Spatial variations of total and dissolved trace elements and their distributions amongst major colloidal forms along and across the Lower Athabasca River

by

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Abstract

The Athabasca River (AR) is the longest river in Alberta with a wide variety of natural and potential anthropogenic inputs. The purpose of this study was to quantify the spatial variation of trace element (TE) concentrations and forms in this aquatic system. Water samples were gathered along a 125-km stretch of the river and at three points across the river, in locations upstream, alongside and downstream from the industrial region. The samples were collected using novel, metal-free sampling methods. With respect to water quality and the uptake/toxicity of trace elements, and to determine the biological significance of trace elements in the river, their size-based distribution amongst different colloidal forms (i.e. truly dissolved, primarily organic, and primarily inorganic) was measured in the dissolved fraction (i.e., < 0.45 μm by filtration). In addition, total concentrations of trace elements were normalized to that of thorium (Th) to determine the extent of enrichment relative to natural ratios in the earth's crust.

Differences in the concentrations of dissolved and total TEs were observed between the transects upstream, midstream, and downstream of industry, and on the east and west sides of the river. Total concentrations of Al, As, Co, Cu, Fe, Mn, Ni, Pb, Th, Tl, and V were significantly ($p < 0.05$) more abundant downstream of industry, compared to upstream. With the exception of As and Cu, these elements occurred predominantly in the particulate fraction (i.e. > 0.45 μm). Normalization to Th showed that no trace elements were enriched in the particulate fraction. In the dissolved fraction (< 0.45 μm), concentrations of As, Co, Cu, Ni, Pb, Re, and V were significantly ($p < 0.05$) more abundant downstream of industry. Within the dissolved fraction, Fe and Pb were found mainly as primarily inorganic colloids, while the other trace elements occurred predominantly in the mainly ionic/truly dissolved fraction (i.e., < ca. 1 kDa). The average concentrations of the investigated trace elements were far below the surface water quality guidelines in the Athabasca River. The PCA analysis indicated that tributaries contribute meaningful amounts of total and dissolved trace elements to the AR.

Preface

The following thesis is composed of original data generated and analyzed by Marjan Ghotbizadeh and includes one paper prepared for publication. The research project, of which this thesis is a part, received research ethics approval from the University of Alberta Research Ethics Board, Project Name “Spatial variations of total and dissolved trace elements and their distributions amongst major colloidal forms along and across the Lower Athabasca River”, March 2020.

Chapter 2 of this thesis is intended to be published as “Ghotbizadeh, M., Cuss, C. W., Grant-Weaver, I., Noernberg, T., Ulrich, A., and Shotyk, W. (2020). Spatial variations of total and dissolved trace elements and their distributions amongst major colloidal forms along and across the Lower Athabasca River”, and it is expected to be submitted to “Science of the Total Environment”. I was responsible for the data collection and analysis as well as the manuscript composition. Dr. Ania Ulrich, and Dr. William Shotyk were the supervisors and were involved with concept formation and manuscript composition. Dr. Chad Cuss also gave analytical and statistical advice and he contributed to manuscript edits. He and Tommy Noernberg assisted with the data collection. Iain Grant-Weaver assisted in the analysis of samples.

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1 CHAPTER 1 INTRODUCTION

1.1 **Research background and rationale**

1.1.1 Trace Elements in aquatic systems

Trace elements (TEs) are elements with very low concentrations in the earth's crust. In natural waters, these elements are found at concentrations lower than 1 ppm (Gaillardet et al., 2014, Cuss et al, 2019). These elements have important roles in biochemical mechanisms, and they could be essential elements, toxic, or both (Guengerich, 2009; Farooq et al., 2016). Essential trace elements are those that are generally required by plants and animals. They are necessary for life, through various enzymes and protein activities (Bicknell, 1942; Kramer et al., 2007; Farooq et al., 2016). As fundamental components of biological structures, essential trace elements can also be toxic, if their concentrations go beyond the necessary amounts for their biological functions (Fraga, 2005).

During recent decades, elevated concentrations of trace elements have been observed in different environmental compartments such as soils, water, sediment, air, and biota (Pfeifer et al., 2000). Through natural sources, like erosion processes and volcanism, and anthropogenic sources, such as industrial and human activities, trace elements enter natural waters (Foster and Charlesworth, 1996; Gaillardet et al., 2014; Meng et al., 2016; Kumar et al., 2017; Wang et al., 2017). In aquatic systems, identification of the main sources of trace elements might remain challenging, specifically when there is a wide variety of potential anthropogenic and natural inputs. Moreover, the contributions of some rocks (e.g., shales) that are rich in some particulate trace elements, could sometimes be considered as anthropogenic contamination, by mistake (Pfeifer et al., 2000).

1.1.2 Environmental threats to global freshwater

Water is the most important natural resource in the world (Vörösmarty et al., 2010). Freshwater sources including rivers, streams, lakes, wetlands, ponds, and springs are home to thousands of species. These aquatic ecosystems are crucial sources for providing a productive environment for plants, animals and the human population, as well as an adequate food supply for them (Pimentel et al., 2007; Aylward et al., 2005). Inevitably, worldwide freshwater demand has increased rapidly with the growth of the human population (Hinrichsen et al. 1998, Postel, 1999, Rosegrant et al. 2002, Gleick, 2003).

In spite of the importance of these resources, they have been heavily altered, due to the elevated environmental threats in the past decades (Carpenter et al, 2011; Pimentel et al. 2007). These threats have raised the management of global freshwater resources to a critical level (Gleick and Singh, 2001). Generally, these menaces include climate change, human population growth, and human activities that contribute to the degradation and destruction of freshwater ecosystems (Gleick and Singh, 2001; Vörösmarty et al., 2010; Russi et al., 2013). But more specifically they include:

i) Agricultural runoff, ii) wetland destruction as a result of agricultural expansion and urban growth, iii) groundwater contamination, iv) unsophisticated dam planning and constructions, and v) poor industrial and household pollution management, which affects freshwater resources (Matthews, 2016).

The protection of the freshwater resources, although challenging, is essential both from a global and local perspective (Vörösmarty et al., 2010; Gleick and Singh, 2001).

1.1.3 The Lower Athabasca River and its inputs

The Athabasca River (AR), a major river in Canada, is the longest river (1538 km) in Alberta (Newton, 2016). The AR is a wide river (375-900 m at Fort McMurray), with several deep channels (up to 6 m). Depending on the season, flow rates of the river fluctuate between 100 to 2000 $m^3 s^{-1}$ (Government of Alberta, 2015). The Athabasca River is one of the largest river systems in Alberta with immense resource draws by various industries, such as the oil sands, natural gas, and forestry sectors. Therefore, this unique aquatic environment has been the center of provincial, national and global attention (Government of Alberta, 2015).

With a significant influence on the culture, history, and economy of the province of Alberta (Shotyk et al., 2017), the Athabasca River has been prone to a growing number of environmental threats, such as agriculture, mining, municipal and industrial wastewater discharges, urban development, forestry, and oil sands developments (Bonnell and Keith, 2000; Spaling et al., 2000; Culp et al., 2000; Dubé, 2003; Alberta Government, 2012, Squires et al., 2013, Lima and Wrona, 2019).

The Athabasca River receives considerable inputs from the bitumen-laden bank erosion alongside the river, combined with inputs of saline groundwater and tributaries enriched in trace elements, potentially toxic metals, dissolved organic matter, hydrocarbons, and salt (Gibson et al., 2011; Headley et al., 2005; Jasechko et al., 2012; Gue et al., 2015; Sun et al., 2017; Cuss et al., 2018; Nagel et al., 2019). Some of the tributaries of the Athabasca River are suspected to be receiving inputs of wastewater seeping from tailings ponds (Ross et al., 2012) or atmospheric deposition of contaminants (Addison and Puckett, 1980). The impact of regional climate change on the hydrology of the AR watershed, has also been suggested to be a relevant reason for the inputs to the river (Shrestha et al., 2017; Comeau et al., 2009). Therefore, the water quality of the AR watershed (tributaries, groundwater) and its effect on ecological and human health has been a serious concern recently (Wrona et al., 2000; Kelly et al., 2009, 2010; Wiklund et al., 2014).

Specific activities of concern include: i) industrial development and urban growth, and intensified agricultural activities (Cessna et al., 2011; Forrest et al., 2011); ii) direct or indirect influences of logging (Kreutzweiser et al., 2008; Silins et al., 2014); iii) inputs from pulp and paper effluent (Wrona et al., 2001; Chambers et al., 2006); iv) wastewaters from coal mining (Casey, 2005); v) bitumen extraction from bituminous sands (Kelly et al., 2010), and; vi) municipal and industrial drainage waters (Chambers et al., 1997) into the Athabasca River watershed (Shotyk et al., 2017). The potential impacts of these activities have sparked interest and debate amongst the public, scientists, and government (Lima and Wrona, 2019; Bonnell and Storey, 2000; Schindler and Donahue, 2006; Squires et al., 2010).

It has been claimed that the concentrations of trace elements in the Athabasca River were more abundant near the industrial zone and among the mentioned industrial activities, the mining and upgrading of bitumen from bituminous sands, have been criticized as probable sources of direct and indirect release of trace metals into the Athabasca River and its tributaries (Timoney, 2007; Kelly et al., 2010; Schindler, 2013). The source attribution and the amount of the contributions from industrial activities, however, were not explained sufficiently in those studies.

On the other hand, some recent studies have shown contradictory results. For instance, in research done by Cuss et al. (2018), the contribution of tributaries to trace element releases to the Athabasca River was pointed out. In other studies, in spite of the focus on industrial contributions to water quality in the Athabasca River, except for a few trace elements that are enriched in bitumen (Ni, Mo, Re, and V), erosion and dust were the origins of the majority of trace metals in the particulate fraction in the AR and snowfall (Shotyk et al., 2016; Javed et al., 2017; Donner et al., 2017). Analysis of surficial bottom sediments samples from the Peace Athabasca Delta, showed that fluvial deposition of some of the elements (Be, Cd, Cr, Cu, Pb, Ni, Zn, V) had peaked many years prior to industrial development (Wiklund et al., 2014).

Distinguishing the sources of trace elements, despite decades of research, still continue to be debated among scientists. To explain the contradictory reports and uncertainty across various studies, high-quality, comprehensive, and scientifically sound investigations are required. A very important consideration is that the Athabasca River is a unique aquatic system with potential inputs from industrial activities, combined with tributaries enriched in high concentrations of dissolved organic matter (DOM) and iron oxyhydroxide (FeOOH). The inputs from each of these sources could react with trace elements in the river, alter their behavior, leading to vertical and horizontal stratifications in the concentration of trace elements (McKnight and Bencala, 1990; Vuori, 1995; Rondeau et al., 2005; Gaillardet et al., 2014, Cuss et al., 2018). Therefore, it goes without saying that with this immense variety of potential anthropogenic and natural inputs to the river, measuring the concentration of trace elements alone, which was considered as the primary evidence to show the industrial contributions, is not enough. It is essential for engineers and scientists to have a firm understanding of these anthropogenic and natural inputs of trace elements into the river so that they can better plan for future industrial activities, while appropriately protecting human and ecological health.

To detect the probable sources of trace elements in the Athabasca River, some other parameters such as the aquatic chemistry of these elements in the river, their form, speciation, and their size distribution are critical to consider (Donner et al., 2017; Javed et al., 2017; Shotyk et al., 2017; Cuss et al., 2018). Trace elements could be in the particulate, dissolved, colloidal, and truly dissolved forms. Their size distributions in these fractions are commonly defined as > 0.45 µm, < 0.45 µm, 1 nm or 1 kDa to 0.45 µm, and < 1 kDa (~ 1 nm), respectively (e.g., Buffle and Van Leeuwen, 1992; Stumm, 1993; Yang et al., 2014; Shotyk et al., 2017, Javed et al., 2017, Cuss et al., 2017; Cuss et al., 2018). Within the dissolved fraction, which is potentially toxic, mobile, bioaccessible, and bioavailable (Javed et al., 2017), the truly dissolved fraction (1 nm or 1 kDa) can directly affect aquatic life (Gélabert et al., 2007). In previous studies these factors, as well as the geography of the Athabasca River, geology and its hydrogeological settings had been insufficiently considered.

1.2 **Research goals and objectives**

1.2.1 Overall goal

The overall goal of this work is to investigate the spatial variation in the total (dissolved+particulate), dissolved, and colloidal concentrations of 18 trace elements in the Athabasca River (AR). Considering their common ecological functions, behavior and their sources, these trace elements are classified as belonging to one of the following groups: TEs of environmental concern (As, Cd, Pb, Sb, and Tl), TEs that are enriched in bitumen (Mo, Ni, Re, V), micronutrients (Cu, Zn), lithophile elements which are expected to be found predominantly in colloidal forms (Al, Co, Cr, Fe, Mn), and selected actinides (Th, U). One of the main contributions proposed in this work is to detect different sources. Size based distribution of these elements amongst total, dissolved and dissolved colloidal fractions, will help to distinguish natural from industrial sources.

1.2.2 Specific Objectives

1. To quantify spatial variation in the concentrations of TEs in total, dissolved, and colloidal forms along the 125-km stretch of the AR that passes from Fort McMurray, past oil sands mining and upgrading, and downstream to the Firebag River. The distribution of dissolved trace elements amongst major colloidal fractions and the spatial variation in the concentration of each fraction were also investigated along the river.
2. To quantify spatial variation in the concentration of trace elements in total, dissolved, and amongst the colloidal forms across the AR. For this purpose, surface and middle water layers were sampled at five transects (two transects upstream, one midstream and two downstream of industry) at the east, middle, and west side of the river.
3. To indirectly assess the probable contribution of industrial operations to the spatial variation of trace element concentrations in the AR, considering the observed increases in TE concentrations from upstream to downstream, cross-river spatial variation, and contributions from tributaries.

1.2.3 Significant aspects

The acquisition of reliable data related to the existing water quality of the Athabasca River has been one of the major challenges associated with past investigations in this river (Timoney, 2007; Dillon et al., 2011; Schindler, 2013; Shotyk et al., 2017). According to these studies, one reason for this inadequacy has been the lack of high-quality, comprehensive, and scientific sampling and analysis. In this study with precise metal free sampling and cutting-edge analytical methods in the metal-free, ultraclean SWAMP lab, we could overcome this shortcoming.

Measuring bioavailability, bioaccessibility and forms of trace elements in natural waters is a challenging task, considering the complex behavior of trace elements (Buffle and Van Leeuwen, 1992; Gaillardet et al., 2014). In this study, we were able to determine the concentration of trace elements in various colloidal forms. This information leads us to better knowledge of the potential impacts of different forms of trace elements on aquatic life.

For decades, First Nations (Indigenous communities) in northern Alberta have raised significant concerns about water quality in the Athabasca River, especially regarding the consequences of oil sands development on a wide range of issues related to water quality, water diversions, and potential health effects (Droitsch & Simieritsch, 2010). By measuring the spatial variation in the concentration of trace elements downstream of industry, and considering the surface water quality guidelines, that are intended to protect the aquatic ecosystems (CCME, 2003), present information the water quality which is relevant to Indigenous communities.

1.2.4 Research Questions and Hypotheses

In this study the research questions are:

- What are the physical forms (particulate, dissolved, and dissolved colloidal fractions) of trace elements? How are the elements distributed amongst these fractions?
- Do the forms of the investigated trace elements differ in abundance downstream compared to upstream?
- Could the industrial activities related to the Athabasca bituminous sands (e.g. mining and upgrading) be important sources of these elements to the lower Athabasca River?
- Do the concentrations of these trace elements in different forms change across the river, at different sides?
- Do the tributaries contribute to spatial variations in the concentration of elements across or along the river and give rise to the observed differences?

In terms of the hypotheses, we expect that:

- The dissolved and total V, Ni, Re, Mo (the elements that are enriched in bitumen) increase from upstream to downstream, probably due to the natural occurrence of bitumen (Shotyk et al., 2016; Donner et al., 2017; Javed et al., 2017), oil sand industry (Kelly et al., 2010; Guéguen et al., 2011, 2016), or both.
- Within the dissolved fraction, the elements that are expected to be found in colloidal forms (e.g. Al, Fe, Mn) increase from upstream to downstream, probably due to the influence of tributary inputs, depends on flow rates (Tondu, 2017; Cuss et al., 2018).

- The total, dissolved, and colloidal concentrations of some elements (e.g. Al, Fe, and Mn) that are more abundant in some tributaries, (e.g. Clearwater River (Tondu, 2017) and Mclean Creek (Cuss et al., 2018) on the east side, or McKay River (Cuss et al., 2018) on the west side) will be different at opposite sides of the river.

1.2.5 Research Approach

In order to properly address the questions outlined above, the following investigations were required across the river and along a transect from upstream to downstream:

a. Determine total and particulate (> 0.45μm) concentrations of trace elements in Athabasca River water, from upstream to downstream.

b. Determine dissolved (< 0.45μm) concentrations of the elements in Athabasca River water, from upstream to downstream.

c. Determine concentrations of elements in the colloidal fraction (1 kDa – 0.45μm), and their distributions amongst mainly ionic (< 1 nm or 1 kDa), organic associated (~1–10 kDa), and inorganic associated (~10 kDa – 0.45 μm) fractions, in Athabasca River water, from upstream to downstream.

d. Determine the contributions of tributaries or industrial activities, by statistical analysis, and comparing the element concentrations with thorium (Th), as a conservative, lithophile element. The reason why we compare the elements to Th is that this element is a physical weathering indicator. If the element to Th ratios downstream of industry reflect crustal values, predominantly natural sources are inferred.

e. To address any probable health risks, the concentrations of the elements were compared with the surface water quality guidelines.

1.2.6 Thesis outline

In Chapter 1, the focus is on the research background and rationale for the study. Chapter 2 is presented as an individual research manuscript. In this chapter, the research methodology, results and corresponding discussion will be presented. Finally, the conclusions and engineering significance of the research work will be summarized in Chapter 3.

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2 CHAPTER 2[*]

SPATIAL VARIATIONS OF TOTAL AND DISSOLVED TRACE ELEMENTS AND THEIR DISTRIBUTIONS AMONGST MAJOR COLLOIDAL FORMS ALONG AND ACROSS THE LOWER ATHABASCA RIVER

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[*] This Chapter is prepared for journal submission and so it is presented as an individual research manuscript.

2.1 **Abstract**

The Athabasca River (AR) is the longest river in Alberta with a wide variety of natural and potential anthropogenic inputs. The purpose of this study was to quantify the spatial variation of trace element (TE) concentrations and forms in this aquatic system. Water samples were gathered along a 125-km stretch of the river and at three points across the river, in locations upstream, alongside and downstream from the industrial region. The samples were collected using novel, metal-free sampling methods. With respect to water quality and the uptake/toxicity of trace elements, and to determine the biological significance of trace elements in the river, their size-based distribution amongst different colloidal forms (i.e. truly dissolved, primarily organic, and primarily inorganic) was measured in the dissolved fraction (i.e., < 0.45 μm by filtration). In addition, total concentrations of trace elements were normalized to that of thorium (Th) to determine the extent of enrichment relative to natural ratios in the earth's crust.

