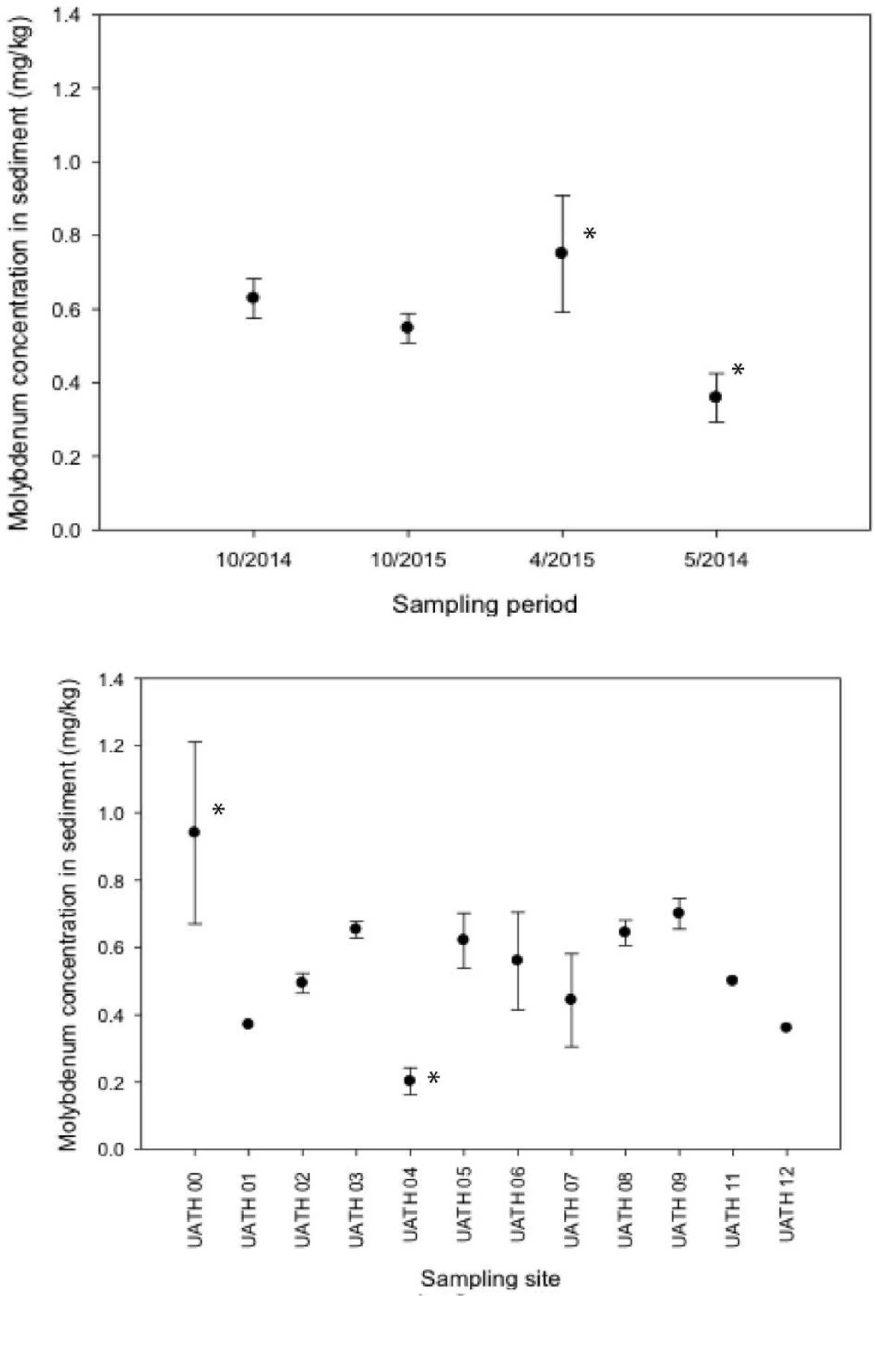

Figure 5. Mean molybdenum concentration in sediment in mg/kg over time in top panel and shown for Upper Athabasca Community Based Monitoring Project sampling sites along Athabasca, McLeod and Freeman Rivers in bottom panel. Where asterisks denote Holm-Sidak post hoc significances and bars indicate standard error.

