In situ measurements of trace metal species in the Athabasca and Mackenzie Rivers using diffusive gradient in thin films (DGT) devices

A Thesis submitted to the Committee of Graduate Studies in Partial Fulfillment of the Requirements for the Degree of Master of Science in the Faculty of Arts and Science.

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Abstract

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This study assesses the bioavailable metal (Cu, Ni, Zn, Pb) species in the Athabasca-Mackenzie watersheds using diffusive gradient in thin films (DGT) devices. Metal toxicity is not only based on the concentration of metal in natural waters, but also on the nature of metal species. Four main forms in aquatic systems are: free ion, inorganic species, DOM bound (humic) species and metal colloidal species. The free ion and inorganic species and very small humic species are known as DGT-labile species and, are considered to be more bioavailable to micro-organisms due to the size and thus may be toxic to microorganisms. In this study, DGT devices were applied to (1) monitor the DGT-labile metal species in the lower Athabasca River and the Mackenzie River watershed and (2) assess the DGT-labile metal concentrations on temporal and spatial scales. In the lower Athabasca River, comparison between the DGT results and the Windermere Humic Acid Model (WHAM) calculation indicated good agreements for all metals when the precipitated iron(III) hydroxide was assumed as an active binding surface. No significant variations in labile species were found over 2003-2012 (RAMP database) despite the development of oil sands. In the Mackenzie River, no significant difference in DGT-labile metal concentrations and DOC concentrations was found in yearly basis 2012-2014. Only DOC was lower in August (6.98 and 3.85 ppm, respectively; p< 0.05) due to dilution from heavy rain events. Spatially, DGT-labile Cu and Ni in the downstream
Mackenzie River were higher than upstream (1.79 and 0.58 ppb for Cu, 1.68 and 0.77 ppb for Ni, 4.06 and 6.91 ppm for DOC; p < 0.05). Overall the in situ measurements of metals constitute a benchmark for future studies in water quality and be helpful in environmental management in Alberta and the Northwest Territories in Canada.
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1.1. Speciation of trace metals

Metal ions in natural waters exist in four main forms: free ion species, dissolved inorganic species, humic complexes (organic species) and inorganic colloidal species. They interact with inorganic and organic molecules and colloidal particles and form different types of complexes which will have different residence time in aquatic ecosystems. For example, free or hydrated ions have longer residence time compared to colloidal species. Metals associated with dissolved organic matter (DOM) are typically less toxic than free and inorganic metal species (Koukal et al., 2003; Tessier and Turner, 1995). In contrast, smaller species (i.e. free metal ions and inorganic metal ions or labile species) are more bioavailable as they can more easily diffuse through cell membranes (Tessier and Turner, 1995). The chemical form of trace metals (i.e. speciation) is important in assessing their toxicity in natural aquatic ecosystems (Forsberg et al., 2006; Ospina-Alvarez et al., 2014). The toxicity of trace metals in natural waters is not only based on their concentration, but also the nature (i.e. speciation) and respective concentrations of the metal species (Magalhaes et al., 2015).

This study will focus on the speciation of four transition metals (Cu, Ni, Zn and Pb) in natural waters. Copper (Cu), nickel (Ni) and zinc (Zn) are important elements for micro-organisms but excess amounts of these metals may induce significant stress and/or death of the organisms (Meylan et al., 2003; Neira et al., 2014). Lead (Pb) is more toxic to aquatic life compared to the former three metals (Antunes and Kreager, 2014).
1.2. Dissolved organic matter in aquatic systems

Dissolved organic matter (DOM) is an important component of aquatic environments and it plays a critical role in biogeochemical processes (Kullberg et al., 1993; Perude and Gjessing, 1990). Structurally, DOM is a complex mixture of aromatic and aliphatic hydrocarbon structures with functional groups like amide, carboxyl, hydroxyl, ketone, etc. (Leenheer and Croué, 2003). The DOM molecular weight ranged from 100’s to >100,000 Da (Leenheer et al., 1989; Leenheer and Croué, 2003; Leenheer et al, 2001). Recently, Guéguen and Cuss (2011) determined the average molecular weight of DOM from the Athabasca River ranged from 1093 to 1557 dalton (Da) with asymmetrical flow field-flow fractionation (AF4) coupled to UV-Visible spectrophotometer. Dissolved organic carbon (DOC) constitutes one of the greatest reservoirs of organic carbon in marine and freshwater systems (Hedges, 1992). About 50% of DOM is composed of DOC (Thurman, 1985). Humic acid (HA) and fulvic acid (FA) are the two main DOM components complexing trace metals in aquatic systems. In this study, the influence of DOM concentration (i.e. DOC) and quality (FA:HA ratio) on metal speciation was assessed.

1.3. Approaches to determine metal speciation

Trace metal speciation can be determined directly using in situ passive technique such as diffusive gradient in thin films (DGT) and by modeling calculation (e.g. Windermere Humic Acid Model; Tipping, 2011). DGT is a time-integrated, passive
sampler technique for in situ monitoring of metal speciation in aquatic environments (Davison and Zhang, 1994). It consists of a polypropylene piston with a layer of 0.45 μm membrane filters for blocking unwanted material like dust and large debris (e.g. twigs and branches), a diffusive hydrogel and a binding gel to accumulate metal ions (Figures 1.1.-1.2). The DGT-accumulated (or DGT-labile) species include free metal ion, metal-inorganic molecules and a small fraction of humic (metal-organic) molecules. DGT has been widely used for in situ metal speciation assessment in freshwaters (Bourgeault et al., 2013; Bruizer et al., 2014; Guéguen et al., 2011; Ohlander et al., 2012). Compared to direct measurements, the diffusion of large complexes (e.g. humic species) is significantly reduced (Balch and Guéguen, 2014; and references therein) whereas the biologically concerned complexes (e.g. free ions and inorganic ion species) are readily accumulated on the DGT samplers. This approach also can minimize the possible sources of contamination as well as potential loss and degradation during sample collection and storage.

The nature of the DGT binding gel allows us to target specific elements. For example, most cations will be measured using Chelex-based DGT (Cusnir et al., 2014; Wu et al., 2014) whereas anionic species will be determined using ferrihydrite-based DGT (Wu et al., 2014; Zhang et al., 1998). Chelex binding gel will be used in this study. Moreover, although short-term (typically three-four days) DGT deployments are not typically affected by formation of biofilm (caused by algal clustering on the surface of DGT windows over time), longer deployments may happen due to site inaccessibility such as forest fire and flood. Pichette et al. (2007) found biofouling
problems for long-term deployment (> 30 days) in very productive waters (i.e. fish farm water).

DGT as a passive sampler based on diffusion requires enough water flow (0.02-0.26 m s\(^{-1}\); Buzier et al, 2014; Gimpel et al, 2001; Uher et al, 2013) to minimize the formation of diffusive boundary layer (DBL). The DBL is the space between the diffusive gel layer and filter membranes. Thick diffusive boundary layers could influence the efficiency of ion transportation and diffusion. Deployment in stagnant waters (flow velocity below 0.02 m s\(^{-1}\)) may result in a low uptake of metal ions to the binding gel. The study of Gimpel et al (2001) also indicated that the water flow velocity of most river and streams exceeds 0.02 cm s\(^{-1}\) which lowers the scrupulosity of DGT deployment in freshwaters.

Metal speciation could be also determined using modeling calculations such as Windermere Humic Aqueous Model (WHAM) VII (Tipping et al, 2011). WHAM assesses the speciation of trace metals based on input parameters such as pH, DOC, dissolved concentrations of major and trace elements, obtained from \textit{in situ} measurements. The model combines several sub-models including humic ion-binding model V (Tipping and Hurley, 1992; Tipping, 1993a, 1993b), models of inorganic solution chemistry, precipitation of aluminum, iron oxyhydroxides, cation-exchange on representative clay, and the adsorption-desorption reactions of fulvic acids (FA) (Tipping and Woof, 1990; Tipping and Woof, 1991). In WHAM calculation, humic concentration is assumed to be 1.2 times that of DOC concentration (Nagai et al, 2007; Aung et al, 2008). The ratio of FA to HA varies from 50:50 to 100:0 (Doig and Liber,
Reasonable agreements (+/- 1 order of magnitude) between DGT measurement and WHAM calculation were typically found in natural waters (Han et al, 2014; Stockdale et al., 2015; Warnken et al, 2009).

1.4. DGT-labile metal

Literature studies (Balistrieri et al., 2012; Han et al., 2013; Odzak et al., 2002; Tonello et al., 2011) showed DGT-labile metal concentrations in Japanese rivers, Lake Greifen (Switzerland) and Silver Bow Creek (Montana, US) ranged from 1 ppb to 12 ppb for Cu, 0.12 ppb to 31 ppb for Ni, 14 ppb to 736 ppb for Zn < 1 ppb for Pb, with DOC ranged from 0.82 ppm to 8.1 ppm and pH ranged from 6.58 to 8.32. The abundance of DGT-labile metal (i.e. ratio DGT-labile concentration / ICP-MS directly measured dissolved concentration) ranged from 1% to 30% for Cu, 30% to 90% for Ni, 40% to 85% for Zn and >1% to 40% for Pb. Of the four metals, both Cu and Pb have low DGT-labile percentages for different reasons. Cu is preferentially associated with DOC whereas Pb is strongly adsorbed by larger surface particles, such as, metal-colloids (Mackenzie, 1980).