Differences in the concentrations of dissolved and total TEs were observed between the transects upstream, midstream, and downstream of industry, and on the east and west sides of the river. Total concentrations of Al, As, Co, Cu, Fe, Mn, Ni, Pb, Th, Tl, and V were significantly ($p < 0.05$) more abundant downstream of industry, compared to upstream. With the exception of As and Cu, these elements occurred predominantly in the particulate fraction (i.e. > 0.45 μm). Normalization to Th showed that no trace elements were enriched in the particulate fraction. In the dissolved fraction (< 0.45 μm), concentrations of As, Co, Cu, Ni, Pb, Re, and V were significantly ($p < 0.05$) more abundant downstream of industry. Within the dissolved fraction, Fe and Pb were found mainly as primarily inorganic colloids, while the other trace elements occurred mainly in the mainly ionic/truly dissolved fraction (i.e., < ca. 1 kDa). The average concentrations of the investigated trace elements were far below the surface water quality guidelines in the Athabasca River. The PCA analysis indicated that tributaries contribute meaningful amounts of total and dissolved trace elements to the AR.

2.1.1 Keywords

Trace elements, Athabasca River, Water quality, Bituminous sands, Field-flow fractionation, ICP-MS, Colloids, Suspended solids

2.1.2 Bullet points

- Total concentrations of Al, As, Co, Cu, Fe, Mn, Ni, Pb, Th, Tl, and V were more abundant downstream of industry, but mostly in the particulate fraction. No anthropogenic enrichment of any of these elements was observed along or across the river.
- Dissolved concentrations of As, Co, Cu, Ni, Pb, Re, and V were more abundant downstream with apparent variations of Fe, Ni and Re across the river.
- Except for Fe and Pb, which were mainly found in the primarily inorganic colloidal fraction, the ionic fraction (< 1kDa) was the dominant form for the rest of the elements.
- Trace elements in the river did not exceed the surface water quality guidelines.
- Tributaries contribute meaningful amounts of total and dissolved trace elements to the river.

2.2 **Introduction**

Trace elements (TEs) have very low concentrations in the earth's crust. In natural waters, these elements are characterized by concentrations lower than 1 mg L^{-1} (Gaillardet et al., 2014, Cuss et al, 2019). Trace elements enter aquatic systems through natural sources, such as volcanism and erosion processes, and through anthropogenic sources, like industrial activities (Foster and Charlesworth, 1996; Gaillardet et al., 2014; Meng et al., 2016; Kumar et al., 2017; Wang et al., 2017).

Water is broadly considered as the most fundamental of natural resources (Vörösmarty et al., 2010). In the past several decades, the world's freshwater resources management has come to a critical stage, as new environmental threats face water managers and policymakers. These threats include climate change, human activities, and the degradation and destruction of freshwater ecosystems (Gleick and Singh, 2001). Although it is challenging, the protection of the world's freshwater resources requires the diagnosis of threats over a wide range of scales, from global to local (Vörösmarty et al., 2010; Gleick and Singh, 2001).

The Athabasca River (AR) is the longest river (1538 km) in Alberta and a major river in Canada (Newton, 2016). The AR has been the center of recent attention due to serious concerns about water quality throughout the AR watershed (Wrona et al., 2000) and impacts on ecological and human health (Kelly et al., 2009, 2010). The AR has been exposed to a growing number of environmental threats (Spaling et al., 2000; Alberta Government, 2012, Squires et al., 2013).

Anthropogenic activities along the Athabasca River and its watershed have also increased in recent decades, including: i) intensification of industrial and urban development, as well as agricultural activities (Cessna et al., 2011; Forrest et al., 2011); ii) impacts of logging (Kreutzweiser et al., 2008; Silins et al., 2014); iii) inputs from pulp and paper mills (Wrona et al., 2000; Chambers et al., 2006); iv) drainage waters released from coal mining (Casey, 2005) and oil sand development and bitumen mining (Kelly et al., 2010), and; v) municipal wastewaters (Chambers et al., 1997; Bonnell and Storey, 2000; Schindler and Donahue, 2006; Squires et al., 2010; Shotyk et al., 2017; Lima and Wrona, 2019). Among these activities, the mining and upgrading of bitumen from Canada's bituminous sands have been criticized as potential sources of trace metals into the AR and its tributaries (Timoney, 2007; Kelly et al., 2010; Schindler, 2013; Guéguen et al., 2016). Although studies have been conducted by many researchers, the extent of contributions from industrial activities, is still insufficiently explored.

Despite the focus on industrial contributions to water quality in the AR, recent investigations have shown that the majority of trace metals in the particulate fraction in the AR and snowfall come from dust, or erosion, with the exception of a few trace elements that are enriched in bitumen (Ni, Mo, Re, and V) (Shotyk et al., 2016; Javed et al., 2017; Donner et al., 2017).

Moreover, a study of sediments gathered from the Peace Athabasca Delta demonstrated that elements (Be, Cd, Cr, Cu, Pb, Ni, Zn, V) had been deposited for many years prior to the development of industry (Wiklund et al., 2014). Another investigation into the distribution of trace elements amongst dissolved colloidal fractions also pointed out the contribution of tributaries to TE in the AR (Cuss et al., 2018).

Natural processes such as impacts of climate change on the hydrology of the AR watershed (Shrestha et al., 2017), and natural discharges from tributaries and groundwaters, alter the release of TEs, dissolved organic matter, hydrocarbons, and salt into this aquatic system (Jasechko et al., 2012; Gibson et al., 2013; Gue et al., 2015; Sun et al., 2017; Cuss et al., 2018; Nagel et al., 2019).

The contradictory reports and uncertainty across different studies intensify the importance of high-quality, comprehensive, and scientifically sound research. In previous reports, the concentrations of trace elements in the AR and snow samples have been considered evidence of industrial influence on trace element concentrations and their distribution among the colloidal fractions, with a lack of attention paid to the geography, geology, and hydrogeology of the AR. The AR is very wide (375–900 m at Fort McMurray), with deep channels up to 6 m, and various flow rates at different points across the river. Besides the discharges from industrial activities, tributaries release high concentrations of dissolved organic matter (DOM) and iron oxyhydroxide (FeOOH) to the main stem of the river. These inputs could react with the trace elements in the river, change their behavior and cause spatial variation in the concentrations of trace elements (McKnight and Bencala, 1990; Vuori, 1995; Porcelli et al., 1997; Rondeau et al., 2005; Gaillardet et al., 2014, Cuss et al., 2018). Considering the immense variety of potential anthropogenic and natural inputs to the AR, concentration measurements alone are not sufficient. To rectify the mentioned oversight and to determine the probable sources of trace elements, factors such as their form, speciation, and size distribution should also be taken into account (Donner et al., 2017; Javed et al., 2017; Shotyk et al., 2017; Cuss et al., 2018).

In aquatic systems, some part of trace elements are transported in complexed forms (Gaillardet et al., 2014). Understanding the partitioning of trace elements into different phases is challenging because it depends on many factors such as pH, ionic strength, temperature, and salinity (Buffle and Van Leeuwen, 1992; Gaillardet et al., 2014). Among these factors, as former studies showed, increasing water pH promotes the sedimentation of colloids (Baalousha et al., 2006; Cuss et al., 2019). Likewise, sedimentation tends to increase with increasing ionic strength, in response to increasing salinity (Baalousha et al., 2006; Stolpe and Hassellöv, 2007; Cuss et al., 2019). Temperature changes and temporal variations could also affect the trace elements forms, their distribution, and their behavior by altering redox conditions (Warren and Haack 2001; Shiller and Stephens 2005; Cuss et al., 2019). The particulate, dissolved, colloidal, and truly dissolved fractions are commonly defined as > 0.45 µm, < 0.45 µm, 1 nm or 1 kDa to 0.45 µm, and < 1 kDa (~ 1 nm), respectively (e.g., Buffle and Van Leeuwen, 1992; Stumm, 1993; Yang et al., 2014; Shotyk et al., 2017, Javed et al., 2017, Cuss et al., 2017; Cuss et al., 2018). Among these fractions, truly dissolved fraction can directly affect aquatic life (Gélabert et al., 2007). To accurately measure the distribution of trace elements amongst the mentioned major colloidal fractions, reliable and precise methods are needed (Cuss et al., 2017).

Asymmetric flow field-flow fractionation (AF4) is potentially able to separate a wide variety of macromolecules and colloids (Wahlund and Giddings, 1987; Fraunhofer and Winter, 2004; Cuss et al., 2017). Coupling AF4 with the smallest membrane pore size (300 Da) to inductively coupled plasma mass spectrometry (ICPMS) enables us to measure the size-based distribution of dissolved trace elements among colloidal fractions based on their size (Beckett et al., 1991; Cuss et al., 2017). The 0.45-µm filterable materials that are retained in the channel and eluted to the ICP-MS are colloidal (i.e. ~1 kDa–0.45µm) (Buffle and Leppard, 1995; Cuss et al., 2017). Colloids, with at least one dimension in size range of 1 to 1000 nm (IUPAC, 1997), have a high specific surface area and unique properties. They play critical roles governing the speciation, transport, toxicity, and bioaccessibility of trace elements in aquatic systems through the adsorption or complexation reactions (Gaillardet et al., 2014; Cuss et al., 2019).

The bioavailability and bioaccessibility of the trace elements in natural waters depend on their chemical speciation and their forms (Worms et al., 2006; Cuss et al., 2019). In aquatic systems, the bioavailability of an element is related to the element's ability to cross biological barriers, such as plasma membrane (Worms et al., 2006; Cuss et al., 2019). According to the United States Environmental Protection Agency (USEPA), the bioaccessible fraction is the fraction of total metal that interacts at the contact surface of an organism, and is potentially environmentally available for absorption or adsorption (McGeer et al., 2004).

To better investigate water quality in the Athabasca River, comprehensive sampling and precise analysis are required. Although the need and the importance of conducting such a thorough survey have been pointed out (Timoney, 2007; Dillon et al., 2011; Schindler, 2013; Shotyk et al., 2016), not enough information has been presented.

Therefore, in this study, our primary objectives were:

1- To quantify spatial variation in the concentrations of trace elements in total, dissolved, and dissolved colloidal forms along the 125-km stretch of the AR that passes from Fort McMurray, past oil sands mining and upgrading, downstream to the Firebag River. The distribution of dissolved trace elements amongst major colloidal fractions and the spatial variation in the concentration of each fraction was also investigated along the river.

2- To quantify spatial variation in the concentration of trace elements in total, dissolved, and amongst the colloidal forms across the AR. For this purpose, surface and middle water layers were sampled at five transects (2 transects upstream, one midstream and two downstream of industry) at the east, middle, and west side of the river.

Our final objective was to provide a much needed, thorough measurement of background concentrations and forms, considering the observed increases in TE concentrations from upstream to downstream, cross-river spatial variation, and contributions from tributaries, against which the probable contribution of industrial operations to trace element concentrations in the AR can be assessed.

2.3 **Materials and Methods**

2.3.1 Study area

Water samples were gathered from 5 transects across the stream along the 125-km stretch of the AR that passes from Fort McMurray, past oil sands mining and upgrading, downstream to the Firebag River in October (when tributaries and groundwaters exert more influence) 2017. To account for spatial variation across the river that may be a useful indicator of source inputs, samples were collected at six points for each transect (T1–T5): 3 sides (east, middle and west), and at two depths (surface and middle) (Figure 1). These five transects were chosen to account for tributary inputs (between T1 and T2), as well as potential inputs from industry (T3 at the midstream, in front of tailings ponds and bitumen upgrading facilities), and groundwaters (between T4 and T5, both downstream of industry).

2.3.2 Ultraclean sampling and analysis conditions

A specialized metal-free depth sampler was used for gathering water samples (Figure 2). At each site, a set of two 125 mL polypropylene (PP) bottles, and one 125 mL Teflon FEP (Thermo Fisher Scientific, Waltham, Massachusetts, Cat # 02-924-15A) were collected for a variety of parameters. All bottles were precleaned in a clean-air cabinet, in the SWAMP lab. The PP bottles were soaked in 10% HNO3 acid baths for seven days, followed by a heating process (to 60 °C) for 6-8 hours on a hot plate. These bottles were dedicated to total and dissolved trace metals, with one of them containing the unfiltered water samples to determine the total trace elements (dissolved+particulate), and the dissolved fraction. The FEP bottles were rinsed with milli-Q water (MQW), for determination of the colloidal distribution in the dissolved fraction. FEP bottles were used to minimize the adsorptive losses to container walls, which is problematic for acid-cleaned PP bottles that are not acidified. To separate the dissolved fraction, samples were filtered immediately in the field, using syringe filters (using 0.45 µm (Millex) polytetrafluoroethylene (PTFE) hydrophilic filter, Thermo Fisher Scientific, Waltham, Massachusetts, Cat # SLCR025NS), which were precleaned in the lab, by passing 10 mL of 2% double-distilled HNO3 through the filter followed by MQW.

In the field the FEP bottles were rinsed with filtered river water before gathering the samples. All water samples were kept in a cooler with ice packs and transferred to storage at 4 °C until analysis. All sampling equipment was pre-cleaned, using multi-stage acid cleaning, and packed under ultraclean conditions (Shotyk et al., 2017, Cuss et al., 2017).

To minimize the risk of contamination, all measurements were conducted in the ultraclean, metal-free SWAMP lab facility at the University of Alberta. Based on their common ecological functions, sources, and behavior, trace elements were classified as belonging to one of the following groups: trace elements of environmental concern (As, Cd, Pb, Sb, and Tl), trace elements that are enriched in bitumen (Mo, Ni, Re, V), micronutrients (Cu, Zn), lithophile elements which are expected to be found predominantly in colloidal forms (Al, Co, Cr, Fe, Mn), and selected actinides and lanthanides (Th, U). The concentrations of these trace elements were measured in both the dissolved and total fractions using ICP-MS.

Normalization to Th, as a conservative, lithophile element, was performed to distinguish the potential sources of trace elements, and their probable enrichment, downstream. To detect the contribution of tributaries and better assess the transport, bioaccessibility and reactivity of dissolved trace elements, their distribution amongst truly dissolved, primarily organic, and primarily inorganic colloids were measured using asymmetric flow field-flow fractionation (AF4) coupled to ICP-MS (Cuss et al., 2017, 2018).

The AF4 was equipped with a polyethersulfone (PES) separation membrane with the smallest available pore size (300 Da), to minimize the loss of small colloids and “truly dissolved” organic-trace element complexes through the membrane, and was coupled to both a UV-Visible spectrophotometer (UV) and ICP-MS to measure the size-based distribution of dissolved trace elements among mainly ionic species and small molecules organic colloids, and larger inorganic colloids (Beckett et al., 1991; Cuss et al., 2017). Distribution of trace elements amongst dissolved colloidal species, using statistical fractogram deconvolution are shown in Figure S1. For two samples in upstream and downstream, primarily organic and inorganic fractions were separated using AF4. Three drops of each sample solution, as representations of the whole samples were deposited onto a TEM grid, which was covered by a carbon film, until the complete evaporation, in the clean cabinet in the SWAMP lab.

The morphology, composition, and size of the fractions that were separated by AF4 were also confirmed using transmission electron microscopy (TEM) coupled to Energy-dispersive X-ray spectroscopy (EDX). To expand on existing water quality knowledge and to better understand the behavior of the trace elements, a broad range of chemical and physical parameters, the instrument certified standard reference material (SRM) and their recoveries were measured (e.g., pH, conductivity, and DOC, SRMs; Table S1 and Table 5).

Our measurements regarding the size-based speciation were then used to confirm the results we found from mass transfer computer program, Visual MINTEQ 3.1.

2.3.3 Statistics and trend detection

Data were expressed as average values ± 95% confidence. Considering the challenges with standard statistical approaches for outlier detection, for complex data involving mixing from multiple sources, with potential spatial variation, five independent methods, including: histogram, Grubbs' test (or ESD, the extreme studentized deviate), GESD test (the generalized extreme studentized deviate), the median absolute deviations, and the mean absolute deviations (MAD) were used to determine the potential outliers in the total and dissolved dataset. These methods were implemented using MATLAB R2017 and SPSS (Table S2).

Among these methods, histograms were used to assess outliers given expected distribution bimodality. Bimodal distributions is normally an indication of heterogeneous samples, different populations or samples with high variability, and it could suggest that the observations may come from two or more distributions (Murphy, 1964; Wang, 2017).

Considering the nature of our data, with bimodal distributions expected along the river and specifically after the inputs from tributaries, groundwater or industry, and also considering the assumptions of all of these methods (Table S2), outliers were identified and removed.

To test the significance of apparent differences, the data were subjected to one sided t-test (for normal data) or Wilcoxon signed rank test (for non-normally distributed data, after the transformations), and Multivariate analysis of variance (MANOVA) with the significance level of $p < 0.05$, using analytical software SPSS statistics (Version 17.0, SPSS Inc. Chicago, IL, USA). The results of these two analyses were then compared to each other, and MANOVA was chosen as the optimal approach because there was more than one explanatory factor (Sthle and Wold, 1990) (Table S3). In our investigation, the location (upstream, midstream, and downstream) and the sides (west, middle, east) were our fixed factors (independent variables), and the concentrations of trace elements were dependent variables.

Relationships between total TE concentrations and Th as a conservative, lithophile element, were evaluated using Spearman's correlation coefficients, to distinguish the potential sources of trace elements, and their probable enrichment, downstream of industry, compared to upstream. Principal Component Analysis (PCA) and correlation analysis were also performed, using MathWorks MATLAB R2017a, to investigate associations between sample sites and TE concentrations, and the influence of tributaries on the AR.

2.4 **Results**

2.4.1 Total concentrations

The average concentrations (μg L^{-1}) of trace elements in the total fraction are presented in Table 1, organized according to their locations upstream, midstream, and downstream of industry, and on different sides of the AR (west, middle, and east). In this fraction, the MANOVA analysis showed no statistically significant ($p < 0.05$) interactions between trace element concentrations along and across the stream (interpret), on the combined dependent variables: F (72, 16) = 0.84, p = 0.7; Pillai's trace = 3.16 (Table 2).

2.4.1.1 Spatial variation along the AR (Upstream, Midstream, Downstream)

The concentrations of Al, As, Co, Cu, Fe, Mn, Ni, Pb, Th, Tl, and V were significantly ($p < 0.05$) higher downstream compared to upstream. Aluminum, As, Fe, Mn, Ni, and Th also increased significantly ($p < 0.05$) from upstream to midstream.