References

AEP (Alberta Environmental Protection). 1997. Environmentally significant areas of Alberta, volume 2. Prepared by: Sweetgrass Consultants Ltd. Calgary, AB for: Resource Data Division Alberta Environmental Protection Edmonton, AB.

Aemera.org. 2015. River quality stations map. Last visited November 26, 2015 url: http://aemeris.aemera.org/map/

Badich, H., Stotzky, G., Ehrlich, H.L. 1980. Environmental factors that influence the toxicity of heavy metals and gaseous pollutants to microorganisms. CRC Critical Reviews in Microbiology **8** (2): 99-145.

Canadian Council of Ministers of the Environment (CCME). 2001. Canadian Water Quality Guide-lines for the Protection of Aquatic Life: CCME Water Quality Index 1.0. Techical Report, Canadian Council of Ministers of the environment Winnipeg, MB, Canada. Available at: http://www.ccme.ca/sourcetotap/wqi.html

Chapman, D. 1996. Assessments- A guide to use of biota, sediments and water in environmental monitoring- second edition. United Nations Educational, Scientific and Cultural Organization World Health Organization United Nations Environment Programme. Available at: http://www.who.int/water_sanitation_health/resourcesquality/watqualassess.pdf

Chambers, P.A., Dale, A., Scrimgeour, G.J., Bothwell, M.L. 2000. Nutrient enrichment of northern rivers in response to pulp mill and municipal discharge. Journal of Aquatic Ecosystems Stress and Recovery **8**: 53-66.

Dube, M., Johnson, B., Dunn, G., Culp, J., Cash, K., Munkittrick, K., Wong, I., Hedley, K., Booty, W., Lam, D., Resler, O., and Storey, A. 2006. Development of a new approach to cumulative effects assessment: a northern river ecosystem example. Environmental Monitoring and Assessment **113**: 87-115.

Eggleton, J., and Thomas, K.V. 2004. A review of factors affecting the release and bioavalability of contaminants during sediment disturbance events. Environment International **30**: 973-980.

Eisler, R. 1998. Copper hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Geological Survey, Biological Resources Division, Biological Science Report USGS/BRD/BSR—1997-0002. 98 pp.

Gueguen, C., Clarisse, O., Perroud, A., and McDonald, A. 2011. Chemical speciation and partitioning of trace metals (Cd, Co, Cu, Ni, Pb) in lower Athabasca river and its tributaries (Alberta, Canada). Journal of environmental monitoring **13**:2865-2872.

Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., and Nielsen, C.C. 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. PNAS **107** (37): 16178-16183.

Kim, R.Y., Yoon, J.K., Kim, T.S., Yang, J.E., Owens, G., and Kim, K.R. 2015. Bioavailability of heavy metals in soils: definitions and practical implementation—a critical review. Environmental Geochemical Health **37:**1041-1061.

Schindler, D.W. 2013. Geoscience of climate and energy 12. Water quality issues in the oil sands region of the lower Athabasca River, Alberta. Geoscience Canada **40**: 202-214

Squires, A.J., Westbrook, C., and Dubes, M.G. 2009. An approach for assessing cumulative effects in a model river, the Athabasca River basin. Integrated Environmental Assessment and Management **6** (1):119-134.

Vuori, K.M. 1995. Direct and indirect effects of iron on river ecosystems. Annales Zoologici Fennici **32** (3): 317-329.

Walsh, H. 2012. Alberta's Oil Sands development is not responsible- moratorium needed. Keepers of the Athabasca. [Online] last accessed November 13, 2015 http://www.keepersofthewater.ca/files/cumulativeeffects2012.pdf

Wang, S., and Mulligan, C. 2006. Occurrence of arsenic contamination in Canada: Sources, behavior and distribution. Science of the Total Environment **366:** 701-721.

Wrona, F.J., Gummer, W.D., Cash, K.J., and Crutchfield, K. 1996. Northern River Basins Synthesis Report No. 11. Cumulative impacts within the northern river basins. Northern River Basin Study, Edmonton.