Overall, DGT-labile metal concentrations are inversely related to DOC concentration. However, due to the affinity of Pb for inorganic colloids, DOC concentration has a smaller effect on Pb. DGT-labile metal concentrations in the lower Athabasca River in the Athabasca Oil Sand Region (AOSR) (AB) and the Mackenzie River (NWT) were relatively low due to the high DOC concentration.
1.5. Objectives

The Athabasca River drains through the world’s third largest oil sand region, the Athabasca’s oil sand region (AOSR). Previous studies (Kelly et al., 2009; Kelly et al., 2010) showed higher metal concentrations near oil sands development. The potential risks cannot be ignored due to the predominant process of extracting bitumen from oil sand uses large amounts water (Anderson et al., 2012; Loganathan et al., 2015). Bitumen contains high concentrations of trace metals such as V, Cr, Zn, Cu, Pb which may be released from tailing ponds into aquatic system (Asubiojo and Adebiyi, 2014; Kelly et al., 2010). The Mackenzie River Basin located downstream of the AOSR is also experiencing mining explorations, mainly near Fort Good Hope-Norman Wells and near the river mouth. Therefore, regarding the disparity of development of oil sands and mining exploration, this study will focus on the assessment of the trace metal speciation by using DGT devices in the Athabasca and Mackenzie watersheds (Figure 1.3).

In Chapter 2, the in situ assessment results (DGT-labile concentration) and WHAM VII modeled labile metal concentration were compared in the summer months of 2011-2012. The Regional Aquatic Monitoring Program database (www.ramp-alberta.org) was also used to assess the potential changes in metal speciation between 2003 and 2012 due to the exponential growth of oil sands (Energy Alberta, 2008, Canadian Energy Research Institute, 2014). However, the presence of high DOC concentrations in the Athabasca River decreases the concentration of labile metal. Indeed, DOC binds strongly to metals and thus diminishes the availability to aquatic microorganisms (Omanovic et al, 2015).
In Chapter 3, the metal speciation in the Mackenzie River basin on both temporal (2012-2014) and spatial scales (from the Great Slave Lake shores to the Arctic Ocean) was assessed, for the first time, in a region undergoing mining exploration and gas production which are expected to increase in the next decade. This study will constitute a benchmark for policy makers, environmental management and future research.

1.6. Study sites

This study focused on eight sites along the Mackenzie River and three sites in the Lower Athabasca River (Figure 1.3). The Athabasca River covers over 1300 km in Alberta, from southern Alberta where it flows north to the Lake Athabasca and empties into the Great Slave Lake via the Slave River in the Northwest Territories. The Alberta oil sand industry established in 1967 is active in three major oil sand deposits: Peace River Oil Sands, Athabasca Oil Sands and Cold Lake Oil Sands, which are all located in the Athabasca River watershed. In this study, metal speciation was assessed in situ using DGT samplers deployed in the Clearwater River (CLR-1), Mackey River (MAR-1) and Muskeg River (MUR-1). Guéguen et al. (2011) found a rapid decrease in DGT-labile metal concentration due to the high DOC level at Athabasca oil sand region. Also, there was a significant fraction of non DGT-labile species found which was considered as colloids. This study (Chapter 2) determined the significance of the inorganic metal colloidal in metal speciation in aquatic systems.

The input WHAM parameters (pH, temperature, pCO₂, DOC, dissolved
concentrations of major and minor elements) were provided by the Regional Aquatics Monitoring Program (RAMP) (www.ramp-alberta.org), an industry-funded, multi-stakeholder environmental monitoring program designed to monitor water quality in the Athabasca oil sands regions. RAMP was used to assess the potential changes in metal speciation over the last 10 years upon the development of oil sands.

The Mackenzie River (NWT) flows north into the Arctic Ocean but very little is known about metal speciation in the Mackenzie River despite the fact that it is located downstream from the Athabasca oil sand region where potential risks of metal pollution cannot be ignored (Schindler, 2010). Additionally, although there were limited studies showed the gas and mining operations along the Mackenzie River, industries and oil leaking constitute a threat to water quality (Omanovic et al., 2014). In the present study, the assessment of bioavailable trace metal ions in the Mackenzie River watershed was part of a community-based program funded by the Government of the Northwest Territories. This community-based program involves 20 different communities in the NWT, ENR (government of NWT) and other water partners. The main focus is to monitor the water quality (including trace metals) in the Mackenzie River from threats of local, regional and outside-the-NWT sources with simple sampling techniques that can be used by personnel with limited scientific background. The DGT technology was proposed as it is simple, reliable and less prone to contamination during handling, deployment and storage (Davison and Zhang, 2012).
1.7. Significance

This study will be the first to assess metal speciation using DGT and WHAM in the lower Athabasca River, a system under the influence of the rapid expansion of the Athabasca’s oil sands activities. It is also anticipated that this study will be the first study on speciation of dissolved trace metals in the Mackenzie River in the Northwest Territories on both spatial and temporal scales. Results of this study could constitute a benchmark in future study in water sciences and be helpful in environmental management in Alberta and the Northwest Territories in Canada.
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Figure 1.1: Components of DGT devices (Cited from Xu et al, 2013)
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Figure 1.3: Map of study sites in Athabasca River and Mackenzie River with locations of DGT deployments (Green dots: Athabasca River sampling sites (Chapter 2); Red dots: Mackenzie River sampling sites (chapter 3))
Chapter 2. Assessment of dissolved trace metal speciation using diffusive gradient in thin films and WHAM in the lower Athabasca River (Alberta, Canada).

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Chapter 2 Abstract

The diffusive gradient in thin films (DGT) technique was evaluated for the determination of labile metal (Cu, Ni, Zn, Pb) species in three tributaries in the Athabasca’s oil sands region (AOSR). The DGT-labile metal concentrations were evaluated against the modeled concentrations as predicted by the Windermere Humic Acid Model (WHAM VII). The best agreements (92 ± 8%) between DGT-labile and WHAM calculated concentrations were found assuming the formation of FeOx. The agreement was only 70 ± 7% in the presence of inorganic colloidal AlOx and in the absence of any colloids. The influence of dissolved organic matter (DOM) composition (i.e. fulvic:humic ratio) on modeled Cu and Ni speciation showed a negligible effect (<1 to 7%) on labile concentration which is within the acceptable error in DGT measurements. Together these results suggest that a change in DOM composition had limited impacts on modeled free metal (Cu and Ni) ion concentrations. Although the main metal ligand, DOM, varied from 9 to 40 ppm between 2003 and 2012, no significant differences in the abundance of WHAM-modeled labile species were found, suggesting no significant change in mobility and bioavailability of Cu, Ni, Pb and Zn in the three AOSR rivers.
2.1. Introduction

Metal ions exist in different forms in natural waters which impact their toxicity and mobility (e.g. Chakraborty et al., 2014; Frohne et al., 2014; Guéguen et al., 2011). Free metal ion is typically considered as the most bioavailable species and thus the best indicator of its toxicity (Chen and Liao, 2014; Moorthy et al., 2014). Metal speciation can be assessed using several analytical techniques including ion-selective electrodes (Bakker and Pretsch, 1998), voltammetry (Huang et al., 2003; Meylan et al., 2004), Donnan membrane technique (Temminghoff et al., 2000) and diffusive gradients in thin films (DGT) (Davison and Zhang, 2012; Ferreira et al., 2013; Guéguen et al., 2012; Han et al., 2013; Sherwood et al., 2009). Metal speciation can also be assessed using thermodynamic models such as the Windermere Humic Aqueous Model (WHAM; Tipping, 1993a, b). One of the challenges in WHAM modeling has been a reliable description of dissolved organic matter (DOM) in terms of humic:fulvic ratio ranged from 0:100% to 20%:80% (Kalis et al., 2006; Lofts and Tipping, 2000; Unsworth et al., 2006). The presence of inorganic colloids is another variable affecting from chemical speciation (Han et al., 2013). Previous studies (e.g. Guéguen et al., 2011; Han et al., 2013) have shown a good agreement between the DGT-labile concentrations of metals and WHAM modeled values.

Alberta’s oil sands production increased from 1.126 million barrels per day (mbd) in 2006 (Energy Alberta, 2008) to 1.8 mbd in 2012 and is expected to grow to 3.70 mbd by 2020 (Canadian Energy Research Institute, 2014). However, the rapid growth in the Athabasca oil sands region (AOSR) have raised some concerns about the
potential impact on water quality of natural water bodies (Kelly et al., 2009; Kelly et al., 2010; Kirk et al., 2014; Schindler, 2010). Kelly et al. (2010) found that priority pollutants exceeded guidelines for the protection of aquatic life near in snowpack (e.g. Ni) and in streams downstream of highly developed areas (e.g. Cu, Ni, Zn and Pb). Although elevated concentrations of these metals may be toxic, investigation of their dissolved speciation is a prerequisite to evaluating their bioavailability and mobility in natural waters.

In this study, the objectives were to (1) determine the metal speciation (Cu, Ni, Zn and Pb) in the Athabasca River using the DGT technique and WHAM during summers 2011 and 2012 and (2) assess the temporal changes in metal speciation using WHAM and the parameters from oil sands regional aquatic monitoring program (RAMP) over the 2003-2012 period. RAMP is an industry-funded, multi-stakeholder environmental monitoring program focuses the assessment of variables such as pH, suspended solids, conductivity, concentration of major ion and nutrients in the AOSR year round. The effects of DOM composition (i.e. ratio fulvic: humic; FA:HA) on labile Cu and Ni concentrations and the influence of colloidal aluminum and iron oxides were considered in WHAM modeling.

2.2. Methodology and Techniques

2.2.1. Sample collection

Surface water sampling was carried out at the mouth of three tributaries of the Athabasca River (Clearwater River, CLR-1; Muskeg River, MUR-1; Mackay River,
MAR-1) in the AOSR in July and August 2011, and July 2012 (Figure 2.1). Surface water filtration was performed immediately in the field through a 1 m acid-washed Nuclepore filter into a 60 mL acid-washed polypropylene bottle. Similar manipulations were performed with Milli-Q water under field conditions to assess for contaminations.