The rest of the elements downstream were comparable to upstream, and their spatial variations along the river were not significant ($p < 0.05$).

2.4.1.2 Spatial variation Across the AR (West, Middle, East)

The differences in total trace element concentrations were not significant ($p < 0.05$) across the transects at different sides for the length of the river investigated. In this fraction, As was more abundant on both sides of east and west, compared to the middle side of the upstream. In midstream total concentrations of As, Co, U, and V were more abundant on the west side, compared to the east side. The spatial variation in the total concentration of elements downstream was not significantly ($p < 0.05$) different at different sides.

Of the investigated elements with statistically significant ($p < 0.05$) spatial variations along the AR, by far the majority (Al, Co, Fe, Mn, Ni, Pb, Th, Tl, and V) were found mainly in the particulate fraction, from 55% (Ni) to 99.7% (Al) (Figure 3). Additionally, none of the investigated trace elements enriched significantly ($p < 0.05$) downstream compared to upstream or midstream of industry (Figure S2).

2.4.2 Dissolved concentrations

Table 3 provides the average concentrations ($\mu g\ L^{-1}$) of trace elements in the dissolved fraction upstream, midstream, and downstream of industry, and on different sides of the AR (west, middle, and east). There was no statistically significant interaction effect between trace element concentrations along and across the stream on the combined dependent variables: $F (72, 36) = 1.1$, $p = 0.38$; Pillai's trace = 2.75 (Table 4).

2.4.2.1 Spatial variation along the AR (Upstream, Midstream, Downstream)

In the dissolved fraction, the concentrations of As, Co, Cu, Ni, Pb, Re, and V increased significantly ($p < 0.05$) from upstream to downstream. Dissolved concentrations of Co, Re, and V were also significantly ($p < 0.05$) more abundant downstream compared to both upstream and midstream.

While declining from upstream to midstream, the dissolved concentration of Re increased nearly two-fold from midstream to downstream (2.3–4.4 ng L^{-1}). The average dissolved concentration of Re in midstream is comparable to the global average river concentration (2.1 ng L^{-1}) (Miller et al., 2011). Moreover, the dissolved concentrations of Mo increased significantly ($p < 0.05$) from midstream to downstream. Among all elements, Ni, Mo, and U were also more abundant downstream compared to midstream of the river. Dissolved concentrations of the remaining elements downstream were comparable to upstream.

2.4.2.2 Spatial variation Across the AR (West, Middle, East)

Dissolved concentrations of Mo, Ni, Re, Sb, and U were significantly ($p < 0.05$) more abundant on the west side of the river, compared to its east side, while dissolved Fe was more abundant on the east side of the river. Dissolved concentrations of the other elements did not significantly ($p < 0.05$) change across the river stream (at different sides).

In this fraction, Ni and Sb were more abundant ($p < 0.05$) on the west side, upstream compared to the east and middle sides. Dissolved concentration of U was also more abundant ($p < 0.05$) on middle, compared to the east side, upstream. In midstream, dissolved concentrations of Cr was more abundant ($p < 0.05$) on the east side, while the concentrations of Cu, Cd, Mo, Re, Sb, and U were significantly higher ($p < 0.05$) on the west side. Dissolved concentrations of Ni and Zn were also significantly higher ($p < 0.05$) on the west side of midstream compared to the middle side. In downstream, dissolved concentrations of Mn and Mo were more abundant ($p < 0.05$) on the west side, compared to the east side.

2.4.3 Dissolved colloidal fractions (Inorganic/DOM/Mainly Ionic and small)

Spatial variations in the distributions of dissolved Al, Fe, Mn, Ni, Mo, As, U, Cu, Pb, Co, Cr, V, Zn, and Th amongst primarily inorganic colloids, primarily organic colloids, and mainly ionic species and small molecules were investigated along and across the AR (Table 5; Figure 4).

2.4.3.1 Spatial variation along the AR (Upstream, Midstream, Downstream)

In the primarily inorganic colloids, almost all of the elements (except for Al, Cr, Mo, and Zn) increased slightly from upstream to downstream. But among them only Mn and Pb increased significantly ($p < 0.05$) from upstream to downstream. Having used TEM-EDX, comparison between the composition of colloids in the primarily inorganic colloidal fractions also showed higher concentrations of V, Mn, and Fe downstream compared to upstream (Figure 5a).

Likewise, these element concentrations increased in the primarily organic colloidal fraction, with the average increase factor of ~1.25. Figure 5b shows the differences in the shape and morphology of the particles in primarily organic (1–10 kDa) and primarily inorganic (10 kDa–0.45 μm) size fractions in a sample collected upstream from industry. Except for Fe, which increased significantly ($p < 0.05$) from upstream to midstream, the variation in the concentrations of the rest of elements along the river was not significant ($p < 0.05$).

Except for Fe and Pb, which were mainly found in the primarily inorganic colloidal fraction, the mainly ionic/truly dissolved fraction was the dominant (> 50%) form for the rest of the elements. In the length of the river investigated, the ionic fraction of As, Cu, Fe, Mn, and V increased slightly but not significantly ($p < 0.05$) from upstream to downstream of industry.

2.4.3.2 Spatial variation across the AR (West, Middle, East)

In the primarily inorganic colloidal fraction, concentrations of As, Cu, Fe, and V were more abundant on the east side of the river compared to the west side. While the concentrations of Co, Mn, Ni, Pb, Th, and U observed were higher on the west side of the river compared to the east side. In the length of the river investigated, these variations were not significant ($p<0.05$).

In the primarily organic colloidal fraction, a very slight, but not significant ($p > 0.05$) variation was observed across the river. In this fraction, As, Mn, and V were more abundant on the east side, and Co, Cu, Fe, Ni, Mo, Pb, Th, and U, on the west side of the length of the river investigated. At each individual section (upstream, midstream, and downstream) the concentrations of the elements in this fraction were not significantly ($p < 0.05$) different at different sides.

In the mainly ionic fraction, for the length of the river investigated, the concentrations of Co, Fe, Ni, Pb, and Th were higher on the east side of the river compared to the west side, while As, Cu, Mo, Mn, U and V were more abundant on the west side of the river, compared to the east side. These changes, however, were not significant ($p > 0.05$). At each individual section (upstream, midstream, and downstream) the concentrations of the elements in this fraction were not significantly ($p < 0.05$) different at different sides. Most of the variations in these fractions were not significant, which was due to the large variations of our data across and along the river.

Normalization analysis was not conducted in the dissolved fraction, since only ~ 25% (2.9 ± 1.8 ng L^{-1}) of the dissolved Thorium (11.8 ± 0.8 ng L^{-1}) was associated with primarily inorganic size fraction.

2.4.4 Multivariate trends

Principal component and Spearman correlation analyses were applied to the dissolved and total concentrations of trace elements, to investigate their multivariate relationships and detect different sources. Principal component analysis (PCA) is used for the data set with many variables that are correlated with each other. It is a mathematical method with the main idea of reducing data dimensionality (Jolliffe, 2002). This reduction is accomplished by identifying directions which are called principal components. Using these components enables each sample to be represented by a few numbers, instead of values for lots of variables. To visually determine if samples can be grouped, or to assess similarities and differences between them, PCs can be plotted (Ringnér, 2008). PC results are normally reported as loadings (the values that each standardized original variable should be multiplied by), and component scores (the transformed variable values) (Shaw, 2003). As mentioned before, tributaries with high concentrations of DOM and Fe release trace elements into the Athabasca River. The concentration of trace elements in the tributaries are shown in Tables 1 and 2.

According to the results, PCs explained 87% of total variations of both dissolved (4 PCs) and total (3PCs) fractions. For each of these PCs, the variable loadings with absolute values lower than the 30% of that for the maximum loading were not considered during the interpretation. (Jolliffe, 2002, Cuss et al., 2018). The results for PCA and the Spearman correlation (correlation coefficients for trace elements and their probability of no correlation) are shown in Tables 6–9 for dissolved and total fractions.

2.4.4.1 Total trace elements

The first principal component (PC1) explained 62% of total variation and with positive loadings on Al, As, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, Sb, Th, Tl, U, V, Zn, the Tar River, and the river that's north of Pierre River (Table 6). This PC revealed variation in the overall concentration of trace elements. With the exception for Mo, Re and Sb, the Spearman correlation analysis indicated that there was a significant positive association ($p < 0.05$) among Th and these elements (Table 7). The average scores of PC1 increased from -0.43 in upstream to 2.3 in downstream of the Athabasca River, with the largest change from upstream to midstream (from -0.4 to 1.6), and specifically on the west side of the river (from -0.1 to 2.65). The maximum score for PC1 is reported for the east side of T4 (downstream), and the river that is north of Pierre River, and then the Tar River.

PC2 (with 17% of variation) had positive loadings on As, Fe, Mn, Mo, Ni, Re, and U. The scores were positive for most tributaries, except for the Steepbank River, McKay River, and the Clearwater River. The highest positive loadings were observed for the Re (0.45), Mn (0.42), U (0.4), and the highest scores for north of Pierre River, Pierre River, and Tar River. The negative loadings on PC2 were on Al, Cr, Pb, and Th, which were positively correlated with each other ($p < 0.01$). These loadings increased from east side to the west side, and decreased from upstream to downstream.

PC3 had 8% of the total variation, with positive loadings on As, Co, Fe, and Mn and the highest scores on the east side of T3 (0.7). The highest loadings were observed for Fe, and Mn, and the highest scores were found for the Clearwater River and the Tar River. The Spearman correlation analysis also indicated that there was a significant ($r = 0.97$, $p < 0.01$) positive correlations among these two elements in the total fraction (Table 7). PC3 had negative loadings on Cd, Mo, Ni, Re, Sb, Zn, and negative scores on Ells, Pierre, McKay, Muskeg, Steepbank, and the north of the Pierre River.

Considering all of these results, the tributaries in the AR could be distinguished as sources of the mentioned trace elements in the dissolved and total fractions.

2.4.4.2 Dissolved trace elements

The first principal component (PC1) explained 47% of total variation and with positive loadings on Al, As, Cd, Co, Cu, Fe, Mo, Ni, Pb, Re, Sb, Th, Tl, U, V, Zn, and positive scores on the Horse River, Tar River, Pierre River, and the north of the Pierre River. This PC was probably related to overall concentration of trace elements. The average scores of PC1 increased from -0.4 in upstream to 0.6 in downstream on the Athabasca River, with the largest change from midstream to downstream (from -0.3 to 0.6), and specifically on the middle and the east side of the river. Based on Table 8, the maximum score is reported for the west side of T4 (downstream), the unnamed river that's north of Pierre River (15.6), and the Horse river (2.7), possibly as a result of mixing zones from upstream to downstream.

PC2 (with 23% of variation) had positive loadings on Co, Cr, Mn, Ni, Re, and U, and all of the tributaries except for the Horse River and the Clearwater River. A positive correlation among the Co, and Cr, Mn, Ni, and Re was also confirmed by the Spearman correlation analysis (Table 9). The maximum positive loading was observed for Mn (0.42), and the highest score was on Tar River (7.5). The negative loadings of PC2 were on Al, Cd, Cu, Pb, Th, and V, and the negative scores were on the Horse River and the Clearwater River. Except for the Al, the rest of these elements were positively correlated ($p < 0.05$) with each other (Table 9).

PC3 with 11% of the total variation, had positive loadings on Al, As, Fe, and Th, with the highest score amounts for on the east side of T2 (0.82), and negative loadings on Cu, Cd, Sb, and U. The most negative scores were on Ells River, Tar River and Pierre River. Compared to the other elements with positive loadings, the scores for Fe (0.57) and Th (0.45) were found considerably higher, as was also observed for the Horse River. Indeed, the Steepbank River, the Clearwater River, and Horse River had the highest positive loadings. Given the relative concentrations of trace elements in these tributaries compared to the mainstem, and the fact that the highest score for the AR samples was found for the site on the east side of T2 ~ 20 km downstream of the Clearwater and Horse River inputs, this PC is likely an indicator of inputs from these tributaries. Notably, the other upstream samples had negative scores on PC3, whereas most of the downstream sample scores were between these two extremes. The Spearman correlation analysis indicated that there was a negative association between Fe and Cd, Sb, and U, in the dissolved fraction. Additionally, it showed a significant ($p < 0.05$) positive correlation of As, with Fe and Th (Table 9).

Finally, PC4, with 6% of the total variation had positive loadings on Cr (0.8) and the highest positive scores on the Horse River, Clearwater River, Pierre River, and the Ells River, with the highest scores on the east side of the midstream (T3) and Ells river. The average scores of PC4, like PC1, increased from upstream to downstream on the Athabasca River, with the largest change from upstream to midstream (from -0.15 to -0.28), and on the east side of the river (from -0.2 to 1.4).

2.5 **Discussion**

Industrial activities have been criticized as potential sources of trace elements in the AR and its tributaries (Timoney, 2007; Kelly et al., 2010; Schindler, 2013; Guéguen et al., 2016). The evidence of this assumption, however, is limited. To test this hypothesis, water samples were collected in 2017 from the main stem of the AR. Water samples were collected in autumn when flows of the AR are low and tributaries and groundwater exert more influence. In this study, the spatial variation in total and dissolved concentrations of 18 trace elements in the main stem of the AR were studied to determine whether downstream values were significantly higher than those upstream. The results were then compared with the corresponding Canadian Council of Ministers of the Environment (CCME) and Surface water quality guideline (SWQG) values for the protection of aquatic life. Throughout the text, Alberta SWQG refers to Surface Water Quality Guidelines for the Protection of Aquatic Life outlined in the Environmental Quality Guidelines for Alberta Surface Waters (Alberta Environment & Sustainable Development, 2014) as part of the Canadian Environmental Quality Guidelines set by the Canadian Council of Ministers of the Environment (CCME). Applying these guidelines to the dissolved concentrations of elements is more appropriate than to the total concentrations as the particulate fraction is mostly natural and also of limited bioavailability (Alberta Environment & Sustainable Development, 2014).

The average concentrations (μg L^{-1}) of trace elements in the total and dissolved fraction, upstream, midstream, and downstream of industry and on different sides (west, middle, and east) are presented in Table 1 and 2.

2.5.1 Spatial variation along and across the AR

In the total fraction, Al, As, Co, Cu, Fe, Mn, Ni, Pb, Th, Tl, and V, and in the dissolved fraction As, Co, Cu, Ni, Pb, Re, and V were more abundant downstream compared to upstream of industry. In the total fraction, normalization analysis to Th as a conservative, lithophile element showed no enrichment downstream of industry. In fact, analysis of these more abundant trace elements in the total fraction revealed similar concentrations downstream and upstream of industry, with concentrations proportional to Th. Additionally, the meaningful ($p < 0.01$) correlation among Th, as a physical weathering indicator, and these elements in the total fraction, suggested that natural processes like physical weathering and erosion were the primary sources of metals in the AR, both upstream and downstream of industry (Table 7).

Among the elements with higher concentrations downstream in the total fraction, except for As, and Cu, the rest of these investigated elements were found mainly in the particulate fraction and therefore with limited bioaccessibility (Shilla et al., 2008). Considering the percentages of the particulate fractions for these elements and the PCA analysis shows the contribution of natural sources of trace elements into the river, both upstream and downstream of industry.

Regarding the variations of element concentrations along or across the analyzed transects, it should be noted that T1 and T2 are both considered “upstream” sites, and yet the Clearwater and Horse rivers contribute considerable dissolved concentrations of trace elements (e.g., Fe, Mn) between these two sites. Hence, the averages for the concentration of the elements in the upstream section exhibited high variability, limiting the detection of changes in the concentration of these elements from upstream to downstream.

2.5.1.1 Al, Fe, Mn (colloidal carriers):

Of the investigated elements, colloidal carriers such as Al (the major components of phyllosilicate clays), and Mn and Fe (the dominant components of oxides/oxyhydroxides) are associated with mineral structures. Therefore, they are less prone to being released into natural waters, with limited bioavailability and bioaccessibility (Kostka et al., 1999; Ehlers and Luthy, 2003; Semple et al., 2004; Reeder et al., 2006; Driscoll et al., 2014, Cuss et al, 2019).

With a percentage of 99.7%, almost all of the Al in the river was found in the particulate fraction. Given the strong association of the dissolved Al with suspended solids, which are naturally high in Alberta Rivers, (Tondu, 2017; Alberta Environment & Sustainable Development, 2014), SWQG is applied to the dissolved form of the Al. For water with a pH more than 6.5, the guideline is 50 $\mu g\ L^{-1}$ (CCME, 2018). With dissolved concentration of $6.8 \pm 0.7\ \mu g\ L^{-1}$, Al was far below this guideline. The PCA analysis for total concentration of Al showed the contribution of tributaries (especially the Clearwater, Steepbank and McKay River) to its higher concentration downstream of the AR.

According to the latest reports, long-term SWQGs for dissolved manganese is in a range between 240-270 $\mu g\ L^{-1}$ (CCME, 2019), based on the hardness of the AR which typically changes between 80 and 180 mg $CaCO_3\ L^{-1}$ (Cuss et al., 2019). Moreover, in drinking water (DW), the maximum acceptable total concentration of 120 $\mu g\ L^{-1}$ has been defined for Mn, (Health Canada, 2019). With the average concentrations of 4.79 ± 1.2 and $47.5 \pm 8.1\ \mu g\ L^{-1}$, dissolved and total Mn, respectively, were below these guidelines. In line with the research done by Tondu (2017), total concentration of Mn was also significantly higher downstream compared to upstream. As previous studies showed, the higher total concentration of Mn in the AR could be due to natural (groundwater) or anthropogenic inputs, or a combination of the two. In the total fraction, Mn enters the environment from geological weathering or tributaries (Noton & Saffran, 1995; Headley, 2005; Tondu, 2017), as well as point sources related to coal mining, bitumen extraction, steel manufacturing, pulp and paper mills, and wastewater and sewage discharge (Nagpal, 2001; NPRI, 2016; WHO, 2004; UKTAG, 2012). In our study, with the largest mean score, the PCA analysis showed the contribution of the Tar River to the higher concentrations of Mn in the both dissolved and total fractions. In the colloidal fractions, Mn was mainly found on the east side of the river, probably because of the tributaries such as Clearwater River (66.4 m^3 s^{-1}).

For dissolved Fe, the SWQG is 300 μg L^{-1} (Tondu, 2017; CCME, 2018). Water in the Athabasca River did not exceed this guideline (Dissolved Fe=112.6 ± 32.4 μg L^{-1}). As also observed before, the concentrations of Fe in the total form increased significantly ($p < 0.05$) from upstream to downstream. In the dissolved fraction, Fe just varied across the river, and it was more abundant on the east side. The concentration of Fe in the different colloidal fractions was also more abundant downstream. In the primarily inorganic and mainly ionic fractions its concentration was higher on the east side, while in the DOM-associated fraction it was more abundant on the west side. A possible explanation for the higher concentration of the dissolved Fe on the east side of the river as the PCA and correlation analysis for the dissolved fraction also showed could be the contribution of the tributaries such as the Horse river, which is located on the east side of the river. A similar conclusion was also reached by Tondu (2017) and Cuss et al., (2018). Moreover, the roughly similar constant Cl^-/Fe ratios of 0.065 and 0.08 in the Clearwater River and along the AR, from upstream to downstream up to A5, where it increases due to saline inputs suggested that there is not any other major source of Fe or Cl^- and that dissolved Fe also behaves conservatively in this region of the river (Figure S3).

2.5.1.2 Pb and Th (physical weathering indicators):

In the total, dissolved, and dissolved primarily inorganic fractions, Pb, as a physical weathering indicator, was significantly ($p < 0.05$) more abundant downstream compared to upstream. Considering the particulate percentage (94%), the higher total concentration of Pb downstream of industry can be explained predominantly by natural processes, such as erosion and chemical weathering (Javed et al., 2017). In this fraction, according to the PCA analysis (PC2), an apparent relationship between the concentration of this element and the Steepbank, Clearwater, and McKay River was observed (Table 8). In the dissolved form, again the contribution of tributaries (the Horse and Clearwater Rivers) were observed in the river (PCA analysis, Table 8). On the other hand, almost all of the anthropogenic Pb released to the atmosphere from high-temperature combustion processes is in the sub-micron sizes (Nriagu, 1990). Therefore, the higher dissolved concentration of Pb (the sub-micron fraction) downstream compared to upstream could probably be contributed to the industrial activities. Regardless of the exact source of this element, it should be noted that Pb concentration in the river was far below the available guidelines. The Alberta SWQG for total lead is dependent on hardness (Alberta Environment & Sustainable Development, 2014). For water with a hardness >180 mg/L, the SWQG for total Pb is 7.0 $\mu g\ L^{-1}$ (Tondu, 2017; CCME, 2018). Total lead concentration in the Athabasca River ($0.53 \pm 0.09\ \mu g\ L^{-1}$) were far below this guideline during our survey.

With the same behavior as Pb, the total concentration of Th increased from upstream to downstream, and again the contribution of the Steepbank, Clearwater River, and the McKay River were apparent in this fraction. Thorium is supposed to be highly correlated with TSS in the total fraction (Tondu, 2017), and considering the PCA results, tributaries could be the main sources of total Th into the river. In the primarily organic and inorganic colloidal fractions the concentration of this element increased along the river and it was more abundant on the east side, where the Horse River and the Clearwater River are located. The contribution of these two tributaries were also observed in the PCA analysis for the dissolved fraction of Th. Unfortunately, there is no Alberta or Canada SWQGs for total or dissolved thorium, however, based on the former studies, the dissolved concentration range to be expected in freshwater (pH values generally 5–8) is from 0.01 to 1 $\mu g\ L^{-1}$ (Langmuir and Herman, 1980).

Based on the average dissolved and total concentrations along the AR, almost all of the Pb (94%), and Th (97%) concentrations were associated with the particulate fraction (Figure 3). In previous studies, however, as a result of their association with DOM, these trace elements were found to be mainly in the dissolved fraction (Bau, 1999; Leybourne and Johannesson, 2008).

2.5.1.3 Mo, Re, and V:

Re, Mo, and V considered highly mobile elements, with high formal oxidation states (V, Mo, Re). Therefore, these elements are supposed to be found in mainly ionic forms (Hem, 1985). Rhenium is one of the extremely rare platinum group elements (PGE), with an abundance of 0.2 $\mu g\ kg^{-1}$ in the Upper Continental Crust (Rudnick and Gao, 2014). Unfortunately, there was no guideline for Re (CCME, 2018); however, its dissolved concentration in the AR (3.2 ± 1.02 ng L^{-1}) was comparable to the global average river water (2 ng L^{-1}) (Miller et al., 2011). In the dissolved fraction, its concentration was more abundant downstream compared to both upstream and midstream, specifically on the west side of the river. With an average total concentration of 3.9 ± 0.8 ng L^{-1}, the majority of Re was in the dissolved fraction (Figure 3). With a slight insignificant declining from upstream to midstream, Re dissolved concentration just duplicated ($p < 0.05$) from midstream to downstream (2.3–4.4 ng L^{-1}), which shows a probable source of Re in midstream. Interestingly, and in accordance with findings reported by Shotyk et al., (2017), chloride also exhibited an approximate two-fold increase in concentration downstream probably due to the saline groundwater seepage into the river (Gibson et al., 2011; Jasechko et al., 2012; Gue et al., 2015; Shotyk et al., 2016, 2017). Similarly, the significantly ($p < 0.05$) higher concentration of chloride was observed only on the west side, as a slightly higher concentration of dissolved Re was also observed on this side for upstream to downstream. The PCA results showed the contribution of the tributaries (except the Horse River and the Clearwater River) to higher concentration of Re in dissolved fraction in the AR (Table 8). The only thing that should be noted is, the most significant increase of the chloride was observed from upstream to midstream, which could be a result of inputs from tributaries (Noton & Saffran, 1995), such as the Clearwater river with the most significant influence (179 tonne Cl^{-}/day) on the AR water quality (Tondu, 2017), saline groundwater, with the discharge rate of 100 ± 20 L s^{-1} into the Clearwater River and 134 ± 68 L s^{-1} into the Athabasca River (Gue, et al., 2018), or artesian saline springs (at midstream), or even anthropogenic inputs like treated water (Tondu, 2017) or oil sands operations inputs (Squires et al., 2010; Dube and Wilson, 2013; Lima and Wrona, 2019). While the increase of Re was notable

($p < 0.05$) from midstream to downstream. Unfortunately, at this stage, it remains unclear to which degree the Re increase is attributed to the natural or anthropogenic inputs.

Mo, another mobile element, also known as one of the elements enriched in bitumen, increased significantly ($p < 0.05$) from midstream to downstream, with a higher dissolved concentration on the west side compared to the east side of downstream. Like Re, most of Mo in the main stem AR was found in dissolved form (90%), which was consistent with the findings in other studies (Pokrovsky et al., 2006; Archer and Vance, 2008). Total concentration of Mo, however, did not change along the stream and it was similar to total concentrations of this element reported for sites far upstream of industry (Cooke et al., 2016). The average total concentration of Mo in the AR (0.61 ± 0.07 $\mu g\ L^{-1}$) was less than 1% of the CCME guideline value for the protection of aquatic life (73 $\mu g\ L^{-1}$ Mo; CCME, 2018).

Following the findings reported by Shotyk et al. (2017) for V, our results showed a significant ($p < 0.05$) increase in the total (48%) and dissolved (31%) concentrations of this element, from upstream to downstream of ABS mining and upgrading activities. Unfortunately, there is no CCME guideline for V (CCME, 2018). Therefore, we used "Federal Environmental Quality Guidelines" of 120 $\mu g\ L^{-1}$ total V (FEQG, 1999). Our results showed that the average total concentrations of V along the AR (4.6 ± 0.8 $\mu g\ L^{-1}$) were far below this value. Considering the redox potentials of V (which will be explained in detail, in the size-resolved speciation part), and also the pH of the river water (8.2), V is supposed to be found predominantly in the dissolved fraction, as was observed for Mo and Re (Figure 3) (Paton, 1978; Hem, 1985; Takeno, 2005). However, with the particulate percentage of 94.4%, it was just the opposite and V was dominated by particulate forms (Figure 3). This could show that V was mainly released into the river by physical weathering processes and erosion. The increasing dust generation and emission near the open-pit mines in midstream of the AR which are dominantly produced due to industrial activities (Mullan-Boudreau et al., 2017a, 2017b; Javed and Shotyk, 2018) and atmospheric deposition of V, which is also mostly in the particulate fraction, could be other potential sources of V in the AR in the total fraction (Watson et al., 2014; Shotyk et al., 2014; Wang et al., 2015; Lynam et al., 2015; Shotyk et al., 2016). In the dissolved fraction, however, the PCA analysis showed the contribution of the Horse River and the Clearwater River to the AR (Table 8). Nevertheless, again, it should be noted that the average total concentrations of V along the AR were far below the guidelines (FEQG, 1999).

2.5.1.4 Co, Cu, and Ni (Essential elements):

Co, Cu, and Ni, as essential elements to animals and plants, have limited mobility and solubility in aquatic systems. These trace elements can be adsorbed easily by DOM and inorganic colloidal carriers such as clays and oxyhydroxides (Scholz and Kahler, 2015). In both the total and dissolved fractions, all of these elements were significantly ($p < 0.05$) more abundant downstream compared to upstream. Dissolved concentration of Ni was more abundant on the west side of the river, but for the two other elements the spatial variation across the AR, was not significant ($p < 0.05$) in the total and dissolved fractions. Copper (Cu) was dominantly found on the east side, and Ni on the west side of downstream in primarily organic and inorganic colloidal fractions.

According to Gue et al, (2018), saline groundwater is not considered a major source of total concentrations of these elements to the AR (Gue et al., 2018). However, natural deposition from tributaries especially from the Clearwater, Muskeg, and Ells rivers, with flow rates of 66.4, 0.2, and 6.6 m^3 s^{-1} respectively, could be an acceptable explanation for the higher concentration of these elements in the total fraction (Tondu, 2017). Physical weathering processes and erosion or even anthropogenic deposition might be other potential sources of these elements, specifically on the east side of downstream. Moreover, we observed the contribution of tributaries (the Horse River, Clearwater River, Ells River, Tar River, and Pierre River) for higher dissolved concentrations of Cu, on the east side. The contribution of tributaries were also observed in the total and dissolved concentrations of Ni (Table 6). Tondu (2017) also pointed out the most considerable inputs of total and dissolved Co from the Clearwater River to the river (Tondu, 2017).

Comparison between dissolved and particulate fractions showed that the majority of Co and Ni were found in the particulate forms (83%, and 55%, respectively) (Figure 3) which is generally viewed as less toxic (Ehlers and Luthy, 2003; Semple et al., 2004; Reeder et al., 2006). The average total Ni concentration in the main stem of the AR (2.12 ± 0.53 µg L^{-1}) was similar to the value (1.9 ± 1.4 µg L^{-1}) reported by Guéguen et al., (2011), and it was far below the CCME guideline value for the protection of aquatic life (25 µg L^{-1} Ni; CCME, 2018). Total concentrations of Co and Cu, (0.51 ± 0.09 µg L^{-1}, and 1.42 ± 0.17 µg L^{-1}, respectively) did not exceed Alberta SWQGs (2.5 µg L^{-1}, and 7 µg L^{-1}) either, during the survey (Alberta Environment & Sustainable Development, 2014).

2.5.1.5 As, U (Highly soluble and mobile with variable behaviors):

As and U are highly mobile trace elements, with more than one oxidation form in aquatic systems. So, it is challenging to predict their behavior in the dissolved fraction, as they are potentially associated with the colloidal carriers (Hem, 1985; Li, 2000; Gaillardet et al., 2014; Cuss et al., 2019). In the total, dissolved, and the colloidal fractions, As concentrations were significantly ($p < 0.05$) higher downstream compared to upstream, being more abundant on the east side in the colloidal fractions. In terms of the spatial variation along the river from upstream to downstream, our findings were in contradiction with the results reported by Donner et al. (2017). In their research, they did not find any significant ($p < 0.05$) spatial variation in the As concentration along the river. Additionally, their reported total concentration of As (12.7 ± 2.8 µg L^{-1} in 2014 and 3.3 ± 0.65 µg L^{-1} in 2015) was much higher than what we have found. One reason for these contradictory results could be natural variations, such as the changes in the water flow rate at different years. Another probable difference between these results could be related to our sampling methods, filters and the way our site locations were chosen. In the work done by Donner et al. (2017), samples were gathered from one depth (surface layer), in the middle of the river from upstream to downstream. In contrast, we tried to select the most representative locations along and across the river. They also used used hydrophobic filters instead of hydrophilic filters for the dissolved samples. According to the surface water guideline values, the permissible concentration of total As is 5 µg L^{-1} (CCME, 1999) for the protection of aquatic life. In the AR, with the predominant form of As (V) in surface water, the average concentration of As was 0.67 ± 0.06 µg L^{-1} in the total fraction, and far below the guideline values. As expected due to the limited interaction with clay minerals that have negative surface charges (Paton, 1978), As was predominantly found in the dissolved fraction (Figure 3). Yet, given the particulate percentage of 24%, it seems that there should be some other dominant sources of As into the AR, rather than mineral materials (i.e., > 0.45 µm). The PCA results (PC3) showed the contribution of tributaries to this element's higher concentration in the dissolved and total forms.

2.5.1.6 Cd, Cr, and Tl:

Among these trace elements, the total concentration of Tl increased significantly ($p < 0.05$) from upstream to downstream. However, no significant variation was observed across the river. This element was mostly in the particulate fraction (85.5%). According to Tondu (2017), total Tl is highly associated with TSS, therefore, its higher concentration was likely a result of high levels of suspended solids occurring downstream.

With the average total concentrations of 23.3 ± 3.9 and 20.3 ± 3 ng L^{-1} for Tl and Cd, respectively, these elements were far below the surface water quality guidelines (Table 10). Unfortunately, there is no Water Quality Guideline for the Protection of Aquatic Life for total or dissolved concentration of Cr; however, the maximum acceptable concentration (MAC) of 50 µg L^{-1} has been established for total chromium in drinking water (Pawlisz et al., 1997). The total concentration of Cr in the AR (2.32 ± 0.45 µg L^{-1}) was far below this level.

As mentioned before, the concentrations of the rest of the elements (Cd, Cr, Sb, U and Zn) downstream were comparable to upstream in the both total and dissolved forms. With the exception of dissolved U, which was significantly more abundant ($p < 0.05$) upstream compared to midstream, the other mentioned elements did not have any notable spatial variations across and along the AR. The concentration of these trace elements in the Athabasca River did not exceed the surface water quality guidelines (Table 10).

2.5.2 Size-resolved speciation

2.5.2.1 Measured results

Being associated with mineral structures, as mentioned in the previous part, Al, Fe, and Mn are less prone to be environmentally available (Kostka et al., 1999; Ehlers and Luthy, 2003; Semple et al., 2004; Reeder et al., 2006; Driscoll et al., 2014). In the dissolved form, **Al** was predominantly found in the truly dissolved fraction (< 1kDa) (Table 10), which concurs well with earlier findings (Cuss et al., 2018). In aquatic systems, Al is expected to be in the anion $Al(OH)_4^-$ form, above neutral pH (Hem, 1985). As also reported by Scholz and Kahler (2015), at pH~8-8.4, log(solubility)Al ~ log(solubility) of $Al((OH_2)_3(OH)_3$ is roughly -6.5, so that the maximum dissolved concentration of Al (which is predominantly in ionic form) is supposed to be 8.54 µg L^{-1} (Scholz and Kahler, 2015). With an average Al dissolved concentration of 6.8 ± 0.7 µg L^{-1} and the river pH value of 8.2, the evidence we found pointed to a complete agreement with the previous findings in terms of the pH-dependent behavior and the form of Al. The dissolved fraction of **Mn** was mainly in the ionic form. Unlike Mn, dissolved concentration of **Fe** was predominantly (66%) found in the primarily organic and inorganic colloidal fractions with particles mostly between 10 kDa and 0.45 µm. Likewise, more than half of the dissolved **Pb** (32.7 ± 4.2 ng L^{-1}), as a non-mobile indicator of weathering processes (Cuss et al., 2019), was associated with the primarily organic and inorganic colloidal fractions, and the most bioaccessible (truly dissolved) concentration of Pb was on the order of 5.2 ng L^{-1}. These results are consistent with what has been found in previous findings related to Pb concentrations in the AR (Javed et al., 2017; Cuss et al., 2018). The dissolved fraction of **Th**, another physical weathering indicator, however, was mostly

(60%) associated with the mainly ionic fraction (< 1 kDa). Although it is believed that complexation with organic and inorganic ligands tends to increase thorium mobility, its aqueous geochemistry still remains poorly understood (Langmuir and Herman, 1980; Hem, 1985). The comparison between different behaviors of Th and Pb, both as physical weathering indicators, could possibly show that Fe as a colloidal carrier was not released to the river by physical weathering processes and was likely due to the increasing influence of tributaries or groundwater (Cuss et al., 2019).

Mo and **V** are highly mobile elements, specifically in mainly ionic forms, with high formal oxidation states (Hem, 1985). Considering their redox potentials and also the pH of the water in the AR, the following elements should all be found mainly in the form of anionic species with a negative charge (VO_4^{3-} and MoO_4^{2-}) (Hem, 1985; Takeno, 2005). Therefore, the interaction of these species with clay minerals and dissolved organic matter in the suspended sediments (with negative surface charges) is expected to be limited (Paton, 1978). Consequently, these anionic trace metals should exist predominantly in the dissolved fraction, as could be observed for Mo and Re. Our results showed that in the dissolved fraction, both of these elements were mainly in truly dissolved form (< 1 kDa) with percentages of 90 and 99% for V and Mo, respectively (Figure 3).

Zn, Co, Ni, and Cu with limited mobility and solubility in aquatic systems. Within the dissolved fraction, the majority (> 50%) of **Ni** and **Cu** concentrations were found in the mainly ionic and DOM associated fractions. In natural waters, these essential elements could easily react with DOM and adsorb to the surfaces of inorganic colloidal carriers such as clays and oxyhydroxides (Scholz and Kahler, 2015; Cuss et al., 2019). So they are expected to be predominantly associated with the DOM fraction (1–10 kDa), as also reported by Cuss et al.

(2019). However, as also is shown in the research done by Pokrovsky et al. (2010), some of these trace elements might remain in the ionic fraction (< 1 kDa) possibly associated with the 10–54% of 'truly dissolved' DOC (Pokrovsky et al., 2010).

The concentrations of the mainly ionic fraction of Ni decreased from 1.57 µg L^{-1} in upstream to 0.49 µg L^{-1} in downstream (Table 5, Figure 4). The highest concentration of the mainly ionic fraction was observed on the east side of the upstream, with an average concentration of 2.6 µg L^{-1}. The concentration of the mainly ionic fraction on the east side of the T2 transect, where the Horse River and the Clearwater River have already merged with the main stem of the AR (Figure S4) is 4.9 µg L^{-1}, which shows the influence of tributaries on Ni inputs within this fraction. In the T1 station (transect), which is far upstream, Ni was mainly in DOM associated form, as also reported by Cuss et al., (2019).