DGT devices (DGT Research Ltd, UK) were deployed in triplicate directly in the rivers in summer months (July and August) and suspended 10–20 cm below the surface at each study site for 2-3 days (Guéguen et al., 2011). Upon retrieval, the DGTs binding gels were placed in acid-washed centrifuged tubes using acid-washed Teflon tweezers, and stored at 4 °C until analysis. The elution was performed, following Buzier et al. (2014), with 1M triple distilled HNO₃ in a 10'000 class clean room for 24 hours to allow extraction of metals from the resin before analysis. Non-exposed DGT units were used to assess possible contamination during assembling, deployment, retrieval and extraction.

### 2.2.2. Chemical analysis

Metal concentrations (Cu, Ni, Zn, Pb) were measured by high resolution ICP-MS (XSeries II, Thermo; Trent Water Quality Centre) with indium and rhodium used as internal standards. The accuracy of the ICP-MS measurements was assessed using 1643e (National Institute of Standards and Technology, USA) and SLRS-4 reference water (National Research Council, Canada). Dissolved organic carbon (DOC) concentration was measured by high temperature combustion method using a
Shimadzu TOC-VCPH analyzer. The absorption spectral slope ($S_{275-295}$; Helms et al., 2008) was calculated using exponential decay fitting in SigmaPlot. Major cations (Ca, Mg, Na, K) were measured by ICP-OES (Varian Vista MPX). Nutrients ($NO_3^-$, $PO_4^{3-}$, $Si(OH)_4$) were measured by ion chromatography (Dionex). Conductivity, pH and temperature were measured using an AP85 Accumet (Fisher, Canada).

2.2.3. Speciation modeling using WHAM VII

Metal speciation was modeled using WHAM VII (Tipping et al. 2011; Lofts and Tipping, 2011). The input parameters including the dissolved concentrations of major (Ca, Mg, K, Na) and trace metals ions (Cu, Ni, Pb, Zn, Al, Fe), nutrients ($NO_3^-$, $PO_4^{3-}$, $Si(OH)_4$), $P_{CO2}$ ($3.5 \times 10^{-4}$ atm; Tipping et al., 2011) and physical chemical parameters (i.e. pH, temperature) were measured (2011-2012) or provided by RAMP (2003-2012). The RAMP sampling was conducted in Spring and Fall (i.e. September). Only the September monitoring data were used in this study.

The effects of DOM composition on metal speciation were evaluated by changing FA:HA ratio from 1:0 to 9:1 to 3:1 to 1:1 (Kalis et al., 2006; Lofts and Tipping, 2000; Unsworth et al., 2006). The impact on the concentration of $Cu^{+2}$ and $Ni^{+2}$ was monitored because of their great affinity to DOM (Doig and Liber, 2005; Ferreira et al., 2013; Han et al., 2013). The presence of colloidal iron and colloidal aluminum oxides (FeOx and AlOx, respectively) was also assessed as they can compete with humics to bind metals (Tipping et al., 2002). WHAM calculations were conducted under three conditions (Han et al., 2013):
1. Both dissolved iron (III) and aluminum (III) were assumed to be hydrated and would not be able to compete with DOM for binding to trace metals.

2. Dissolved iron (III) was assumed to be hydrated whereas dissolved aluminum (III) would form colloidal aluminum oxide AlOx (1 mole of precipitated aluminum (III) hydroxide will form 61 g of aluminum oxide (Tipping et al., 2011)) to compete with DOM to bind metals.

3. Dissolved iron (III) was assumed to form colloidal iron oxide FeOx at the ratio of 1 mole of precipitated iron (III) hydroxide forming 90 g of iron oxide (Dzombak and Morel, 1990) to compete with DOM in binding metals and ignore the formation of AlOx.

The default solubility constants of iron (III) hydroxide and aluminum (III) hydroxide were those programmed in WHAM VII (Tipping et al., 2011).

Comparisons of thermodynamically-based WHAM concentrations with DGT results were conducted using the maximum dynamic concentration $C_{\text{Dyn max}}$ from DGT measurements (Balistrieri and Blank, 2008; Han et al., 2013; Unsworth et al., 2006):

$$C_{\text{Dyn max}} = C_{\text{free ion}} + C_{\text{inorg}} + \frac{C_{\text{FA}}D_{\text{FA}}}{D_{\text{inorg}}} + \frac{C_{\text{HA}}D_{\text{HA}}}{D_{\text{inorg}}}$$  \hspace{1cm} (1)

$C_{\text{Dyn max}}, C_{\text{free ion}}, C_{\text{inorg}}, C_{\text{FA}}$ and $C_{\text{HA}}$ refer to the concentration of maximum dynamic and concentrations of free metal ion and metal complexes with inorganic ligands and, fulvic and humic acids respectively. $D_{\text{FA}}, D_{\text{HA}}$ and $D_{\text{inorg}}$ are diffusion coefficients of fulvic acid, humic acid and inorganic species, respectively. In the absence of Fe or Al colloids formed (assumption 1), only $C_{\text{free ion}}$ and $C_{\text{inorg}}$ were considered. Equation (1) could be converted to
\[C_{\text{Dyn max}} = f_{\text{free}} C_{\text{total}} + f_{\text{inorg}} C_{\text{total}} + \frac{f_{\text{FA}} C_{\text{total}} D_{\text{FA}}}{D_{\text{inorg}}} + \frac{f_{\text{HA}} C_{\text{total}} D_{\text{HA}}}{D_{\text{inorg}}} \quad (2)\]

where \(f_{\text{free}}, f_{\text{inorg}}, f_{\text{FA}}\) and \(f_{\text{HA}}\) (assuming \(f_{\text{free}} + f_{\text{inorg}} + f_{\text{FA}} + f_{\text{HA}} = 1\)) are the fraction of each species modeled using WHAM VII and \(C_{\text{total}}\) is the dissolved metal concentration. \(D_{\text{inorg}}\) was provided by DGT research (http://www.dgtresearch.com) whereas \(D_{\text{FA}}\) and \(D_{\text{HA}}\) were set at \(1.13 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}\) and \(0.58 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}\), respectively (Zhang, 2004). In the presence of colloidal species (i.e. aluminum or iron oxides), equation (2) can be rearranged as,

\[C_{\text{Dyn max}} = f_{\text{free}} C_{\text{total}} + f_{\text{inorg}} C_{\text{total}} + \frac{f_{\text{FA}} C_{\text{total}} D_{\text{FA}}}{D_{\text{inorg}}} + \frac{f_{\text{HA}} C_{\text{total}} D_{\text{HA}}}{D_{\text{inorg}}} + \frac{f_{\text{colloid}} C_{\text{total}} D_{\text{colloid}}}{D_{\text{inorg}}} \quad (3)\]

where \(f_{\text{colloid}}\) and \(D_{\text{colloid}}\) are the fraction of colloidal species and diffusion coefficient of the species with \(D_{\text{colloid}} \sim 0.1 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}\) (Sherwood et al., 2009). The comparison was made between negative log of maximum dynamic metal concentration (pDyn max) and negative log of DGT-labile concentration (pDGT-labile) under the above three assumptions (i.e. no colloids, in the presence of iron or aluminum oxides).

2.3. Results and Discussion

2.3.1. Dissolved organic matter

The dissolved organic carbon (DOC) concentration (Table 2.1) ranged from 17.2 to 37.5 ppm in the summer months of 2011 and 2012 across the three sites, congruent with the 10-year RAMP average (22 ± 9 ppm) and previous boreal studies (Millot et al., 2003). The DOC concentrations at CLR-1 (15.6 ± 6.9 ppm) were lower than at the
other two sites whereas the highest mean DOC concentration was in MAR-1 during 2012-2014.

The spectral slope parameter, $S_{275-295}$, an indicator of molecular weight of the DOC (Guéguen and Cuss, 2011; Helms et al., 2008), decreased from 0.0154 -0.0161 nm$^{-1}$ at MUR-1 to 0.0134-0.0143 nm$^{-1}$ at CLR-1 and 0.0136-0.0149 at MAR-1. The decrease in $S_{275-295}$ between MUR-1 and CLR-1 and MAR-1 suggests an increase in molecular weight (MW) and terrestrial influence (Helms et al., 2008). DOM found in CLR-1 and MAR-1 showed similar $S_{275-295}$ values, suggesting comparable MW and source.

2.3.2. Dissolved and DGT-labile concentrations

Metal concentrations in DGT blanks ($n=2-5$) were under the analytical detection limit (ppt range), suggesting negligible metal contamination during sampling and storage. Metal and DOC concentrations were relatively variable between sites in the summers of 2011-2012 (Table 2.1). The dissolved metal (Cu, Ni, Zn, Pb) concentrations found were comparable with those reported by RAMP (http://www.ramp-alberta.org/RAMP.aspx). Results showed that DGT-labile Cu concentrations ranged from 0.09 to 0.51 ppb, representing 0.074 to 0.18% of dissolved Cu concentrations (Table 2.2). The DGT-labile Ni concentration ranged from 0.187 to 0.447 ppb in 2011-2012, representing from 49.2 to 78% of Ni dissolved concentrations. DGT-labile Zn concentrations ranged from 0.49 to 3.21 ppb whereas DGT-labile Pb concentrations ranged from 0.0001 to 0.05 ppb. Comparable DGT
labile fractions were found for Zn and Pb (9.56-25.5 \% and 12.5-37.2 \%, respectively). DGT-labile concentrations in this study were comparable to previous studies in the Athabasca River (Guéguen et al., 2001) and other worldwide rivers (Dragun et al., 2008; Han et al., 2013; Ponton and Hare, 2009).