In the dissolved phase, **As** could be found in more than one oxidation state (Cuss et al., 2019). Moreover, considering the pH of the water in the AR, As may be found mainly in the form of anionic species with a negative charge ($HAsO_4^{2-}$) (Hem, 1985). In terms of the distribution of As among the colloidal fractions, As is mostly associated with the truly dissolved fraction (< 1 kDa) (96% and 95%, respectively) in both upstream and downstream of industry (Figure 3). This finding is consistent with the research done by Pokrovsky et al. (2010) and Cuss et al. (2019). In the study carried out by Cuss et al. (2019) more than 90% of dissolved As was associated with the primarily < 1 kDa fraction, and < 10% was associated with the 10 kDa–0.45 µm fraction (the primarily inorganic colloids) upstream of industry.

U was predominantly found in the ionic fraction (99%), which is consistent with previous results presented in former studies, in baseflow conditions (Pokrovsky et al., 2010). In several prior studies, the geochemistry of U has been studied extensively (Hem, 1985). The dominant U species depend on the pH-Eh conditions and the concentration and availability of complexing ions (Gascoyne, 1992; Markich, 2002). Based on the solubility and pH-Eh diagrams published by Garrels and Christ (1965), at high pH values, more highly oxidized forms of U, such as the uranyl ion, UO_2^{2+}, or the anionic species are more soluble (Garrels and Christ, 1965). Other findings revealed that at high pH values (>7.5) $UO_2(OH)_3^-$ is calculated to be the dominant uranyl species which is more soluble and much more mobile in natural waters (Silva and Nitsche, 1995; Markich and Brown, 1999; Markich, 2002; Mühr-Ebert et al., 2019). Uranyl complexes with carbonate and sulfate (Sillen and Martell, 1964) might alter the behavior of dissolved uranium. In most natural water, uranium is present in concentrations between 0.1 and 10 μg L^{-1}.

2.5.2.2 Predicted Results (Visual MINTEQ)

The percentage distribution among dissolved and adsorbed species of trace elements, and their concentrations and activities of aqueous inorganic species (mmol L^{-1}) are shown in Table 11a and 11b, respectively. Comparison between the predicted speciation of the investigated trace elements in the AR, and the measured speciation (Table 10) indicated good agreement.

2.6 **Conclusions and implications**

To quantify spatial variations in the concentration of 18 trace elements in the AR, water samples across transects upstream, alongside and downstream from the industrial region, were gathered in fall 2017. The total and dissolved concentrations of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Re, Sb, Tl, Th, U, V, and Zn, and their spatial variations along and across the river were measured in the ultraclean metal-free SWAMP laboratory, using ICP-MS. We also measured the spatial variation in the distribution of trace elements amongst dissolved colloidal fractions using AF4-UV-ICPMS. The analyses and their interpretations lead to the following conclusions:

1- In the total fraction, the concentrations of Al, As, Co, Cu, Fe, Mn, Ni, Pb, Th, Tl, and V were significantly ($p < 0.05$) more abundant downstream of industry, compared to upstream. Among these elements Al, As, Fe, Mn, Ni, and Th were also significantly ($p < 0.05$) more abundant in midstream compared to upstream. In this fraction, the variation in concentration of the investigated elements was not significant ($p < 0.05$) across the transects, at different sides.

2- Among the elements with higher total concentrations downstream, the majority (Al, Co, Fe, Mn, Ni, Pb, Th, Tl, and V) were mainly in the particulate fraction. Moreover, none of these elements showed enrichment downstream, compared to upstream, after normalization to Th, an indicator of silicate minerals.

3- In the dissolved fraction, the concentrations of As, Co, Cu, Ni, Pb, Re, and V were significantly ($p < 0.05$) more abundant downstream of industry, compared to upstream. Dissolved concentrations of Co, Re, and V were also significantly ($p < 0.05$) higher downstream compared to both upstream and midstream. Among the other elements without any spatial variation from upstream to downstream, the dissolved concentrations of Mo increased significantly ($p < 0.05$) from midstream to downstream.

1- In the dissolved form, the concentrations of Mo, Ni, Re, Sb, and U were significantly ($p < 0.05$) higher on the west side of the river, compared to its east side, while dissolved Fe was more abundant on the east side.

2- The distribution of dissolved trace elements amongst colloidal fractions showed that while Fe and Pb were found mainly in the inorganic colloidal fraction (10 kDa to 0.45 μm), the other trace elements occurred mainly (> 50%) in the ionic fraction (< 1 kDa).

Prior studies showed that the water pH and the inputs to the AR, showed tremendous seasonal variations (Porcelli et al., 1997; Pokrovsky et al., 2006, 2012; Dahlqvist et al., 2007; Stolpe et al., 2013; Gaillardet et al., 2014; Marttila et al., 2016). These variations could alter the behavior of trace elements along or across the AR. So, further studies of the seasonal variation in TE concentrations could be so helpful to clearly identify anthropogenic inputs to the AR.

Moreover, comparison of the distribution of trace elements in the colloidal fractions in the mainstem of the Athabasca River with the corresponding results for the tributaries will help to better understand the natural impact of tributaries on water quality in the river.

2.7 **Supporting Information**

For interested readers a detailed description is presented in the Appendix 1. This part include the mean concentrations of DOC, SRMs, measurement recoveries, measured in the samples from the upstream, midstream, and downstream and at different sides of the river (Table S1), Outlier detection methods, for the total and dissolved fractions of datasets (Table S2), the comparison between one sided t-test and MANOVA with the significance level of $p < 0.05$ (Table S3), the normalization analysis graphs for different elements (Figure S2), Fe-Cl^{-1} relationship in the AR (Figure S3), and spatial variation in the Ni colloidal fraction concentrations, for Upstream of Fort McMurray (T1) and Mclean transects (T2), upstream of industry (Figure S4).

2.8 **References**

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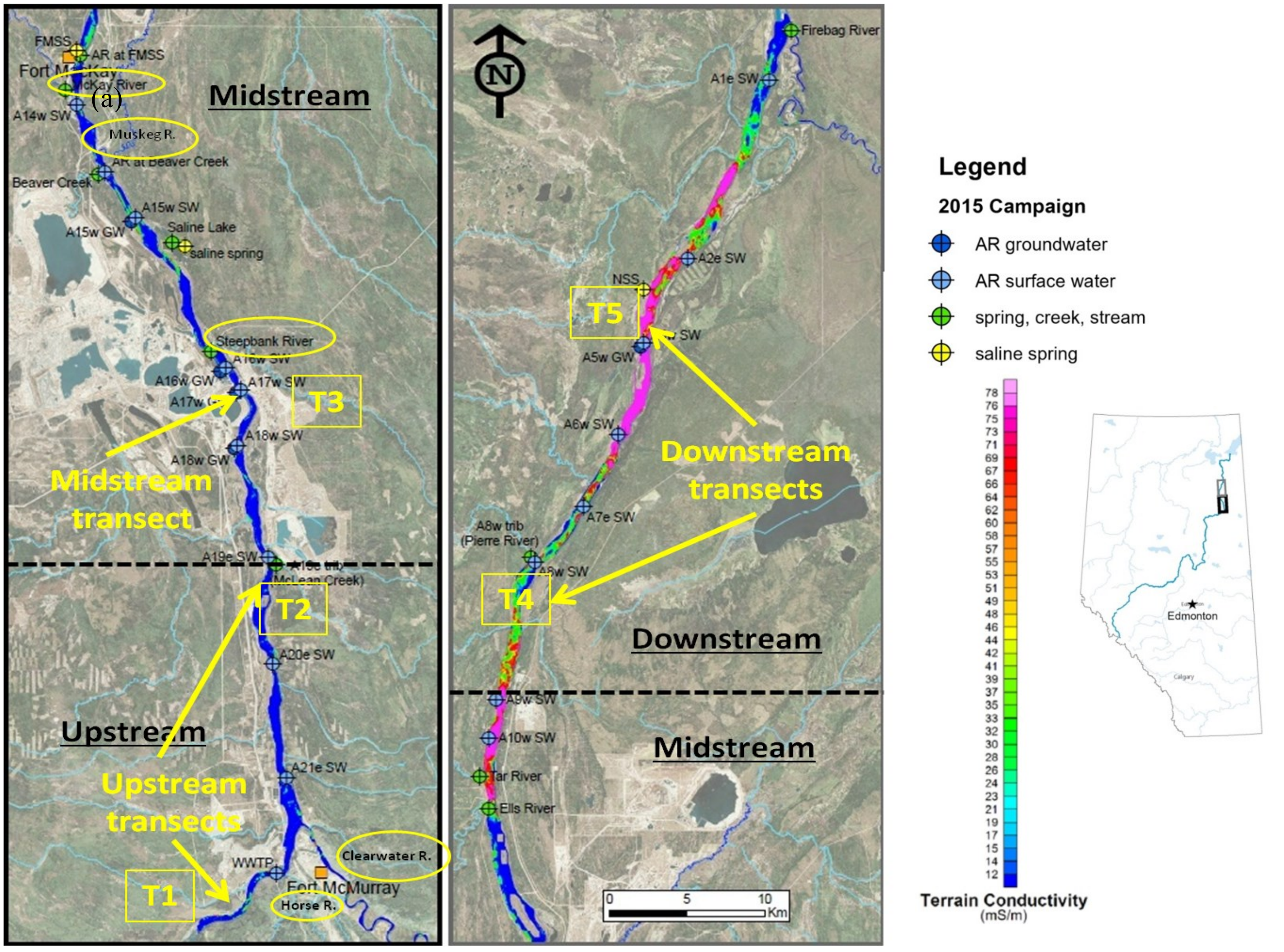
2.9 Figures



(a)

(b)

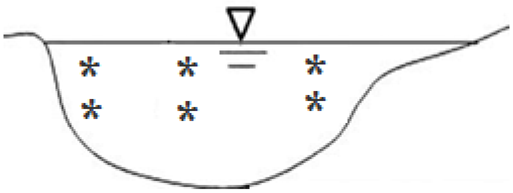


Fig. 1. Map of study area and sampling locations (a). In this map, our study area begins at Fort McMurray moving downstream to Fort MacKay, then from Ells River downstream to the Firebag River. Lower terrain conductivity data were provided by Gibson et al., (2013), modified from Cuss et al., (2018).
The complete perpendicular transect for upstream and downstream of industrial operations (b). Arrow and horizontal lines represent water surface,* designates a sample location at different sides of the river.

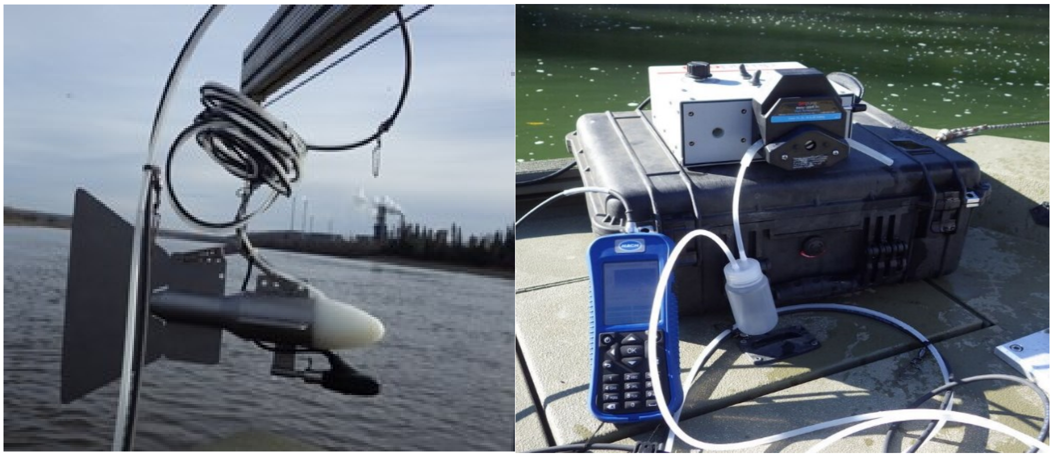


Fig. 2. The SWAMP lab fish, a metal-free depth sampler (left), connected to a peristaltic pump and the velocity meter (right).

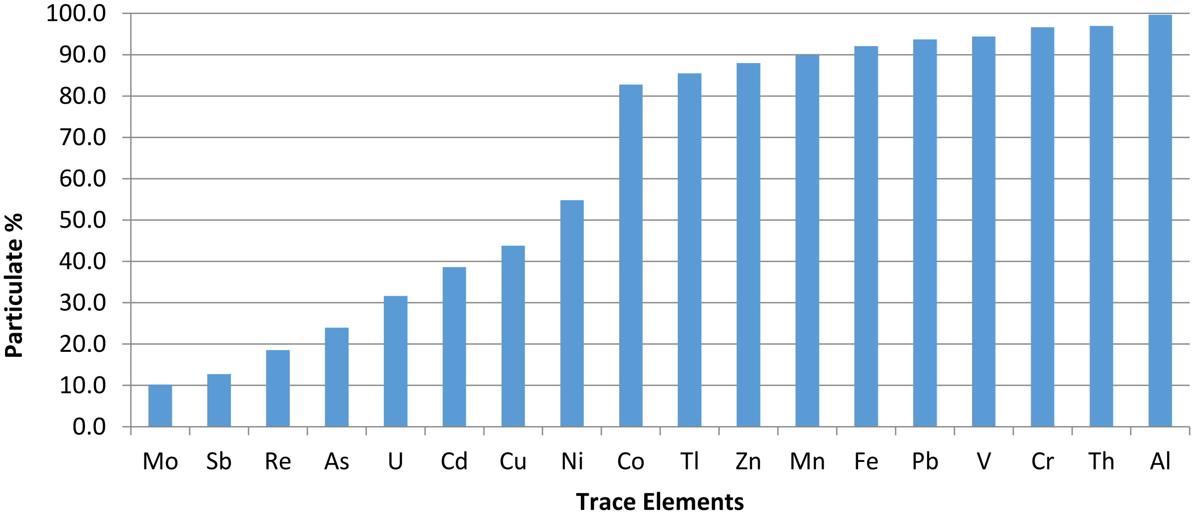


Figure 3. Summary of the relative abundance (percent of total concentration) of trace metals in the main stem of the Athabasca River represented by the particulate fraction (> 0.45 μm).

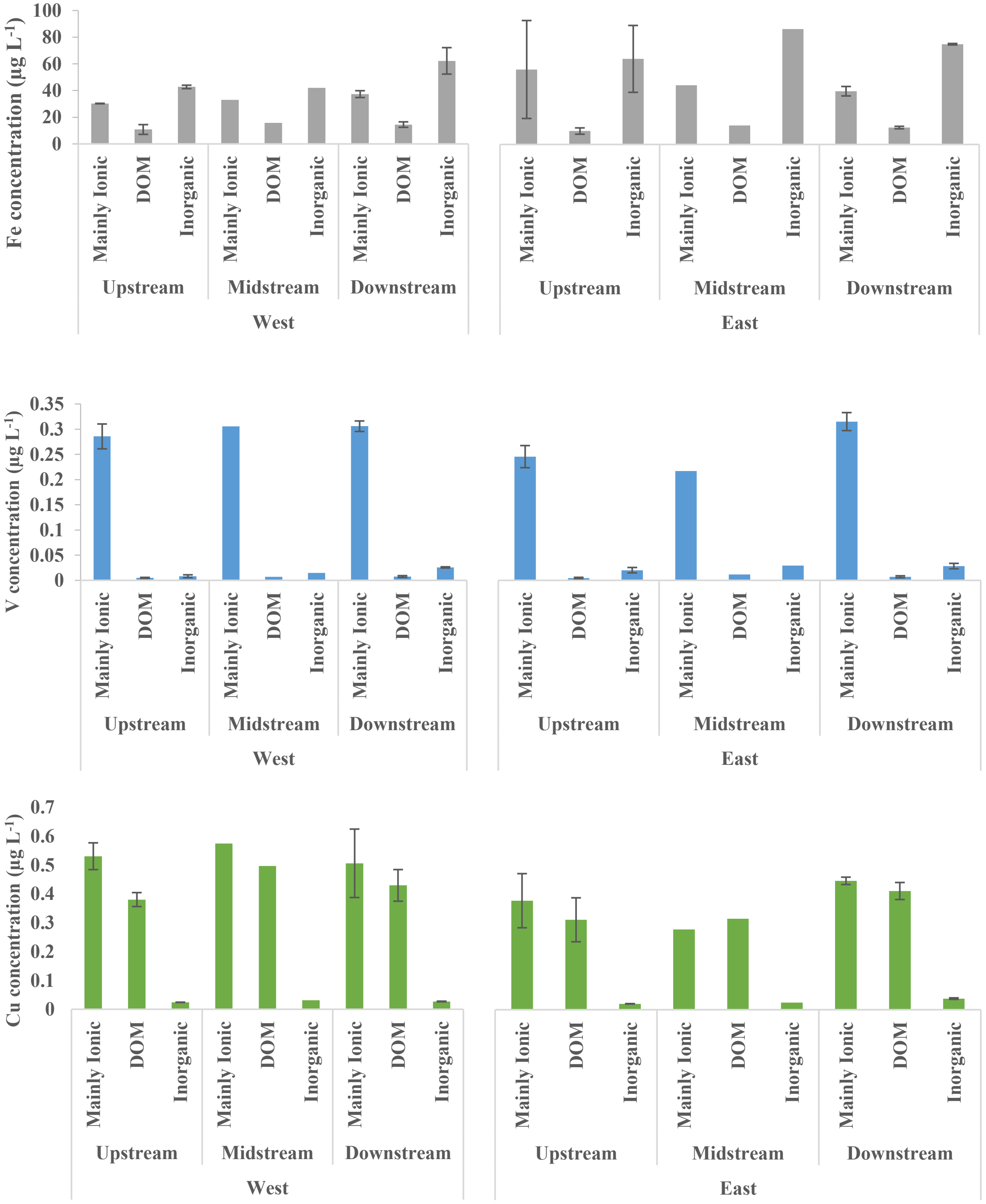


Figure 4. Spatial variation in the distribution of dissolved trace elements amongst colloidal species along and across the Athabasca River. Error bars represent ± one standard deviation).

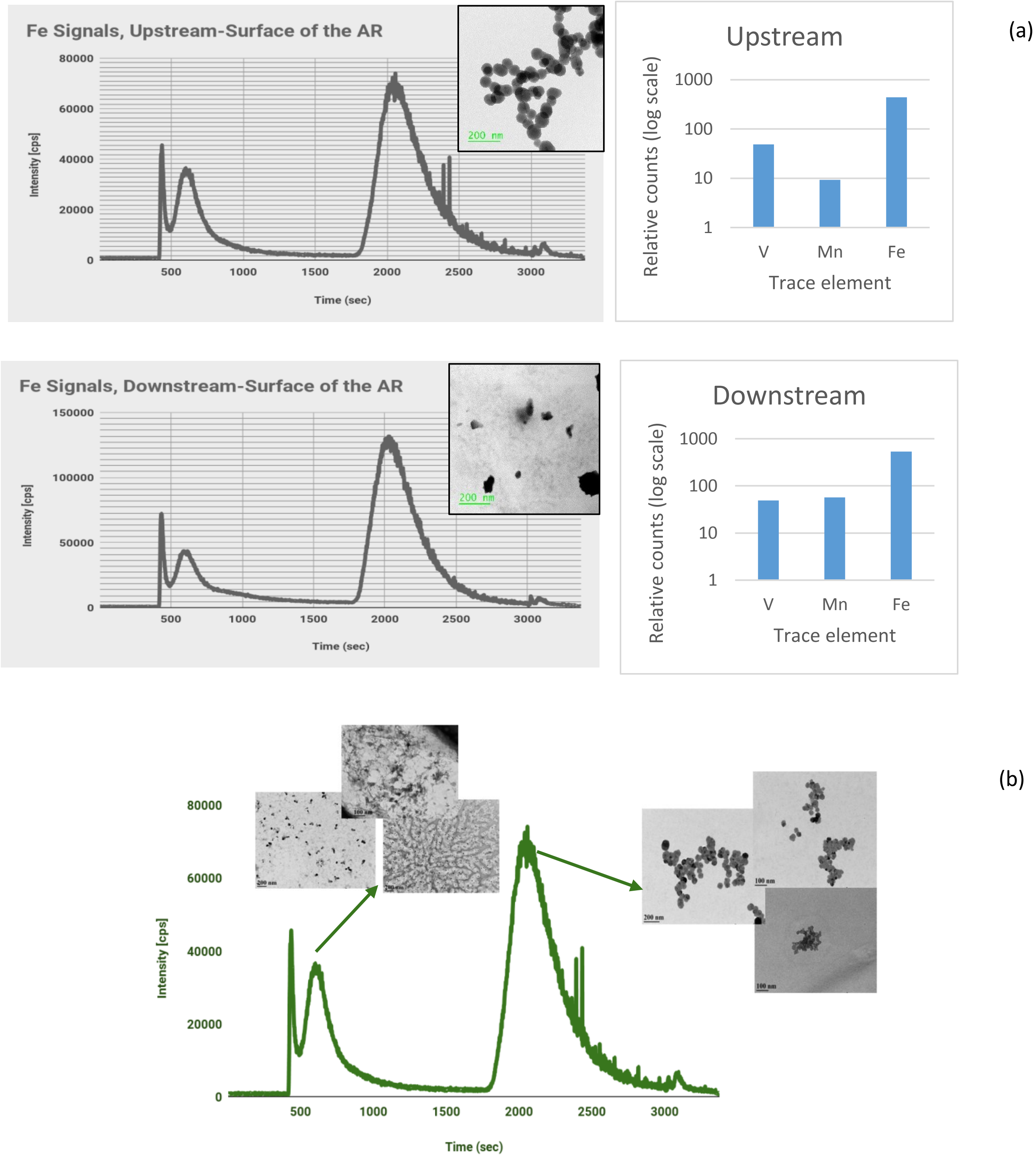


Figure 5. The morphology, composition, and size of the inorganic fraction in upstream and downstream of industry (a), and the shapes and morphology of the particles in organic (1-10 kDa) and inorganic (10 kDa-0.45 μm) fractions using TEM coupled to EDX (b).

2.10 Tables

Table 1. Mean total concentrations of trace elements (µg L^{-1}) in the mainstem (downstream, midstream, and upstream), and in the tributaries.

Trace Elements	**Descriptive Statistics**	**down**			**mid**			**up**		
		East	**Middle**	**West**	**East**	**Middle**	**West**	**East**	**Middle**	**West**
Al	Mean	2475.25	2320.98	2089.76	1905.08	2209.80	2354.45	1575.45	1356.71	1547.10
	Std. Deviation	962.47	503.78	614.55	25.42	129.72	219.78	90.71	177.09	99.37
	N	4	2	4	2	2	2	3	4	4
V	Mean	5.69	5.20	4.88	4.41	5.01	5.29	3.68	3.34	3.64
	Std. Deviation	2.10	0.82	1.40	0.11	0.06	0.32	0.29	0.36	0.20
	N	4	2	4	2	2	2	3	4	4
Cr	Mean	3.07	2.81	2.29	2.05	2.37	2.58	2.35	1.55	1.81
	Std. Deviation	1.66	0.63	1.03	0.09	0.18	0.25	1.00	0.24	0.23
	N	4	2	4	2	2	2	3	4	4
Mn	Mean	54.81	52.71	51.00	51.58	57.41	49.87	38.84	32.95	38.00
	Std. Deviation	16.00	11.41	8.65	1.75	0.93	3.89	5.29	3.02	2.06
	N	4	2	4	2	2	2	3	4	4
Fe	Mean	1715.21	1679.92	1511.45	1533.94	1709.03	1537.82	1128.20	977.69	1045.08
	Std. Deviation	573.28	359.08	353.56	19.83	57.38	92.12	203.63	68.87	20.37
	N	4	2	4	2	2	2	3	4	4
Co	Mean	0.60	0.66	0.53	0.48	0.57	0.56	0.42	0.38	0.41
	Std. Deviation	0.20	0.19	0.12	0.01	0.01	0.01	0.02	0.03	0.00
	N	4	2	4	2	2	2	3	4	4
Ni	Mean	2.88	2.03	1.97	3.19	1.97	2.22	1.59	1.54	1.75
	Std. Deviation	0.79	0.47	0.38	2.00	0.01	0.22	0.03	0.13	0.16
	N	4	2	4	2	2	2	3	4	4
Cu	Mean	1.68	1.50	1.43	1.38	1.46	1.66	1.17	1.20	1.31
	Std. Deviation	0.52	0.31	0.29	0.14	0.13	0.08	0.15	0.10	0.07
	N	4	2	4	2	2	2	3	4	4
Zn	Mean	5.81	7.14	5.01	2.74	4.71	7.02	3.42	5.40	4.16
	Std. Deviation	0.35	1.44	2.03	0.05	2.08	0.04	0.43	1.18	1.47
	N	4	2	4	2	2	2	3	4	4
As	Mean	0.74	0.70	0.68	0.67	0.75	0.73	0.60	0.56	0.59
	Std. Deviation	0.19	0.09	0.09	0.00	0.01	0.00	0.01	0.01	0.02
	N	4	2	4	2	2	2	3	4	4
Mo	Mean	0.61	0.61	0.63	0.49	0.52	0.68	0.64	0.68	0.68
	Std. Deviation	0.04	0.02	0.12	0.03	0.05	0.06	0.16	0.03	0.03
	N	4	2	4	2	2	2	3	4	4
Cd (ng L^{-1})	Mean	24.00	23.50	20.00	16.00	23.00	23.00	16.00	18.25	19.25
	Std. Deviation	8.68	3.54	4.24	1.41	4.24	2.83	0.00	2.50	2.36
	N	4	2	4	2	2	2	3	4	4
Sb (ng L^{-1})	Mean	77.50	60.00	62.50	55.00	70.00	75.00	56.67	67.50	72.50
	Std. Deviation	27.54	14.14	5.00	7.07	14.14	7.07	5.77	12.58	9.57
	N	4	2	4	2	2	2	3	4	4
Re (ng L^{-1})	Mean	4.50	5.00	5.00	3.00	3.00	3.00	3.67	4.25	4.00
	Std. Deviation	0.58	0.00	1.63	0.00	0.00	0.00	0.58	0.50	0.00
	N	4	2	4	2	2	2	3	4	4
Tl (ng L^{-1})	Mean	28.00	27.00	24.50	22.00	25.00	28.00	19.00	17.25	19.25
	Std. Deviation	9.90	5.66	7.00	0.00	1.41	4.24	2.00	2.06	1.50
	N	4	2	4	2	2	2	3	4	4
Pb	Mean	0.63	0.67	0.56	0.50	0.57	0.62	0.43	0.39	0.43
	Std. Deviation	0.20	0.19	0.16	0.02	0.02	0.05	0.01	0.04	0.02
	N	4	2	4	2	2	2	3	4	4
Th	Mean	0.45	0.45	0.39	0.34	0.41	0.45	0.29	0.25	0.28
	Std. Deviation	0.14	0.14	0.10	0.00	0.01	0.05	0.03	0.04	0.03
	N	4	2	4	2	2	2	3	4	4
U	Mean	0.42	0.43	0.40	0.34	0.39	0.48	0.41	0.45	0.47
	Std. Deviation	0.05	0.06	0.05	0.01	0.01	0.04	0.07	0.02	0.02
	N	4	2	4	2	2	2	3	4	4

Table 1 (Continued).

Trace Elements	Little Fishery River	Horse River	Clearwater River	Mclean creek	Steepbank River	Muskeg River	McKay River	Ells River	Tar River	Pierre River	North of Pierre River
Al	398.5	969.7	2073.3	20.3	124.6	97.4	68.6	68.0	1332.8	43.1	2594.2
V	1.3	2.6	4.6	0.3	0.4	0.3	0.4	0.3	3.8	0.4	7.5
Cr	0.9	1.0	2.4	0.2	0.2	0.2	0.1	0.1	1.6	0.1	3.1
Mn	41.3	52.3	71.8	137.1	24.9	51.5	9.9	9.1	299.9	120.0	92.1
Fe	1048.2	1724.2	2216.7	734.2	954.5	270.2	390.3	362.2	3710.1	1186.4	2752.1
Co	0.3	0.3	0.6	0.4	0.2	0.1	0.1	0.1	0.7	0.3	0.8
Ni	1.7	2.1	1.5	1.2	0.6	1.1	1.0	0.9	2.6	3.8	6.7
Cu	0.9	0.8	0.9	0.2	0.2	0.3	0.5	0.4	0.9	0.4	2.3
Zn	1.6	2.7	3.0	0.4	0.6	1.8	0.7	3.9	3.6	1.3	6.8
As	0.5	0.9	0.7	0.3	0.4	0.2	0.5	0.4	1.1	0.8	1.1
Mo	0.2	0.8	0.2	0.3	0.3	0.2	0.4	0.8	1.0	0.9	1.2
Cd (ng L^{-1})	5	6	9	2	2	3	2	2	10	6	33.0
Sb (ng L^{-1})	50	30	20	20	80	40	40	50	60	70	135.0
Re (ng L^{-1})	5	4	1	5	2	8	3	7	10	13	22.0
Tl (ng L^{-1})	6	12	22	2	2	2	2	2	17	3	41.5
Pb (ng L^{-1})	124	332	565	10	46	27	51	57	361	27	866
Th (ng L^{-1})	70	210	390	10	50	10	20	10	240	20	520
U	0.5	0.2	0.1	0.4	0.2	0.4	0.3	0.3	0.9	0.6	0.7

Table 2- Multivariate effects of the variation (location and side) for total concentration of trace elements.

Multivariate Tests[a]

Effect		Value	F	Hypothesis df	Error df	Sig.	Partial Eta Squared
Intercept	Pillai's Trace	1.000	194.322[b]	18.000	1.000	0.056	1.000
	Wilks' Lambda	0.000	194.322[b]	18.000	1.000	0.056	1.000
	Hotelling's Trace	3497.793	194.322[b]	18.000	1.000	0.056	1.000
	Roy's Largest Root	3497.793	194.322[b]	18.000	1.000	0.056	1.000
loc	Pillai's Trace	1.915	2.512	36.000	4.000	0.191	0.958
	Wilks' Lambda	0.001	1.893[b]	36.000	2.000	0.406	0.971
	Hotelling's Trace	102.189	0.000	36.000	0.000		0.981
	Roy's Largest Root	89.619	9.958[c]	18.000	2.000	0.095	0.989
Side	Pillai's Trace	1.812	1.069	36.000	4.000	0.545	0.906
	Wilks' Lambda	0.005	.728[b]	36.000	2.000	0.734	0.929
	Hotelling's Trace	35.483	0.000	36.000	0.000		0.947
	Roy's Largest Root	30.076	3.342[c]	18.000	2.000	0.255	0.968
loc * Side	Pillai's Trace	3.165	0.842	72.000	16.000	0.701	0.791
	Wilks' Lambda	0.000	0.626	72.000	6.289	0.843	0.873
	Hotelling's Trace			72.000			
	Roy's Largest Root	65.207	14.490[c]	18.000	4.000	0.009	0.985

a. Design: Intercept + loc + Side + loc * Side

b. Exact statistic

c. The statistic is an upper bound on F that yields a lower bound on the significance level.

Table 3. Mean dissolved concentrations of trace elements (µg L^{-1}) in the mainstem (downstream, midstream, and upstream), and in the tributaries.

Trace Elements	**Descriptive Statistics**	**down**			**mid**			**up**		
		East	**Middle**	**West**	**East**	**Middle**	**West**	**East**	**Middle**	**West**
Al	Mean	6.21	5.82	7.09	7.55	6.00	8.01	6.78	7.14	6.96
	Std. Deviation	1.19	0.77	0.87		1.73	0.16	0.18	1.62	0.69
	N	5	4	4	1	3	2	4	5	4
V	Mean	0.29	0.28	0.30	0.24	0.25	0.28	0.21	0.22	0.23
	Std. Deviation	0.02	0.02	0.02		0.02	0.00	0.01	0.02	0.01
	N	5	4	4	1	3	2	4	5	4
Cr	Mean	0.08	0.08	0.09	0.17	0.06	0.06	0.06	0.05	0.06
	Std. Deviation	0.05	0.06	0.06		0.01	0.00	0.02	0.00	0.03
	N	5	4	4	1	3	2	4	5	4
Mn	Mean	5.46	5.28	6.75	5.43	4.32	3.87	4.34	2.28	5.38
	Std. Deviation	0.54	0.20	0.57		1.85	0.13	2.56	0.65	4.30
	N	5	4	4	1	3	2	4	5	4
Fe	Mean	120.89	103.64	110.94	173.73	150.72	90.62	121.99	70.37	70.62
	Std. Deviation	11.31	4.41	9.08		21.69	1.55	68.75	6.20	4.58
	N	5	4	4	1	3	2	4	5	4
Co	Mean	0.10	0.10	0.10	0.08	0.08	0.09	0.08	0.08	0.09
	Std. Deviation	0.01	0.01	0.01		0.01	0.00	0.00	0.01	0.01
	N	5	4	4	1	3	2	4	5	4
Ni	Mean	1.05	0.96	1.13	0.92	0.87	1.12	0.79	0.89	0.91
	Std. Deviation	0.14	0.10	0.11		0.04	0.06	0.08	0.02	0.04
	N	5	4	4	1	3	2	4	5	4
Cu	Mean	0.91	0.88	0.98	0.64	0.70	0.98	0.61	0.73	0.77
	Std. Deviation	0.15	0.17	0.19		0.05	0.00	0.14	0.03	0.01
	N	5	4	4	1	3	2	4	5	4
Zn	Mean	0.62	0.69	0.66	0.39	0.36	0.65	0.55	0.77	0.76
	Std. Deviation	0.13	0.32	0.14		0.04	0.10	0.01	0.31	0.19
	N	5	4	4	1	3	2	4	5	4
As	Mean	0.53	0.51	0.55	0.49	0.51	0.56	0.47	0.49	0.48
	Std. Deviation	0.02	0.03	0.04		0.03	0.01	0.01	0.02	0.01
	N	5	4	4	1	3	2	4	5	4
Mo	Mean	0.54	0.57	0.61	0.46	0.45	0.57	0.52	0.61	0.62
	Std. Deviation	0.02	0.01	0.02		0.02	0.00	0.09	0.01	0.01
	N	5	4	4	1	3	2	4	5	4
Cd (ng L^{-1})	Mean	13.20	13.00	14.50	9.00	10.33	15.50	10.25	12.80	13.75
	Std. Deviation	3.03	3.46	3.51	0.00	1.15	0.71	2.63	1.30	0.96
	N	5	4	4	1	3	2	4	5	4
Sb (ng L^{-1})	Mean	58.00	57.50	62.50	50.00	50.00	70.00	47.50	60.00	65.00
	Std. Deviation	4.47	9.57	9.57	0.00	0.00	0.00	9.57	0.00	5.77
	N	5	4	4	1	3	2	4	5	4
Re (ng L^{-1})	Mean	3.60	5.00	4.75	2.00	2.00	3.00	2.50	3.00	3.00
	Std. Deviation	0.89	0.82	0.50	0.00	0.00	0.00	0.58	0.00	0.00
	N	5	4	4	1	3	2	4	5	4
Tl (ng L^{-1})	Mean	3.60	3.50	3.50	3.00	3.33	4.00	3.00	3.00	3.50
	Std. Deviation	0.55	0.58	0.58	0.00	0.58	0.00	0.82	0.00	0.58
	N	5	4	4	1	3	2	4	5	4
Pb (ng L^{-1})	Mean	37.80	34.50	38.75	32.00	31.00	36.50	26.25	28.20	29.25
	Std. Deviation	5.07	3.70	3.77	0.00	5.20	0.71	1.26	4.55	0.50
	N	5	4	4	1	3	2	4	5	4
Th (ng L^{-1})	Mean	14.00	10.00	12.50	10.00	10.00	10.00	10.00	10.00	10.00
	Std. Deviation	5.48	0.00	5.00	0.00	0.00	0.00	0.00	0.00	0.00
	N	5	4	4	1	3	2	4	5	4
U	Mean	0.29	0.27	0.31	0.22	0.24	0.34	0.26	0.33	0.33
	Std. Deviation	0.02	0.02	0.02		0.01	0.00	0.05	0.03	0.03
	N	5	4	4	1	3	2	4	5	4

Table 3 (Continued).

Trace Elements	**Little Fishery River**	**Horse River**	**Clearwater River**	**Mclean creek**	**Steepbank River**	**Muskeg River**	**McKay River**	**Ells River**	**Tar River**	**Pierre River**	**North of Pierre River**
Al	2.9	12.4	7.1	2.7	4.2	1.7	4.3	3.1	3.2	2.5	14.1
V	0.2	0.3	0.2	0.2	0.2	0.1	0.2	0.1	0.2	0.2	0.3
Cr	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.1	0.2	0.1
Mn	27.5	23.9	16.6	130.8	13.8	36.2	5.8	7.2	244.5	95.2	87.1
Fe	188.4	630.1	314.9	56.9	471.9	72.5	186.2	145.5	38.5	64.7	746.1
Co	0.1	0.1	0.1	0.4	0.1	0.1	0.1	0.1	0.3	0.2	0.4
Ni	1.1	1.2	0.4	1.3	0.5	0.6	1.0	1.2	1.9	3.4	9.2
Cu	0.5	0.6	0.2	0.2	0.2	0.2	0.5	0.5	0.4	0.4	1.6
Zn	0.3	0.6	0.5	0.3	0.5	0.2	0.4	1.0	1.1	0.3	1.7
As	0.5	0.9	0.4	0.4	0.5	0.2	0.5	0.5	0.6	0.7	0.9
Mo	0.2	0.8	0.2	0.3	0.3	0.2	0.4	0.9	1.0	0.9	1.5
Cd (ng L^{-1})	2	4	3	2	1	1	2	2	2	3	17
Sb (ng L^{-1})	50	30	20	30	20	20	40	80	60	80	150
Re (ng L^{-1})	4	3	1	4	1	6	3	6	8	10	29
Tl (ng L^{-1})	3	3	1	2	1	1	2	2	3	3	15
Pb (ng L^{-1})	6	61	24	3	11	1	21	21	2	1	69
Th (ng L^{-1})	10	40	10	10	20	0	10	0	0	0	30
U	0.4	0.1	0.1	0.4	0.1	0.3	0.3	0.3	0.8	0.5	0.8

Table 4- Multivariate effects of the variation (location and side) for dissolved concentration of trace elements.