2.3.3. Influence of DOM composition on metal speciation

The significant difference in S_{275-295} (Table 2.1) suggests MW differences in DOM between sites. According to Zhang and Giddings (1987), FA and HA as main components of DOM can be distinguished from each other using Flow Field-Flow Fractionation based on MW. Usually, MW of FAs are about 800 Da whereas HAs are slightly larger, 1500-3000Da. An increase in MW of DOM would elevate HA and reduce the FA:HA ratio. On the other hand, DOM accumulate free metal ion to decrease the concentration of free metal in natural waters. The effects of FA:HA ratio on free metal concentrations were assessed (Figure 2.2). The average pCu (i.e., - log[Cu^{2+}]) increased by 0.32\% when the FA:HA ratio varied from 1:0 to 1:1 (Figure 2.2A). This increase in pCu is consistent with the difference in the formation constant (logK) value between FA and HA (2.16 vs 2.38, respectively; Tipping et al., 2011) as an increase in HA increased pCu. However, the effects on Cu^{2+} concentration were very small (0.32\% or 0.002 ppb) as > 99\% of Cu was bound to DOM. Similarly, the average Ni^{2+} concentration decreased by 5.68\% (3.23 ppb) while HA concentrations increased from 0 to 50\% of DOM (Figure 2.2B), congruent with an increase in the logK value for Ni-HA (1.6 vs 1.43; Tipping et al., 2011). Although the impact of the
FA:HA ratio on Ni speciation was greater relative to Cu speciation, the change in the FA: HA ratio on free metal concentrations was within the 10% experimental error of DGTs (Kreuzeder et al., 2015). The increase in HA has limited effect on Cu and Ni free ion concentrations, suggesting that the change in humic contribution (i.e. $S_{275-295}$; Table 2.1) has limited impact on metal speciation. The following discussion will be based on FA:HA ratios of 9:1 (Dwane and Tipping, 1988).

### 2.3.4. Comparison between WHAM VII calculations and DGT measurements

The WHAM-based concentrations were compared to those measured using DGT under the three assumptions (i.e. no colloids formed, FeOx formed and AlOx formed) (Figure 2.3). In the absence of inorganic colloid formation, the ratio $pC_{\text{Dyn max}} : pC_{\text{DGT}}$ was close to 1 for Cu and Pb (1.18 ± 0.52 and 0.74 ± 0.13, respectively) whereas significantly overestimated $C_{\text{Dyn max}}$ were found for Ni ($pC_{\text{Dyn max}} : pC_{\text{DGT}} = 0.05 ± 0.25$) (Figure 2.3A). Similar results have been found in previous studies (Han et al., 2013; Unsworth et al., 2006; Warnken et al., 2009), possibly due to slow diffusion of DOM (Balch and Guéguen, 2014; Furukawa and Takahashi, 2008; Zhang and Davison, 2001) and dissociation of humic complexes (Fasfous et al., 2004). Zn concentrations were overestimated in WHAM calculation but the difference was found to be less than the typical error associated with DGT measurement for Zn (Balistrieri and Blank, 2008; Han et al., 2013).

Under the assumption of competition between dissolved iron(III) and DOM binding sites for trace metals, and precipitation of iron(III) hydroxide (Figure 2.3B),
the root mean square error (RMSE) was significantly improved for Pb compared to the case where no inorganic oxides were formed (0.23 vs. 0.72). Previous studies (Kaste et al., 2006; Hassellov and Von der Kammer, 2008) found colloidal FeOx was the main vector to remobilize and transport Pb from the atmosphere and natural rivers. The competition with FeOx binding did not affect the predicted Cu and Zn speciation.

Under the assumption of colloidal AlOx competing with humic substances for metal binding, the average $pC_{\text{Dyn max}}:pC_{\text{DGT}}$ ratios were comparable to those found in the absence of inorganic colloid formation (Figures 2.3A,C). The measured dissolved Al concentrations at all sites were quite low compared to dissolved Fe concentrations (3.9-33.1 vs 276-775 ppb; Table 2.1), limiting the formation of AlOx and thus its competition with humic substances. A study in Japanese rivers confirmed the lack of AlOx influence on free/labile metal concentrations (Han et al., 2013). Similarly, Dong et al. (2001) found the contribution of colloidal AlOx to Pb adsorption was insignificant compared to that of colloidal FeOx. As a result, even though dissolved Al (III) can be considered as an essential critical parameter in metal speciation (Han et al., 2013), the $C_{\text{Dyn max}}:C_{\text{DGT}}$ ratios remained unchanged relative to the comparison of no colloids. Also, the best agreement under colloidal AlOx competing with humic substances for metal binding was found in Cu (RMSE 0.27; Table 2.3).

2.3.5. Modeling metal concentration in rivers on a temporal scale by WHAM VII

2.3.5.1. DGT vs RAMP-based speciation in 2011 and 2012

RAMP-based metal speciation in September 2011 and 2012 was modeled in WHAM
and compared to the concentration of DGT measurements. The formation of FeOx was only considered here as it was shown to better predict free/labile metal concentrations (Figure 2.3). Due to the high possibility of contamination, comparison of Zn was not as good but within experimental error (i.e. 10%). Acceptable agreements were found between RAMP-modeled and DGT concentrations for Cu, Ni and Pb when FeOx was considered (pRAMP:pC$_{DGT}$ 1.05 ± 0.23, 1.39 ± 0.25 and 0.80 ± 0.12 for Cu, Ni and Pb, respectively), reinforcing the robustness of the DGT techniques (Figure 2.4).

### 2.3.5.2. Temporal change in metal speciation

The temporal changes in free ion and inorganic and organic complexes were modeled between 2003 and 2012 at the three study sites using yearly RAMP monitoring database (Figures 2.5-2.6). No significant difference was found between no inorganic colloids (AlOx or FeOx) formed (not shown) and AlOx formed (Figure 2.5) due to low Al concentration (0.06 – 1.7 ppb). The largest humic complex contribution was found for Cu followed by Pb (except when colloidal FeOx are formed), Zn and Ni, consistent with the decreasing affinity for FA and HA complexation (Tipping et al., 2011).

In the presence of AlOx (Figure 2.5) or FeOx (Figure 2.6), humic complexes represented > 99% of Cu speciation resulting in less than 1% of Cu as free and inorganic species, consistent with the DGT results in 2011-2012 (Table 2.2). Humic complexes of Ni, Zn and Pb fluctuated by 26.5, 6.1 and 10.7 %, respectively, due to
the inter-annual variation in DOC concentration (Figure 2.7) found between 2003 and 2012. The increase (slopes=0.76 and 0.72) in DOC concentration in CLR-1 and MAR-1 resulted in decreased labile (free ion and inorganic) metal concentrations. The dissolved concentration of Al was very low in both rivers between 2003 and 2012 (Table 2.1), consistent with the negligible effect of AlOx complexes on metal speciation. Under the assumption of FeOx formation, the contribution of FeOx-metal species was significant in Ni, Zn and Pb speciation (Figure 2.6) due to high Fe concentration (Table 2.1).

Ni speciation was controlled by humic complexes due to the presence of high DOC concentration (13-32 mg/L) under the assumptions of the presence of colloidal AlOx (from 20% to 80%; Figure 2.5). Under the assumption of the presence of colloidal FeOx (from 20% to 80%; Figure 2.6), humic species were the dominant forms followed by the inorganic complexes (from 15% - 70% in the presence of AlOx or FeOx; Figures 2.5 and 2.6) and free metal ions (from 1% to 20 % in both the presence of AlOx and the presence of FeOx; Figures 2.5 and 2.6). AlOx bound Ni complexes were negligible at all sites in 2003-2012. The 20% decrease in free/labile Ni species found in 2010 and 2012 relative to the average free/labile Ni ion species was associated with the 2-fold increase in DOC in 2010 and 2012.

Most of the Zn speciation was associated with humic complexes with AlOx forms (89 ± 4.2% in CLR-1, 90.1 ± 3.5% in MAR-1 and 79 ± 6.7% in MUR-1; Table 2.4) and FeOx forms (82 ± 4.7% in CLR-1, 87 ± 3.8% in MAR-1 and 77 ± 5.7% in MUR-1; Table 2.4) and only about 12% to 20% (Table 2.4) of Zn across the three sites
(CLR-1, MAR-1, MUR-1) were free and inorganic metal species under both scenarios.

Pb speciation with AlOx forms was dominated by humic species (89 ± 3.8% in CLR-1, 86 ± 7% in MAR-1 and 68 ± 11% in MUR-1; Table 2.4) whereas inorganic Pb species (9.7 ± 4.1% in CLR-1, 13 ± 6.9% in MAR-1 and 32 ± 11% in MUR-1; Table 2.4) bound the rest of Pb. Less than 1% of Pb was free or associated with colloidal AlOx species. In 2012, approximately 5% Pb complexes were in colloidal AlOx form because the concentration of Al in 2012 was at least 10 times higher than other years, and the extremely high amount of Al (125 ppb) formed large amounts of colloidal aluminum oxide that had to compete with DOM binding sites. The distribution of Pb speciation at each river site varied similarly to speciation of Zn and Ni. A significant different distribution pattern of Pb speciation was found with the presence of FeOx.

Up to approximately 96% of Pb (96 ± 1.4% in CLR-1, 96 ± 2% in MAR-1 and 88 ± 22% in MUR-1; Table 2.4) was colloidal iron oxide instead of humic species, and the remaining Pb was humic species (3.9 ± 1.4% in CLR-1, 3.8 ± 2.1% in MAR-1 and 7.6 ± 12% in MUR-1; Table 2.4) and inorganic species (0.4 ± 0.2% in CLR-1, 0.51 ± 0.3% in MAR-1 and 4.8 ± 9.2% in MUR-1; Table 2.4). The reasons for Pb being associated with colloidal FeOx are the high concentration of Fe (III) detected and the large amount of colloidal iron oxide formed to compete with binding sites on DOM. Pb is strongly adsorbed by metal-colloidal species (Mackenzie, 1980) to lessen association of Pb with humic species. The influence of increments in DOC concentration exists in Pb speciation when considering colloidal iron oxide.
assumption as well. High DOC concentrations raise the percentage of metal that binds to humic species and lower colloidal iron oxide formation. Consequently, colloidal FeOx species in Cu, Ni and Zn were only 4% or less, and humic species dominated in metal (Cu, Ni, Zn) speciation. Moreover, humic binding Pb species in 2011 were relatively high because Fe concentrations were low and could not compete with humic substance, so humic substances bound most of the metal ions. Therefore, humic Pb species in 2011 under colloidal iron oxide assumption were higher than in other years.