Multivariate Tests[a]

Effect		Value	F	Hypothesis df	Error df	Sig.	Partial Eta Squared
Intercept	Pillai's Trace	1.000	5172.987[b]	18.000	6.000	0.000	1.000
	Wilks' Lambda	0.000	5172.987[b]	18.000	6.000	0.000	1.000
	Hotelling's Trace	15518.960	5172.987[b]	18.000	6.000	0.000	1.000
	Roy's Largest Root	15518.960	5172.987[b]	18.000	6.000	0.000	1.000
loc	Pillai's Trace	1.915	8.794	36.000	14.000	0.000	0.958
	Wilks' Lambda	0.000	26.439[b]	36.000	12.000	0.000	0.988
	Hotelling's Trace	544.382	75.609	36.000	10.000	0.000	0.996
	Roy's Largest Root	533.309	207.398[c]	18.000	7.000	0.000	0.998
Side	Pillai's Trace	1.799	3.488	36.000	14.000	0.008	0.900
	Wilks' Lambda	0.007	3.795[b]	36.000	12.000	0.008	0.919
	Hotelling's Trace	28.778	3.997	36.000	10.000	0.012	0.935
	Roy's Largest Root	23.522	9.148[c]	18.000	7.000	0.003	0.959
loc * Side	Pillai's Trace	2.751	1.102	72.000	36.000	0.382	0.688
	Wilks' Lambda	0.002	1.348	72.000	25.950	0.200	0.783
	Hotelling's Trace	23.882	1.493	72.000	18.000	0.171	0.857
	Roy's Largest Root	15.322	7.661[c]	18.000	9.000	0.002	0.939

a. Design: Intercept + loc + Side + loc * Side

b. Exact statistic

c. The statistic is an upper bound on F that yields a lower bound on the significance level.

Table 5. Distribution of the investigated trace element concentrations (µg L^{-1}) among the colloidal fractions (mainly ionic/truly dissolved fraction, mainly organic (DOM), and mainly inorganic fractions).

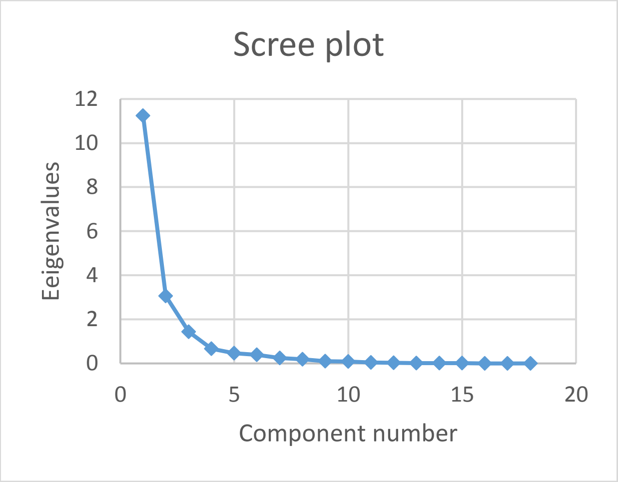
Concentration.(µg/L)			**Al**	**V**	**Mn**	**Fe**	**Co**	**Ni**	**Zn**	**Cu**	**As**	**Mo**	**Pb**	**Th**	**U**
West	**Upstream**	**mainly Ionic**	< LOD	0.286	5.431	30.271	0.082	0.542	< LOD	0.530	0.693	0.748	0.006	0.006	0.411
		stdv	< LOD	0.025	3.852	0.180	0.003	0.022	< LOD	0.046	0.085	0.032	0.001	0.001	0.036
		DOM	< LOD	0.005	0.085	10.811	0.022	0.438	< LOD	0.380	0.014	0.003	0.001	0.002	0.004
		stdv	< LOD	0.001	0.009	3.648	0.003	0.014	< LOD	0.024	0.004	0.003	0.000	0.001	0.001
		mainly Inorganic	< LOD	0.008	0.238	42.732	0.001	0.007	< LOD	0.024	0.010	0.000	0.020	0.004	0.000
		stdv	< LOD	0.003	0.012	1.297	0.001	0.007	< LOD	0.000	0.010	0.000	0.003	0.002	0.000
	Midstream	**mainly Ionic**	< LOD	0.306	2.911	32.959	0.084	0.580	< LOD	0.574	0.642	0.640	0.001	0.006	0.343
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
		DOM	< LOD	0.007	0.105	15.708	0.026	0.492	< LOD	0.496	0.018	0.015	0.002	0.003	0.004
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
		mainly Inorganic	< LOD	0.015	0.382	42.007	0.000	0.017	< LOD	0.031	0.000	0.000	0.025	0.004	0.000
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
	Downstream	**mainly Ionic**	< LOD	0.306	5.016	37.328	0.093	0.459	< LOD	0.506	0.605	0.665	0.002	0.007	0.319
		stdv	< LOD	0.010	0.674	2.556	0.007	0.012	< LOD	0.119	0.005	0.019	0.001	0.000	0.010
		DOM	< LOD	0.008	0.116	14.496	0.016	0.510	< LOD	0.429	0.018	0.000	0.001	0.002	0.003
		stdv	< LOD	0.002	0.001	2.042	0.002	0.041	< LOD	0.055	0.000	0.000	0.000	0.001	0.001
		mainly Inorganic	< LOD	0.026	0.465	62.263	0.002	0.018	< LOD	0.027	0.017	0.000	0.023	0.002	0.001
		stdv	< LOD	0.001	0.049	9.914	0.000	0.000	< LOD	0.001	0.002	0.000	0.002	0.001	0.000
Middle	**Upstream**	**mainly Ionic**	< LOD	0.238	2.248	22.410	0.074	0.471	< LOD	0.392	0.569	0.680	0.002	0.004	0.356
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
		DOM	< LOD	0.006	0.048	7.097	0.014	0.356	< LOD	0.351	0.029	0.008	0.001	0.003	0.004
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
		mainly Inorganic	< LOD	0.014	0.212	41.098	0.000	0.012	< LOD	0.018	0.004	0.000	0.016	0.003	0.000
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
	Midstream	**mainly Ionic**	< LOD	0.270	5.794	56.034	0.073	0.053	< LOD	0.394	0.611	0.525	0.005	0.007	0.255
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
		DOM	< LOD	0.005	0.141	14.425	0.022	0.880	< LOD	0.387	0.040	0.000	0.000	0.002	0.005
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
		mainly Inorganic	< LOD	0.034	0.422	99.077	0.000	0.055	< LOD	0.042	0.000	0.013	0.022	0.006	0.000
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
	Downstream	**mainly Ionic**	< LOD	0.285	4.642	36.636	0.080	0.418	< LOD	0.478	0.593	0.624	0.001	0.006	0.303
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
		DOM	< LOD	0.007	0.089	10.018	0.023	0.607	< LOD	0.487	0.024	0.008	0.001	0.003	0.005
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
		mainly Inorganic	< LOD	0.030	0.350	66.721	0.001	0.035	< LOD	0.037	0.000	0.000	0.024	0.004	0.000
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000

Table 5 (Continued).

East	**Upstream**	**mainly Ionic**	< LOD	0.246	5.114	56.656	0.139	2.601	< LOD	0.396	0.538	0.605	0.011	0.018	0.313
		stdv	< LOD	0.022	3.464	37.017	0.080	2.312	< LOD	0.098	0.026	0.043	0.013	0.012	0.047
		DOM	< LOD	0.004	0.093	10.128	0.018	0.467	< LOD	0.327	0.015	0.002	0.001	0.002	0.002
		stdv	< LOD	0.002	0.026	2.385	0.008	0.087	< LOD	0.080	0.012	0.002	0.000	0.001	0.002
		mainly Inorganic	< LOD	0.020	0.217	64.668	0.000	0.008	< LOD	0.021	0.011	0.000	0.016	0.002	0.000
		stdv	< LOD	0.005	0.047	25.273	0.000	0.008	< LOD	0.000	0.003	0.000	0.001	0.001	0.000
	Midstream	**mainly Ionic**	< LOD	0.217	0.929	44.826	0.040	0.226	< LOD	0.291	0.515	0.488	0.002	0.006	0.227
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
		DOM	< LOD	0.012	0.095	14.306	0.011	0.461	< LOD	0.330	0.032	0.000	0.001	0.001	0.004
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
		mainly Inorganic	< LOD	0.029	0.299	87.312	0.001	0.021	< LOD	0.025	0.026	0.000	0.019	0.001	0.000
		stdv	< LOD	0.000	0.000	0.000	0.000	0.000	< LOD	0.000	0.000	0.000	0.000	0.000	0.000
	Downstream	**mainly Ionic**	< LOD	0.315	5.904	40.251	0.086	0.524	< LOD	0.468	0.672	0.638	0.004	0.006	0.326
		stdv	< LOD	0.018	1.276	3.583	0.006	0.091	< LOD	0.013	0.045	0.068	0.001	0.001	0.035
		DOM	< LOD	0.007	0.121	12.781	0.023	0.471	< LOD	0.431	0.021	0.005	0.001	0.003	0.004
		stdv	< LOD	0.002	0.044	0.937	0.009	0.037	< LOD	0.031	0.004	0.005	0.000	0.001	0.002
		mainly Inorganic	< LOD	0.028	0.466	75.780	0.000	0.011	< LOD	0.040	0.018	0.000	0.026	0.005	0.000
		stdv	< LOD	0.005	0.110	0.544	0.000	0.011	< LOD	0.003	0.002	0.000	0.003	0.001	0.000
LOD			**5.962**	**0.01**	**0.246**	**1.54**	**0.026**	**0.212**	**5.746**	**0.219**	**0.027**	**0.015**	**0.013**	**0.653**	**0.003**
SRMs recovery (%)	**NIST 1640a**		**96**	**99**	**99**	**97**	**98**	**97**	**100**	**100**	**99**	**99**	**97**	**N/A**	**96**
	SPS SW2		**100**	**100**	**99**	**100**	**99**	**97**	**94**	**100**	**100**	**100**	**98**	**100**	**99**

Table 6- PCA analysis of the total concentration of trace elements (Variable loadings, average score by stream sections, scree plot).

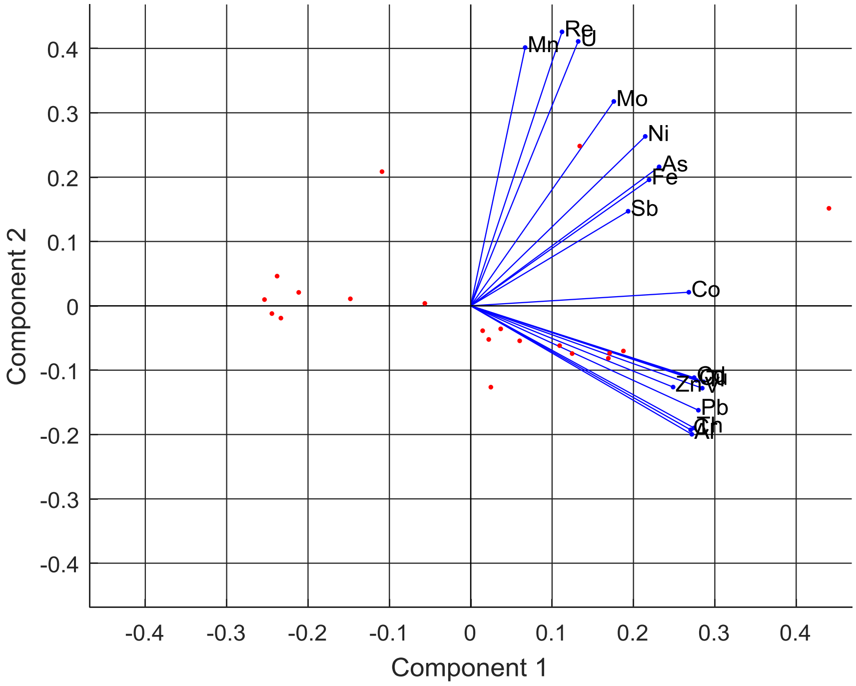
Coeff	PC1	PC2	PC3
Al	0.28	-0.18	0.09
V	0.29	-0.12	0.06
Cr	0.27	-0.16	0.08
Mn	0.06	0.42	0.49
Fe	0.22	0.20	0.43
Co	0.28	0.01	0.23
Ni	0.19	0.27	-0.15
Cu	0.28	-0.12	-0.12
Zn	0.22	-0.12	-0.22
As	0.24	0.22	0.19
Mo	0.16	0.32	-0.27
Cd	0.27	-0.12	-0.19
Sb	0.20	0.12	-0.43
Re	0.08	0.45	-0.27
Tl	0.29	-0.11	0.00
Pb	0.29	-0.15	0.04
Th	0.28	-0.17	0.07
U	0.14	0.40	-0.12



Location	Side	PC1	PC2	PC3
UP	E	-0.59	-0.64	0.12
	M	-0.60	-0.34	-1.02
	W	-0.10	-0.25	-0.83
MID	E	0.38	-0.62	0.71
	M	1.73	-0.98	0.60
	W	2.65	-0.88	-0.26
DOWN	E	2.99	-0.76	0.02
	M	2.59	-1.00	0.29
	W	1.38	-0.67	0.15
TRIBS		-2.56	1.52	0.38

Location	PC1	PC2	PC3
UP	-0.43	-0.41	-0.57
MID	1.59	-0.83	0.35
DOWN	2.32	-0.81	0.15
TRIBS.	-2.56	1.52	0.38

Table 6 (continued).



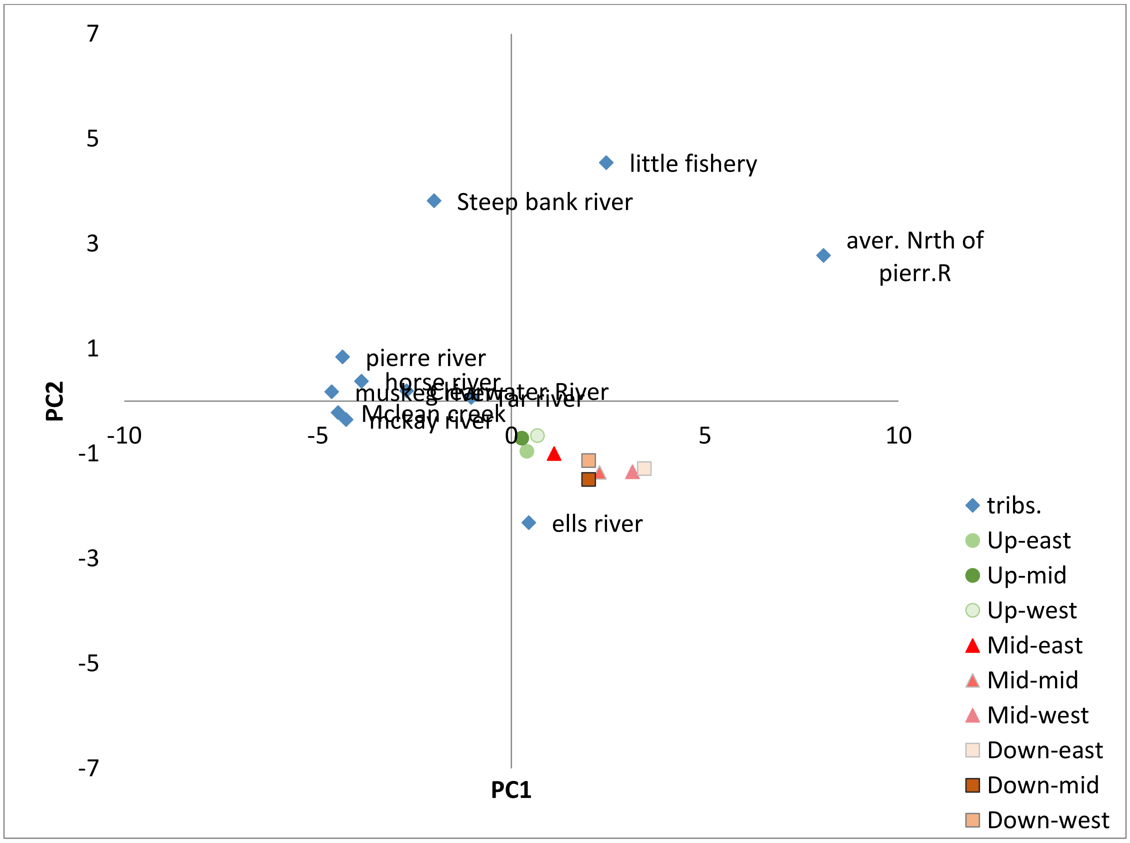


Table 7- Spearman Correlation coefficients for the total trace elements.

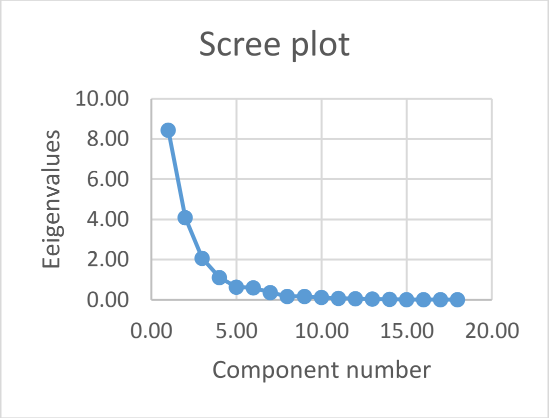
.991**																
.869**	.860**															
.889**	.875**	.712**														
.922**	.914**	.743**	.969**													
.953**	.937**	.784**	.968**	.959**												
.738**	.749**	.618**	.736**	.737**	.746**											
.730**	.740**	.632**	.743**	.665**	.768**	.623**										
0.37	.385*	0.34	0.14	0.22	0.29	0.19	0.23									
.895**	.882**	.794**	.928**	.879**	.941**	.683**	.856**	0.15								
-0.21	-0.18	0.07	-.396*	-.386*	-0.30	-0.17	0.08	0.34	-0.19							
.523**	.538**	.443*	.519**	.493**	.588**	.459*	.724**	.576**	.621**	0.21						
0.21	0.20	0.22	0.20	0.13	0.24	0.25	.576**	.406*	0.35	.418*	.770**					
-0.02	0.00	-0.07	-0.14	-0.11	-0.07	-0.07	0.00	.392*	-0.14	0.31	0.19	0.04				
.980**	.983**	.877**	.842**	.880**	.914**	.689**	.741**	.409*	.871**	-0.11	.550**	0.24	0.01			
.983**	.985**	.814**	.879**	.918**	.939**	.740**	.739**	.402*	.860**	-0.21	.520**	0.16	0.06	.968**		
.963**	.966**	.779**	.864**	.895**	.925**	.718**	.716**	.407*	.847**	-0.21	.509**	0.18	0.08	.959**	.982**	
-0.07	-0.05	0.14	-0.19	-0.25	-0.08	-0.03	0.37	0.34	0.04	.812**	.454*	.689**	0.18	0.01	-0.08	-0.07

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 8- PCA analysis of the dissolved concentration of trace elements (Variable loadings, average score by stream sections, scree plot, and loading plots).