Together the results suggest DGT-labile metal concentrations over 2003-2012 were acceptable under the Water Quality for the Protection of Aquatic Life guidelines (2.36-3.34 ppb, 95.58 - 130.07 ppb for Ni, 30 ppb for Zn, and 3.18 - 5.53 ppb for Pb as CaCO₃ ranged 100-150 ppm, respectively).

2.4. Conclusion

Metals (Ni, Cu, Zn, Pb) speciation were assessed in July 2011, August 2011 and July 2012 at 3 AOSR sites using DGT devices. The abundance of DGT-labile species increased from Cu (0.07% to 0.18%) to Zn (9.56%-25.5%) to Pb (12.5% to 37.2%) and Ni (49.2% to 78%). Acceptable agreements were found between WHAM calculation and DGT measurements. Among the three conditions, the DGT-labile concentrations of Cu, Ni, Zn and Pb were best predicted assuming the presence of FeOx. In the long-term monitoring assessment (2003-2012), no significant variation in metal speciation was found suggesting no noticeable impact on their bioavailability over the study period.
Acknowledgment

Y. Z. is grateful to all the staff in ESC A116 laboratory in Trent University for their cooperation and laboratory technician A. Perroud for all his help during field work in 2011-2012.
Reference


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Guéguen, C.; Clarisse, O.; Perround, A.; McDonald, A. 2011. Chemical


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Table 2.1: Average values and ranges for spectral slope $S_{275-295}$, DOC and total dissolved metal concentrations measured in this study (Summers 2011-2012). The values reported by RAMP (2002-2012) are in parenthesis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CLR-1</th>
<th>MAR-1</th>
<th>MUR-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{275-295}$ [nm$^{-1}$]</td>
<td>0.0134-0.0143</td>
<td>0.0136-0.0149</td>
<td>0.0154-0.0161</td>
</tr>
<tr>
<td>DOC [ppm]</td>
<td>19.3±3.0 (15.6±6.9)</td>
<td>17.2-23.1</td>
<td>36.1±2(31.8±4.9)</td>
</tr>
<tr>
<td>Cu [ppb]</td>
<td>0.73±0.24(0.69±0.2)</td>
<td>0.46-0.91(0.48-0.9)</td>
<td>0.89±0.5(0.67±0.2)</td>
</tr>
<tr>
<td>Ni [ppb]</td>
<td>1.36±0.31 (0.41±0.44)</td>
<td>1.14-1.57(0.10-0.72)</td>
<td>1.51±0.17(0.44±0.02)</td>
</tr>
<tr>
<td>Zn [ppb]</td>
<td>2.16±1.8 (0.5±0)</td>
<td>0.86-4.22(0.501)</td>
<td>3.33±1.45(0.84±0.1)</td>
</tr>
<tr>
<td>Pb [ppb]</td>
<td>0.08±0(0.13±0.04)</td>
<td>0.07-0.08(0.1-0.15)</td>
<td>0.12±0.04(0.11±0.1)</td>
</tr>
<tr>
<td>Al [ppb]</td>
<td>15.1±8.3(65.75±83.8)</td>
<td>8.4-24.3(6.5-124)</td>
<td>23±9.9(32.15±0.01)</td>
</tr>
<tr>
<td>Fe [ppb]</td>
<td>401±210 (296±223)</td>
<td>276-644(139-454)</td>
<td>543±128(692)</td>
</tr>
</tbody>
</table>
Table 2.2: WHAM modeled **average values** and **ranges** for DGT-labile metal concentrations and percentage over 2011-2012.

<table>
<thead>
<tr>
<th>Site</th>
<th>Cu [ppb]</th>
<th>Cu DGT-labile %</th>
<th>Ni [ppb]</th>
<th>Ni DGT-labile %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(No colloids &amp; AlOx)</td>
<td>FeOx</td>
<td>(No colloids &amp; AlOx)</td>
<td>FeOx</td>
</tr>
<tr>
<td>CLR-1</td>
<td>0.17(+/-0.09)</td>
<td>0.105(+/-0.027)</td>
<td>0.1(+/-0.027)</td>
<td>0.31(+/-0.12)</td>
</tr>
<tr>
<td>MAR_1</td>
<td>0.14(+/-0.11)</td>
<td>0.074(+/-0.007)</td>
<td>0.07(+/-0.0074)</td>
<td>0.28(+/-0.11)</td>
</tr>
<tr>
<td>MUR-1</td>
<td>0.33(+/-0.18)</td>
<td>0.18(+/-0.064)</td>
<td>0.18(+/-0.064)</td>
<td>0.33(+/-0.08)</td>
</tr>
<tr>
<td>CLR</td>
<td>0.09-0.26</td>
<td>0.07-0.12</td>
<td>0.074-0.122</td>
<td>0.22-0.44</td>
</tr>
<tr>
<td>MAR</td>
<td>0.07-0.27</td>
<td>0.07-0.08</td>
<td>0.068-0.082</td>
<td>0.18-0.4</td>
</tr>
<tr>
<td>MUR</td>
<td>0.14-0.51</td>
<td>0.11-0.23</td>
<td>0.111-0.232</td>
<td>0.24-0.41</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>Zn [ppb]</th>
<th>Zn DGT-labile %</th>
<th>Pb [ppb]</th>
<th>Pb DGT-labile %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(No colloids &amp; AlOx)</td>
<td>FeOx</td>
<td>(No colloids &amp; AlOx)</td>
<td>FeOx</td>
</tr>
<tr>
<td>CLR-1</td>
<td>1.28(+/-1.11)</td>
<td>12.4(+/-2.27)</td>
<td>12.31(+/-2.25)</td>
<td>0.0054(+/-0.003)</td>
</tr>
<tr>
<td>MAR_1</td>
<td>3.21</td>
<td>9.56(+/-0.2)</td>
<td>9.52(+/-0.2)</td>
<td>0.0011(+/-0.0017)</td>
</tr>
<tr>
<td>MUR-1</td>
<td>1.9(+/-0.36)</td>
<td>25.5(+/-8.23)</td>
<td>25.3(+/-8.11)</td>
<td>0.0345(+/-0.0248)</td>
</tr>
<tr>
<td>CLR</td>
<td>0.5-2.06</td>
<td>9.8-14.2</td>
<td>9.8-14.1</td>
<td>0.002-0.007</td>
</tr>
<tr>
<td>MAR</td>
<td>0-3.21</td>
<td>9.4-9.8</td>
<td>9.3-9.7</td>
<td>0.0001-0.003</td>
</tr>
<tr>
<td>MUR</td>
<td>0-2.15</td>
<td>16.6-32.8</td>
<td>16.5-32.4</td>
<td>0.006-0.05</td>
</tr>
</tbody>
</table>
Table 2.3: Root Mean Square Error (RMSE) of WHAM calculated labile-metal (Cu, Ni, Zn, Pb) concentration under the three assumptions (without any colloids, FeOx forms, AlOx Forms)

<table>
<thead>
<tr>
<th></th>
<th>Without Colloid</th>
<th>FeOx Forms</th>
<th>AlOx Forms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.2735</td>
<td>0.2737</td>
<td>0.2735</td>
</tr>
<tr>
<td>Ni</td>
<td>0.5709</td>
<td>0.5698</td>
<td>0.5710</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5757</td>
<td>0.5774</td>
<td>0.5757</td>
</tr>
<tr>
<td>Pb</td>
<td>0.7170</td>
<td>0.2299</td>
<td>0.6716939</td>
</tr>
</tbody>
</table>
Table 2.4: Average percentage values and standard deviation from WHAM for metal (Ni, Cu, Zn, Pb) speciation on a temporal scale (Summers 2003-2012) under two assumptions: dissolved AlO\textsubscript{x} or FeO\textsubscript{x} forms.

<table>
<thead>
<tr>
<th>Dissolved forms</th>
<th>CLR-1</th>
<th>MAR_1</th>
<th>MUR-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage of total concentration</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
</tr>
<tr>
<td>Free metal ion</td>
<td>15+/−4.2%</td>
<td>6.9E+/−3+/−5.8E−3%</td>
<td>8.4+/−2.7%</td>
</tr>
<tr>
<td>Inorganic metal species</td>
<td>30+/−7.7%</td>
<td>0.14+/−0.05%</td>
<td>4.4+/−1.3%</td>
</tr>
<tr>
<td>Humic species</td>
<td>52+/−9.1%</td>
<td>99.8+/−0.06%</td>
<td>85+/−4.2%</td>
</tr>
<tr>
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<td>6.4E+/−3+/−0.19%</td>
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</tr>
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<td>0.76+/−0.3%</td>
<td>3.9+/−1.3%</td>
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<tr>
<td>Metal-colloidal FeO\textsubscript{x}</td>
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<td>0.76+/−0.3%</td>
<td>3.9+/−1.3%</td>
</tr>
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Figure 2.1: Sampling location and RAMP sites (Red shadow: Athabasca oil sand region, Arrows: Direction of water flow)
Figure 2.2: Influence of FA:HA ratio (Purple, 1:0; blue, 9:1; red, 7.5:2.5 (or 3:1); green, 5:5 (or 1:1)) on (A) Cu$^{2+}$ and (B) Ni$^{2+}$ concentrations in the lower Athabasca River.
Figure 2.3: Free/labile metal concentration (●Cu, ▲Ni, ◆Zn, ■Pb) (μM) assuming (A) no colloidal formed, (B) formation of colloidal FeOx and (C) formation of colloidal AlOx assuming a FA:HA ratio of 9:1. (Dashed line: +/-1 unit deviation lines.) Each dot represents one set of DGT measurement/WHAM calculation.

(A)  (B)  (C)
Figure 2.4: Free/labile RAMP metal concentration (●Cu, ▲Ni, ◆Zn, ■Pb) (uM) assuming formation of colloidal FeOx assuming a FA:HA ratio of 9:1. Each dot represents one set of DGT measurement/WHAM calculation.
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Chapter 3. Assessing labile metal concentrations in the Mackenzie River (NWT, Canada) using diffusive gradient in thin film (DGT).

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Chapter 3 Abstract

The diffusive gradient in thin films (DGT) technique was applied to assess the labile (mainly free ions and inorganic molecules) metal concentrations (of Cu, Ni, Zn and Pb) at 8 sites in the Mackenzie River basin (Northwest Territories, Canada) in the summer months (July to September) of 2012-2014 when ice melted. The in situ DGT-labile metal concentrations (1.37 ± 1.61 ppb, 1.35 ± 1.77 ppb, 4.04 ± 4.22 ppb and 0.06 ± 0.11 ppb, for Cu, Ni, Zn and Pb respectively) were at lower end of the range of previous studies, suggesting the pristine status of the Mackenzie River. In the spatial assessment of labile metal, the 8 sites were grouped in two regions: Great Slave Lake (sites #1-3) and Mackenzie River regions (sites #4-8). A strong latitudinal gradient in DGT-labile Cu, Ni and DOC concentrations was found between the two regions. On the temporal scale, no significant differences (P<0.05) in labile metal concentrations was found in either monthly (July-Sept) or yearly (2012-2014) basis. The only significant difference (p>0.05) was found in DOC concentrations in monthly basis. The lower DOC concentrations led to higher DGT-labile metal levels, confirming that DOC plays a significant role in aquatic systems.
3.1. Introduction

Toxicity of trace metals is not only based on the total concentration of the metals but also their chemical species (i.e., speciation). Among the dissolved metal species, the labile species (i.e. free ion species and inorganic species) are potentially more bioavailable and toxic than complexed species (Bailey et al., 2002; Chen and Liao, 2014; Moorthy et al, 2014) and therefore of primary concern for ecotoxicologists and environmental managers. Consequently, direct determination of metal speciation constitutes a priority in the assessment of risk associated with metal contamination in aquatic systems.

The diffusive gradients in thin films (DGT) (Davison and Zhang, 1994) is a time-integrated, passive sampler technique for in situ monitoring of labile metal species concentrations in aquatic environments (e.g. Balistrieri et al., 2012; Dragun et al., 2008; De Souza et al., 2014; Guéguen et al., 2011). Numerous studies have shown that DGT is an efficient tool for measuring in situ labile metal species, except in waters with strong biofouling potential (Pichette et al., 2007; Uher et al., 2012). This simple technology is ideal for citizen science project as the risks of contamination are very limited compared to water sampling for metal speciation.

The Mackenzie River, the longest river in Canada, flows north to the Arctic Ocean with a yearly average discharge of 325 km$^3$ per year (Environment Canada). The potential risk of metal contamination in the Mackenzie River cannot be ignored due to the intensive surface mining activities (e.g. 1.8 million barrels per day (mbd) in 2012 and expecting 3.7mbd in 2020 (Canadian Energy Research Institute, 2014)) occurring upstream in the Great Slave Lake (Caumette et al., 2011; Caumette et al.,
2012) and in the Alberta Oil Sands regions (e.g. Guéguen et al., 2011; Kelly et al., 2010; Kirk et al., 2014).

The objective of this study was to assess labile (i.e. free ion species, inorganic species and kinetically labile DOM bound species) concentrations of Cu, Ni, Zn and Pb using DGT at eight sites along the Mackenzie River (Northwest Territories, NWT) on both temporal and spatial scales during the summer months of 2012-2014. Although most DGT units were deployed for 2-3 days as recommended (Guéguen et al., 2011; Zhang et al., 1998), some units were retrieved after 3-4 weeks due to forest fires or other logistical issues. These latter units were impacted by biofouling on filters. If DGTs are to be used in conjunction with other passive samplers such as semipermeable membrane devices, longer deployment time (i.e. one month) would be required (O’Toole et al., 2006). There is little published data of long-term DGT deployment (i.e. 1 month) on the DGT performance in DOC-rich waters. The results will constitute a benchmark for future studies in the Mackenzie River basin where exploration of oil, gas and mineral deposits and thus potential ecological threats are expected to intensify over the next decade(s).

3.2. Material and Methods

3.2.1. Site description

Eight sites were sampled as part of a community-based study in the Mackenzie River basin (NWT) (Figure 3.1A). DGT devices made at Trent University were shipped to the northern communities and deployed at eight sites selected by the
communities in the summer month (July to September). The eight sites were grouped into regions: three sites (#1-3) located around the Great Slave Lake and five sites (#4-8) located along the lower Mackenzie River. Gas, oil and mineral operations occurred in the downstream region (Sites # 4-8) whereas the Great Slave Lake region (Sites #1-3) was downstream from the lower Alberta Oil Sands regions (AOSR). It can be noticed that important mining activities occurred near the main NWT city, Yellowknife (Site #3).

3.2.2. DGT preparation and deployment

Diffusive gels were made by mixing 40% acrylamide and DGT cross-linker (DGT Research Ltd, UK) and Milli-Q water at an appropriate ratio (Gao et al., 2011) followed by adding appropriate volume of ammonium persulfate (APS) and N,N,N,N-tetramethylethylenediamine (TEMED) based on the total mixture volume. The mixtures were immediately transferred between two glass plates with a spacer separating the two plates and heated to 45 °C in an oven for 1 hour. The gel was then hydrated in Milli-Q water for at least 24 hours and cut into shape. Metal binding gels were prepared with a similar procedure, except Chelex-100 resin was added to the APS/TEMED mixture. Triplicate DGTs (DGT Research Ltd, UK) were deployed in plastic plates directly in the river during summer months (July-Sept) and suspended 10–20 cm below the surface at eight sites for 1-5 deployments per year (Figure 3.1) and for 2-3 days per deployment in summer 2012-2014 (Guéguen et al., 2011); four sets of DGT were deployed for ~1 month in the Mackenzie River due to forest fires.
and limited site access. Upon retrieval, the DGTs were bagged and shipped on ice to the laboratory. The binding gels were extracted with 1M triple distilled HNO₃ (Buzier et al., 2014) in acid-washed centrifuged tubes for 24h under ultra-clean conditions.

Metal (Cu, Ni, Zn, Pb) concentrations in DGT extracts were analyzed on a high resolution ICP-MS (XSeries II, Thermo; Trent Water Quality Centre) with indium and rhodium used as internal standards. The ICP-MS measurements were assessed with reference water: 1643e (National Institute of Standards and Technology, USA) and SLRS-4 (National Research Council, Canada).

3.2.3. DGT-labile concentration calculation

DGT-labile metal concentration was calculated based on Fick’s laws of diffusion:

\[ C = \frac{M\Delta g}{DtA} \]  \hspace{1cm} (2)

where \( \Delta g \) (0.094cm; DGT research) is the thickness of the diffusive gel and membrane filter, \( D \) represents the diffusion coefficient of metal at a given temperature, \( t \) is the time of DGT deployment (i.e. ranging from 2-3 days to 1 month) and \( A \) is the exposed window area of DGT (i.e. 3.14 cm²). \( M \), the mass of metal accumulated in DGT was calculated based on the volume of 1M triple diluted HNO₃ from elution shown as equation (3),

\[ M = \frac{Ce\left(V_{HNO3} + V_{gel}\right)}{fe} \]  \hspace{1cm} (3)

where \( Ce \) is the metal concentration in 1M triple diluted HNO₃, \( V_{HNO3} \) is the volume of HNO₃ added to elute trace metal ions, \( V_{gel} \) is the volume of resin gel which is 0.15 ml (DGT research) and \( fe \) is 0.8 (DGT research) as the metal elution factor for metals.
(Cu, Ni, Zn, Pb).

After the assembly of a batch of DGT devices, three devices were randomly selected and stored in the laboratory (< 4 °C) as blanks to be analyzed with DGT samples in ICP-MS for signal correction. The triplicate blank DGTs were analysed simultaneously with DGT devices from the same batch that were exposed. DGT field blanks were also analysed for each set of triplicate DGT devices deployed in the field. The DGT field blanks were essentially transported and handled in the same way as DGT devices that were deployed; however, they were not exposed.

3.2.4. DGT Biofouling experiment

Biofouling can greatly affect the performance of the DGT samplers under field exposures (Pichette et al., 2007). In addition to the typical DGT filter (cellulose nitrate; Whatman GmbH; Zhang and Davison, 2001), two 0.45 μm prefilters, AgI coated cellulose nitrate (Whatman GmbH) (Pichette et al., 2007) and polycarbonate (Nuclepore) were used to assess the biofouling effect on DGT performance by determining the mass difference of filters after field exposures. The diffusive and binding gels were the same in all units. Three sets of DGTs were deployed in the Otonabee River which has comparable DOC concentration and water temperature to those found in the Mackenzie River. One set was retrieved each week for three weeks. Each DGT set contained 2 DGT units equipped with one of each of the three types of filters (6 in total). The dry mass of the deployed prefilters was determined and compared to that of non-deployed pre-filters. The diffusive binding gels were also
digested and analysed to assess the impact on metal accumulation.

3.2.5. ANOVA analysis

ANOVA analysis (unequal variance T-test analysis) was used to assess the labile metal concentrations on both spatial (site#1-3 and #4-8) and temporal (yearly between 2012, 2013 and 2014 and monthly between July, August and September) scales. For the ANOVA analysis, a 95% confidence level was applied.

3.3. Results and discussion

3.3.1. Effect of biofouling

Significant changes in filter appearance and mass were observed over a 3-week deployment in the Otonabee River (Figures 3.2-3.3). Both cellulose nitrate membrane and nuclepore filters showed a significant increase (p < 0.05) in their dry mass after 21 days deployment. In contrast, AgI coated filters did not show any significant change in mass after 3-week deployment (p > 0.05), suggesting limited biofouling as reported previously (Pichette et al., 2007; Uher et al., 2012).

The DGT-labile concentration of Cu and Ni (Figures 3.3C-D) was significantly lower after the two-week deployment when using untreated cellulose nitrate membranes whereas a significant difference of the metal accumulation was displayed from the mass elevation after the three-week deployment in water. The values from the DGT with Nuclepore filters showed the mass of filter in day 14 may be lower than it in day 7 due to discrepancies on the masses of new Nuclepore filters from each other and the masses are very small (<0.006g). Increased Cu and Ni concentrations in
day 14 could be caused by leaking from the Nuclepore filter edge due to the poor thickness. Overall, Nuclepore filters confirmed the influence of biofouling on Cu and Ni accumulation on DGT. This contrasts with DGT loaded with AgI coated filter where no significant difference in Cu and Ni accumulation to DGT devices was found after 3-week deployments. Although nuclepore filters showed satisfactory results after two week deployment, they were not recommended due to their very minimal thickness and low dry mass weight (0.005 ± 0.00032g), making it easier to slip through the piston during deployment.

3.3.2. **DOC and DGT-metal concentrations variation on a spatial scale**

The results showed that only the DGT-labile Cu and Ni and DOC concentrations displayed latitudinal changes (Figure 3.4) from the Great Slave Lake region (Sites #1-3) to the downstream sites (Sites #4-8) (0.58 and 1.79 ppb for Cu, 0.77 and 1.68 ppb for Ni, 6.91 and 4.06 for DOC; p < 0.05 unequal variance T-test). In contrast, Zn and Pb were not significantly different between Great Slave Lake region (Sites #1-3) and downstream sites (Site #4-8). The high concentrations were found in the downstream region for all four metals due to relatively low DOC concentrations (Figure 3.4D). The average DOC concentration showed a 1.8-fold decrease from the Great Slave region to the downstream sites. The significant reduction in DOC partly explained the increase in DGT-labile Cu concentrations as DOM is the main ligand of Cu (Chapter 2). Indeed, 99% Cu ion was controlled by humic substance complexation and only 1% was free or as small inorganic species (chapter 2) and thus DGT-labile. Ni (Chapter 2)
and Zn showed less affinity for DOM binding whereas Pb was strongly adsorbed by metal-colloidal species (Mackenzie, 1980). Indeed, Cu is the most correlated metal of all four metals to DOC. A significant increase was found in Cu at site #5 compared to site #6 (2.55 vs 0.55 ppb). It is may be caused by the oil operations at site #5. Although DGT-labile concentrations of Ni and Pb were 3.2 and 4.3 times higher at site #5 compared to site #6, the differences were not significant. Although the DOC concentration at site #8 was one of the highest reported in this study, the DGT-labile metal concentrations were still high, which is likely due to the influence of thaw slumps in Peel River watershed (Kokelj et al., 2013). The slope failure resulting from thawing of metal-rich permafrost (Todd, et al., 2012) was shown to significantly influence water quality of the impacted river (Kokelj et al., 2013) and potential metal speciation.

### 3.3.3. DOC and DGT-labile metal concentrations on a temporal scale

DOC concentrations in the Mackenzie River ranged from <0.02 to 15.03 ppm (Figure 3.5), similar to that in boreal streams (Antunes, et al, 2014; Guéguen et al., 2011; Moore, 2003; Nicolau, Galera-Cunha and Lucas, 2006; Millot et al, 2003). No yearly difference was found in the DOC concentration (Figure 3.6; p > 0.05). On a monthly basis, DOC concentration was significantly higher in September than in August (Figure 3.5; 6.98 and 3.85 ppm, respectively; p< 0.05) due to frequent heavy rain events in August (Ferguson and Marsh, 1991) which diluted DOC concentration. The late summer/early fall peak discharge can last for several days and be greater in
magnitude than the spring breakup.

The average DGT-labile concentrations of Cu, Ni, Zn and Pb (Table 3.1) over the three summers were 1.37 ± 1.61 ppb, 1.35 ± 1.77 ppb, 4.04 ± 4.59 ppb and 0.06 ± 0.11 ppb, respectively, which are at the lower end of the reported range in worldwide rivers (Baslistrieri et al., 2012; Han et al., 2013; Odzak et al., 2002; Tonello et al., 2011). Comparable magnitudes in DGT-labile metal concentrations were found over the three years of monitoring except when DGTs were deployed for several weeks due to site inaccessibility. For example, the labile concentrations from site #1 in August 2014 were lower than when the units were deployed for several days, likely the results of enhanced biofouling as shown in Figures 3.2-3.3. Consequently, only the results of the DGT samplers deployed for 2-3 days will be further discussed.

DGT-labile Cu concentration were well below the Water Quality for the Protection of Aquatic Life and Northwest Territories Water quality guidelines (2.36-3.34 ppb for Cu as CaCO$_3$ ranged 100-150 ppm) except in 1 sample at site #8 and 2 samples at site #5. However, the median concentration at these 2 sites was below the guidelines most of the time. The DGT-labile Ni, Zn and Pb concentrations were below both guidelines (95.58 - 130.07 ppb for Ni, 30 ppb for Zn, and 3.18 - 5.53 ppb for Pb, respectively) for all 8 sites. The DGT-labile metal concentrations were not significantly different on the yearly and monthly bases (p > 0.05), suggesting no significant temporal effects on the DGT-labile concentrations in the Mackenzie River basin during the ice free season.
3.4. Conclusions

Long-term DGT deployments showed abnormally low DGT-labile concentrations, caused by algal and microbial accumulation on the samplers. Short-term deployments (<1 week) were recommended for metal speciation assessments in natural systems. This study reported for the first time, the DGT-labile concentrations in the Mackenzie River basin. The average DGT-labile species were 1.37 ± 1.61 ppb for Cu, 1.35 ± 1.77 ppb for Ni, 4.04 ± 4.22 ppb for Zn and 0.06 ± 0.11 ppb for Pb, respectively, which were at lower end of the range reported previously in urban river studies, confirming the pristine status of the Mackenzie River. The results also showed that no monthly variations in DGT-labile metal concentrations were found (p > 0.05), suggesting that metal speciation remained unchanged during the ice free season. On the other hand, only the DGT-labile Cu and Ni concentrations increased from Great Slave Lake region (sites #1-3) to downstream in the Mackenzie River (sites #4-8) while DOC decreased. This result suggests DOC is a critical role in metal speciation. Additionally, non-anthropogenic sources (e.g. thaw permafrost) of trace metal introduced to the downstream Mackenzie River causing a metal concentration difference at site #8. Finally, the results of DGT-labile metal concentrations (Cu, Ni, Zn, Pb) in this study would contribute to policy maker, water quality managers and future studies upon the economic growth from expected gas and oil production in the NWT.
Acknowledgements

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References


Marsh, P.; Lesack, L.F.W. 1996. They hydrological regime of perched lakes in the


Table 3.1: Average values and ranges for DOC and DGT-labile metal concentrations of this study (NWT, Summers 2012-2014).

<table>
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<td>Range</td>
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<td>Pb [ppb]</td>
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<td>0.05 ± 0.091</td>
<td>0.004-0.49</td>
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Figure 3.1: Map of DGT deployment in Mackenzie River, NWT.
Figure 3.2: Biofouling on Chelex-DGT
Figure 3.3: (A-B) Masses (in gram) of prefilter (cellulose nitrate and AgI coated, nuclepore filter) and DGT-labile concentration of (C) Cu and (D) Ni after 7, 14, 21 day deployment (from darkest to lightest gray). The masses of not deployed prefilters (Purple) are included for comparison.
Figure 3.4: Concentrations of (A) DOC and DGT-labile (B) Cu, (C) Ni, (D) Zn and (E) Pb from upstream of Mackenzie River to downstream. Red line indicated guideline from “Water Quality for the Protection of Aquatic Life” and “Water quality guidelines used by the Northwest Territories”
3.4C

DGT-Labile Ni concentration

Site # 1 2 3 4 5 6 7 8

DGT-Labile Ni concentration

0 2 4 6 8
3.4D
Figure 3.5: Yearly average concentration of DOC (ppm) and DGT-labile (A)Cu (ppb), (B) Ni (ppb), (C) Zn (ppb) and (D) Pb (ppb) on log scales (2012-Gray, 2013-Brown and 2014-Blue). The arrow indicates the latitudinal change (61° – 68° N)
Figure 3.5

A

B

C

D

Labile-Cu

Labile-Ni

Labile-Zn

Labile-Pb
Figure 3.6: Monthly average concentration of DOC (ppm) and DGT-labile A) Cu (ppb), (B) Ni (ppb), (C) Zn (ppb) and (D) Pb (ppb) on log scales (July- Blue, August-Red and September-Orange)
Chapter 4: Conclusion

4.1. DGT-Labile concentrations

The Athabasca River and the Mackenzie River are two major rivers that flow through Alberta and NWT, Canada. The rapid, intensive, industrial developments of the Athabasca’s Oil Sands in the lower Athabasca River and growing mining exploration along the Mackenzie River watershed may have potential on water quality (e.g. trace metal contamination) and thus human and aquatic life in both watersheds.

This study focused on these four metals including three essential metal: Cu, Ni, Zn and a non-essential metal Pb. These metals accumulated onto Chelex-loaded DGTs were monitored in the Athabasca-Mackenzie basin.

The DOC and DGT-labile metal concentrations (Table 4.1) showed the Cu and Ni concentrations in the Athabasca River and in the Mackenzie River were quite comparable to each other, and comparable between sites. Similar ranges were previously found in worldwide rivers (Balistrieri et al., 2012; Han et al., 2013; Odzak et al., 2002; Tonello et al., 2011). The DGT-labile Zn concentration was higher in the Mackenzie River than in the AOSR, but lower than other rivers (Balistrieri et al., 2012; Han et al., 2013). The DGT-labile Pb concentrations in the Athabasca River were slightly higher than other rivers (Balistrieri et al., 2012; Han et al., 2013) but much below than the value calculated in Water Quality for the Protection of Aquatic Life and Northwest Territories Water quality guidelines based on CaCO₃ ranged 100-150 mg/L (3.18 - 5.53 ppb). In contrast, Kelly et al. (2010) found significant increase in
total metal concentrations in the Athabasca River and its tributaries including CLR-1, MAR-01 and MUR-1 (Chapter 2). The disparity may be due to the differences in sampling dates (July-August vs February and June) and the sampling techniques. In present study, DGT devices were applied to measure free/labile metal ions in the Athabasca River and tributaries whereas Kelly et al. (2010) focused on total concentration (particulate + dissolved) in surface rivers. Moreover, the measurements in Kelly et al. (2010) were in February and near tailing ponds which would result in higher metal concentrations.

DOM play a crucial role in aquatic systems. Metal complexes would have greater residence time and less bioavailable due to lack of mobility through cell membrane of organisms (or DGT diffusive layer in this study). The results showed that the DOC concentrations in the Athabasca River were 2-4 fold higher than in the Mackenzie River and higher than in previous studies in temperate rivers (Marie et al., 2015; Pettersson et al., 1997). Higher DOC values were expected as wetlands and bogs dominate the lower Athabasca and Mackenzie watersheds. Indeed, DOC strongly binds to Cu and Ni and thus reduce their toxicity. Within the Mackenzie River sites, Site #5 was located near gas operations where higher DGT-labile Cu and Ni concentrations (2.3 ± 2.06 and 2.12 ± 2.51 ppb, respectively) and low DOC concentration (3.43 ± 1.52 ppm) were found. In contrast, the AOSR sites had 6-12 fold higher DOC concentrations (up to 36.1ppm) and lower of DGT-labile concentrations. Similar results were previously reported (Ahmed et al., 2014; Mlakar et al., 2015; Trenfield et al., 2012). DGT-labile Pb concentration was found slightly
higher than previously reported (Ahmed et al., 2014; Mlakar et al., 2015; Trenfield et al., 2012). Dissolved speciation of Pb was dominated by inorganic colloids (up to 96%; Chapter 2). The DGT-labile metal concentrations did not exceed the water quality guidelines in both study areas except Cu at site #5 in the Mackenzie River. Further investigations would be recommended to confirm the higher Cu levels reported in this study. This would be particularly relevant as gas and mining operations are expected to grow near site #5.

4.2. Metal Speciation on temporal and spatial scales

Due to the AOSR development on the lower Athabasca River, the concentration of bioavailable metal species, i.e. the DGT-labile metal, becomes the most concerned issue to microbiologists. To settle this issue, the AOSR metal speciation trends from 2003 to 2012 are summarized in Figure 4.1. Also, ANOVA statistics analysis unequal variances were applied to determine the significant differences of DGT-labile concentration based on the data provided by RAMP. The result demonstrated no significant differences on the 10-year temporal scale despite some metal speciation fluctuations caused by DOC variations. The DGT-labile metal concentration was below the water quality guidelines suggesting the bioavailable metal level at the three study sites did not significant change over the past ten years.

In addition, the high DOC values were congruent with lower DGT-labile metal concentration. Similar DGT-labile concentrations were found in the lower Athabasca River (Chapter 2) and in the Mackenzie River NWT (Chapters 3) although the DOC
levels were 2-5 fold different (13 - 32 ppm vs 2.5 - 9 ppm). On one hand, no significant difference was found in the average DGT-labile metal and DOC concentrations on a yearly basis (2012-2014). On the other hand, DOC was found significantly lower in August than September (3.85 and 6.98 ppm, respectively; p<0.05). The reason causing the DOC difference could be due to change in river discharge. Water discharge increases in the Mackenzie River during late May or early June when ice melts upstream of the river (Marsh and Hey, 1989; Marsh and Lesack, 1996). This is followed by an increasing in discharge. There is more rain in August than in July or September, which could dilute the concentration of DOC. Moreover, on a spatial scale, there is a significant latitudinal increase (Figure 4.4) in DGT-labile Cu and Ni concentrations from the Great Slave Lake region (Sites #1-3) to the downstream sites (Sites #4-8) whereas DOC significantly decreased. It suggests that Cu and Ni speciation was DOC-influenced but not Zn and Pb. Although the Great Slave Lake region was closer to the AOSR, their DGT-labile metal concentrations were lower than that found further downstream in the NWT (i.e Site #5), suggesting that the AOSR mining operations did not impact significantly the water quality in Great Slave Lake region. Higher DGT-labile metal concentrations downstream of the Mackenzie River (Sites #5 and #8) could be possibly due to the activities associated with the gas and oil industry as oil development can release trace metals into natural waters (Wang et al. 2015). The presence of thaw slump (site #8) also has shown to release metal to surface waters (Kokelj et al., 2013). Therefore, the overall recommendation is to keep monitoring metal speciation at NWT downstream sites,
especially at site #5 and #8, in order to distinguish the natural sources of trace metal from human activities (e.g. oil production). For AOSR, year-round DGT deployments are recommended in order to determine the metal speciation variations especially non-DOC-related metals (e.g. Pb).

4.3. DGT challenges

Biofouling effects (Figure 4.2) on DGT-labile samplers were assessed (Figure 4.3). Over weeks, algae and microbial activities form a film on DGT windows reducing metal ion accumulations. The accumulated metal mass is no longer proportional to the deployment time. It was found that, AgI coated cellulose filter prevented the formation of microbial and algae mats for long time (~1 month) deployments. Even though, the DGT-labile Cu and Ni concentrations from Nuclepore DGT did not decrease significantly, the small thickness of Nuclepore filter would easily cause filter slippages which may cause ion leaking from the edge of the filter. Consequently, AgI coated cellulose nitrate filters are recommended for long term DGT deployments. Moreover, short term (< 3 days) deployments are highly recommended considering the loss from natural caused inaccessibility in long term deployment.

4.4. Significance of this study

This study modelled, for the first time, metal speciation over the past ten years in the Athabasca River using WHAM VII. No significant change in metal speciation was
found which is reassuring despite the significant increase in mining operations over the last decade. The results of this study will help microbiologists and policy makers to assess the potential threat from the bioavailable metal species in the Athabasca River.

On the other hand, this study also reported the use of diffusive gradient in thin films (DGT) samplers in the Mackenzie River located downstream of active oil sand development to determine the metal speciation temporally and spatially. It was found that the DGT-labile metal concentration in these two rivers meet the drinking water quality guidelines with an unexpected higher site in downstream Mackenzie River despite anthropogenic sources (e.g. gas operation at #5). Geomorphological (e.g. thaw slump) and geology reasons would contribute to metal concentration downstream (including not only the four metals) compared to upstream in the Mackenzie River. This study can constitute a benchmark for environmental managements and future researches in Alberta and NWT, Canada and provides an insight on the safety of drinking water along the two rivers.
Reference


Table 4.1: Average DGT-labile metal concentrations in Alberta Oil Sand Region (AOSR) and Mackenzie river watershed and compared with literature values (Balistrieri et al., 2012; Han et al., 2013; Odzak et al., 2002; Tonello et al., 2011)

<table>
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<tr>
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<tr>
<td>CLR-1</td>
<td>0.73±0.24</td>
<td>0.73±0.24</td>
<td>0.73±0.24</td>
<td>0.73±0.24</td>
<td>19.3±3.0</td>
</tr>
<tr>
<td>MAR-1</td>
<td>0.89±0.5</td>
<td>0.89±0.5</td>
<td>0.89±0.5</td>
<td>0.89±0.5</td>
<td>36.1±2</td>
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<td>MUR-1</td>
<td>0.5±0.47</td>
<td>0.5±0.47</td>
<td>0.5±0.47</td>
<td>0.5±0.47</td>
<td>26.57±6.5</td>
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<td>Mackenzie</td>
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<tr>
<td>1</td>
<td>0.73±0.94</td>
<td>0.88±0.79</td>
<td>4.08±5.2</td>
<td>0.06±0.1</td>
<td>9.07±5.75</td>
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<td>2</td>
<td>0.39±0.43</td>
<td>0.59±0.91</td>
<td>3.38±5.34</td>
<td>0.02±0.04</td>
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<tr>
<td>3</td>
<td>0.31±0.24</td>
<td>0.31±0.29</td>
<td>1.13±1.72</td>
<td>0.01±0.01</td>
<td>3.87±0.46</td>
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<td>4</td>
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<td>4.45±3.38</td>
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<tr>
<td>5</td>
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<td>2.12±2.51</td>
<td>4.26±5.11</td>
<td>0.08±0.1</td>
<td>3.43±1.52</td>
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<tr>
<td>6</td>
<td>0.53±0.25</td>
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<td>4.72±2.48</td>
<td>0.03±0.06</td>
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<td>5.36±4.08</td>
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<td>2.46±1.99</td>
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<tr>
<td>8</td>
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<td>0.12 - 31</td>
<td>14 – 736</td>
<td>0.01 – 0.65</td>
<td>0.82 – 8.32</td>
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Figure 4.1: Metal speciation in CLR-1 (First row), MAR-1 (second row), MUR-1 (Third row) assuming formation of colloidal FeOx (purple: metal associated with FeOx; green: metal-DOM complex; red: inorganic complex; blue: free ion).
Figure 4.2: Appearance of biofouling on DGT devices (Uher, et al., 2012)
Figure 4.3: (A-B) Masses (in gram) of prefilters (cellulose nitrate and AgI coated cellulose and nuclepore filter) and DGT-labile concentration of (C) Cu and (D) Ni after 7, 14, 21 days of deployment (from darkest to lighest gray). The masses of not deployed prefilters (Purple) are included for comparison.
Figure 4.4: Map of DGT deployment in Mackenzie River, NWT.