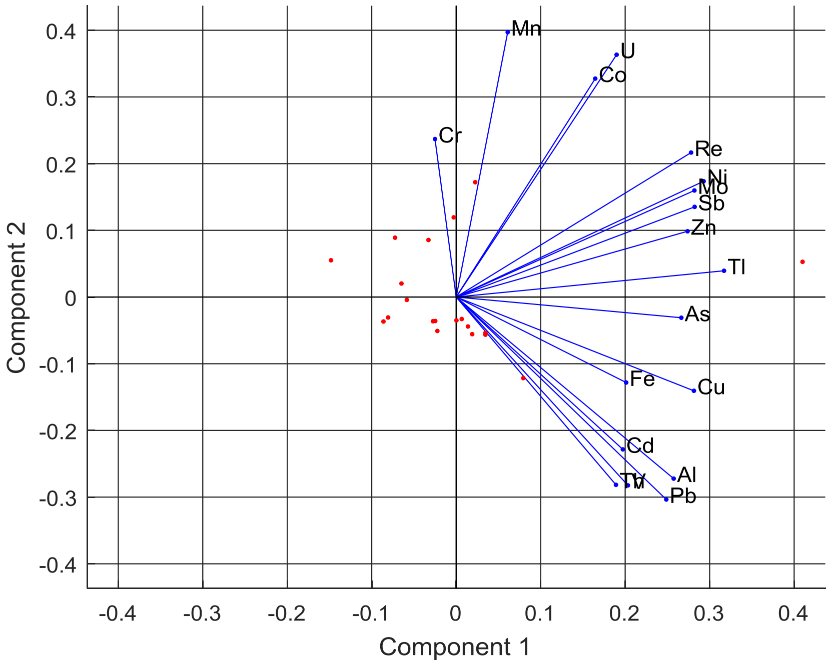
Coeff	PC1	PC2	PC3	PC4
Al	0.24	-0.25	0.17	-0.03
V	0.20	-0.33	-0.09	-0.10
Cr	0.07	0.18	0.03	0.80
Mn	0.06	0.42	0.03	-0.16
Fe	0.18	0.00	0.57	-0.02
Co	0.20	0.34	0.09	-0.23
Ni	0.30	0.19	0.08	-0.12
Cu	0.27	-0.22	-0.26	-0.02
Zn	0.25	0.04	-0.14	0.17
As	0.28	0.02	0.21	0.23
Mo	0.29	0.12	-0.08	0.23
Cd	0.18	-0.31	-0.37	-0.07
Sb	0.30	0.06	-0.27	0.14
Re	0.28	0.22	0.02	-0.12
Tl	0.32	0.01	-0.04	-0.17
Pb	0.24	-0.32	0.09	0.06
Th	0.18	-0.21	0.45	-0.09
U	0.20	0.32	-0.25	-0.18



Location	Side	PC1	PC2	PC3	PC4
UP	E	-1.17	-0.42	0.08	-0.23
	M	-0.19	-0.59	-0.78	-0.18
	W	0.04	-0.53	-0.98	-0.05
MID	E	-0.87	-0.52	0.65	1.40
	M	-1.00	-0.88	0.21	-0.35
	W	1.01	-1.36	-1.05	-0.20
DOWN	E	0.33	-1.14	-0.30	-0.15
	M	0.29	-0.89	-0.68	0.11
	W	1.05	-1.24	-0.64	0.15
TRIBS.		-0.03	2.46	1.39	0.14

Location	PC1	PC2	PC3	PC4
UP	-0.44	-0.51	-0.56	-0.15
MID	-0.28	-0.92	-0.06	0.28
DOWN	0.56	-1.09	-0.54	0.04
TRIBS.	-0.03	2.46	1.39	0.14

Table 8 (continued).



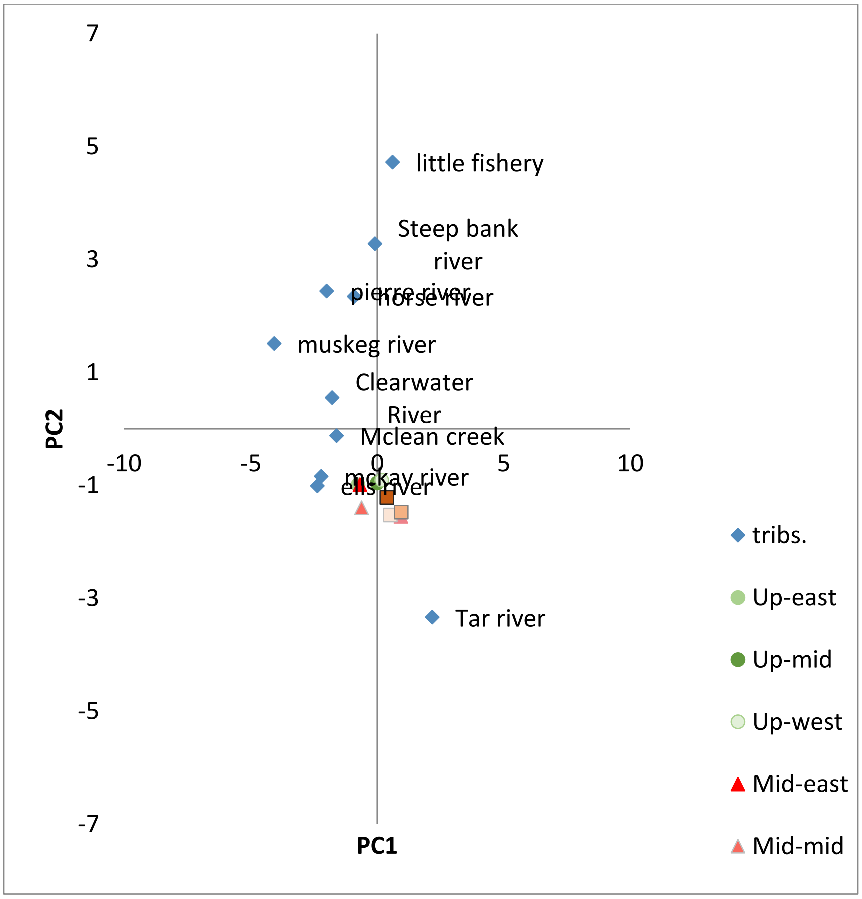


Table 9- Spearman Correlation coefficients for the dissolved trace elements.

0.14																
0.19	.424*															
-0.23	0.26	.475**														
-0.05	0.34	.473**	.585**													
0.04	.753**	.470**	.479**	0.17												
0.16	.812**	.466**	0.33	0.16	.794**											
0.20	.768**	.392*	0.17	-0.08	.844**	.799**										
.362*	0.24	0.28	0.05	-0.27	.516**	.393*	.567**									
0.24	.860**	.484**	.353*	.367*	.761**	.792**	.707**	0.27								
0.25	-0.07	-0.16	-0.18	-.728**	0.20	0.15	0.30	.488**	-0.03							
0.33	.551**	.376*	-0.07	-0.29	.724**	.688**	.874**	.652**	.568**	.425*						
0.28	.375*	.362*	-0.03	-.417*	.582**	.566**	.780**	.691**	.479**	.531**	.865**					
-0.24	.551**	-0.06	0.21	-0.25	.575**	.485**	.532**	0.25	.371*	.419*	0.34	0.32				
0.05	.539**	.561**	0.14	-0.03	.616**	.613**	.712**	0.34	.534**	0.02	.777**	.676**	0.18			
0.29	.959**	.479**	0.27	0.35	.745**	.826**	.781**	0.31	.862**	-0.07	.594**	.415*	.451**	.572**		
0.30	.479**	.369*	0.09	0.27	.454**	.471**	.448*	0.24	.380*	-0.03	.415*	0.20	0.10	.381*	.506**	
0.22	-0.01	-0.01	-0.17	-.657**	0.32	0.31	.444*	.608**	0.19	.769**	.626**	.809**	0.24	0.31	0.03	0.00

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed)

Table 10- Summary of the main findings

TE	Unit	Mean total concentration	Stdv	CCME Guideline (total concentration)	Mean dissolved concentration	Stdv	CCME or US EPA Guideline (dissolved concentration)	Particulate fraction (%)	Dissolved fraction (%)	Dissolved ionic fraction (%)	Dissolved organic associated fraction (%)	Dissolved inorganic associated fraction (%)	increased % in total fraction from Upstream to Downstream	increased % in dissolved fraction from Upstream to Downstream
V	(µg/l)	4.57	0.79	total 120 µg/l (4)	0.26	0.03		94.4	5.6	90.2	2.3	7.5	48	31
Mn	(µg/l)	47.46	8.1	total 50 µg/l drinking water (2)	4.79	1.2	between 240-270 µg L^{-1} (9)	89.9	10.1	90.6	2.1	7.3	44	
Fe	(µg/l)	1426.48	277.8		112.6	32.4	dissolved 300 µg/l, (2)	92.1	7.9	34.1	10.5	55.5	56	
Co	(µg/l)	0.51	0.09	total 120 µg/l (4)	0.09	0.01		82.8	17.2	80.8	18.7	0.5	48	19
Ni	(µg/l)	2.12	0.53	total 25 µg/l (2)	0.96	0.1		54.8	45.2	54.7	43.6	1.7	41	22
Cu	(µg/l)	1.42	0.17	total 7 µg/l (3)	0.8	0.13		43.8	56.2	50.9	45.7	3.4	26	31
As	(µg/l)	0.67	0.06	total 5 µg/l (1)	0.51	0.03		23.9	76.1	94.8	3.7	1.5	21	11
Mo	(µg/l)	0.61	0.07	total 73 µg/l (2)	0.55	0.06		10.2	89.8	99.0	0.7	0.2		
Pb	(ng/l)	533.7	94.2	total 7.0 µg/l (2)	32.7	4.18		93.7	6.3	14.6	3.5	81.8	49	33
Th	(ng/l)	366.4	73.8		10.72	1.4	dissolved 0.01 to 1 µg/l, (5)	96.9	3.1	55.8	17.0	27.2	57	
U	(µg/l)	0.42	0.04	total 15 µg/l (2)	0.29	0.04		31.7	68.3	98.7	1.2	0.1		
Re	(ng/l)	3.94	0.77		3.21	1.02	Global average river water 2 ng/l, (6)	18.5	81.5					57
Tl	(ng/l)	23.33	3.9	total 0.8 µg/l (2)	3.38	0.32		85.5	14.5				43	
Cd	(ng/l)	20.33	3	0.021-0.082 µg/l (7)	12.48	2.04		38.6	61.4					
Cr	(µg/l)	2.32	0.45	Total 50 µg/l, drinking water (8)	0.08	0.03		96.6	3.4					
Al	(µg/l)	1981.6	381.8		6.84	0.7	dissolved 50 µg/l, (2)	99.7	0.3				54	
Zn	(µg/l)	5.04	1.41		0.61	0.14	dissolved 7 µg/l (2)	88	12					
Sb	(ng/l)	66.3	7.67		57.83	7.11		12.8	87.2					

1- CCME, 1999
2- CCME, 2018
3- Alberta Environnent & Sustainable Developement, 2014
4- FEQG, 1999
5- Langmuir and Herman, 1980
6- Miller et al., 2011
7- CCME, 1999
8- Pawlisz et al., 1997
9- CCME, 2019

Table 10 (continued).

Trace elements	**MANOVA results**					
	Means downstream concentrations greater than upstream					
	Total fraction			Dissolved fraction		
	$p < 0.05$	$p < 0.01$	$p < 0.005$	$p < 0.05$	$p < 0.01$	$p < 0.005$
Al	√	√				
As	√			√	√	√
Cd						
Co	√	√	√	√	√	√
Cr						
Cu	√			√	√	√
Fe	√	√	√			
Mn	√	√	√			
Mo						
Ni	√			√	√	√
Pb	√	√	√	√	√	√
Re				√	√	√
Sb						
Th	√	√	√			
Tl	√					
U						
V	√	√		√	√	√
Zn						

Table 11a- Visual MINTEQ results, the expected percentage distribution among dissolved and adsorbed species, based on the Athabasca River average pH (8.2) in fall.

Component	% of total concentration	Species name
UO_2^{+2}	0.016	(6)UO_2^{+2}D(aq)
	96.709	FA1-UO_2(6)(aq)
	3.275	FA2-UO_2(6)(aq)
HFA1-(6)(aq)	43.354	HFA1-(6)(aq)
	56.28	FA1-H(6)(aq)
	0.357	FA1-Fe(II)(6)(aq)
HFA2-(6)(aq)	0.127	HFA2-(6)(aq)
	99.814	FA2-H(6)(aq)
	0.058	FA2-Al(6)(aq)
(6)H+1D(aq)	99.055	(6)H^{+1}D(aq)
	0.181	(6)Al^{+3}D(aq)
	0.698	(6)Fe^{+2}D(aq)
	0.05	(6)Mn^{+2}D(aq)
DOC (NICA-Donnan)	100	DOC (NICA-Donnan)
HFA1-(6)(aq)	100	$HFA1^{-}$(6)(aq)
HFA2-(6)(aq)	100	$HFA2^{-}$(6)(aq)
Al^{+3}	83.401	(6)Al^{+3}D(aq)
	0.09	(6)$AlOH^{+2}$D(aq)
	2.084	FA1-Al(6)(aq)
	14.425	FA2-Al(6)(aq)
HVO_4^{-2}	22.042	$HVO4^{-2}$
	77.958	$H2VO4^{-}$
Cr^{+2}	0.077	Cr^{+2}
	99.923	$CrOH^{+}$
Mn^{+2}	99.406	(6)Mn^{+2}D(aq)
	0.594	FA1-Mn(6)(aq)
Fe^{+2}	63.043	(6)Fe^{+2}D(aq)
	36.957	FA1-Fe(II)(6)(aq)
Co^{+3}	100	$CoOH^{+2}$
Ni^{+2}	98.595	(6)Ni^{+2}D(aq)
	1.391	FA1-Ni(6)(aq)
	0.014	FA2-Ni(6)(aq)
Cu^{+2}	14.124	(6)Cu^{+2}D(aq)
	80.665	FA1-Cu(6)(aq)
	5.211	FA2-Cu(6)(aq)
Zn^{+2}	99.922	(6)Zn^{+2}D(aq)
	0.077	FA1-Zn(6)(aq)

Table 11a (continued).

AsO_4^{-3}	0.024	AsO_4^{-3}
	94.187	$HAsO_4^{-2}$
	5.789	$H_2AsO_4^{-}$
MoO_4^{-2}	99.989	MoO_4^{-2}
	0.011	$HMoO_4^{-}$
Cd^{+2}	80.612	(6)Cd^{+2}D(aq)
	19.355	FA1-Cd(6)(aq)
	0.032	FA2-Cd(6)(aq)
Tl^{+1}	99.999	Tl^{+1}
Pb^{+2}	37.125	(6)Pb^{+2}D(aq)
	43.894	FA1-Pb(6)(aq)
	18.98	FA2-Pb(6)(aq)

Table 11b- Visual MINTEQ results, concentrations and activities of aqueous inorganic species (mmol L^{-1}), based on the Athabasca River average pH (8.2) in fall.

	Concentration	Activity	Log activity
(6)Al(OH)2+D(aq)	1.2083E-13	1.2083E-13	-12.918
(6)Al+3D(aq)	2.071E-07	2.071E-07	-6.684
(6)AlOH+2D(aq)	2.2321E-10	2.2321E-10	-9.651
(6)Cd+2D(aq)	9.3235E-11	9.3235E-11	-10.03
(6)Cu+2D(aq)	1.7781E-09	1.7781E-09	-8.75
(6)Fe+2D(aq)	1.1966E-06	1.1966E-06	-5.922
(6)H+1D(aq)	0.0003397	0.0003397	-3.469
(6)Mn+2D(aq)	8.5043E-08	8.5043E-08	-7.07
(6)Ni+2D(aq)	1.6122E-08	1.6122E-08	-7.793
(6)OH-D(aq)	3.9609E-14	3.9609E-14	-13.402
(6)Pb+2D(aq)	5.3757E-11	5.3757E-11	-10.27
(6)UO2+2D(aq)	1.7949E-13	1.7949E-13	-12.746
(6)UO2OH+D(aq)	2.4405E-17	2.4405E-17	-16.613
(6)Zn+2D(aq)	9.1714E-09	9.1714E-09	-8.038
(UO2)2(OH)2+2	3.0804E-37	3.0673E-37	-36.513
(UO2)2OH+3	1.6253E-42	1.6098E-42	-41.793
(UO2)3(OH)4+2	9.1616E-51	9.1227E-51	-50.04
(UO2)3(OH)5+	3.2402E-46	3.2367E-46	-45.49
(UO2)3(OH)7-	1.822E-46	1.82E-46	-45.74
(UO2)4(OH)7+	8.2023E-60	8.1936E-60	-59.087
Al(OH)2+	2.2466E-18	2.2442E-18	-17.649
Al(OH)3 (aq)	1.4258E-16	1.4258E-16	-15.846
Al(OH)4-	1.1104E-14	1.1093E-14	-13.955
Al+3	1.7752E-24	1.7583E-24	-23.755
Al2(OH)2+4	1.5979E-39	1.5709E-39	-38.804
Al3(OH)4+5	4.558E-53	4.4383E-53	-52.353
AlMo6O21-3	1.9762E-69	1.9574E-69	-68.708
AlOH+2	2.8179E-21	2.8059E-21	-20.552
AsO4-3	8.5607E-13	8.4791E-13	-12.072
Cd(OH)2 (aq)	1.4959E-25	1.4959E-25	-24.825
Cd(OH)3-	2.3408E-30	2.3383E-30	-29.631
Cd(OH)4-2	3.826E-36	3.8097E-36	-35.419
Cd+2	1.177E-21	1.172E-21	-20.931
Cd2OH+3	8.8113E-44	8.7272E-44	-43.059
CdOH+	1.4873E-23	1.4857E-23	-22.828
Co+3	1.8512E-16	1.8335E-16	-15.737
CoOH+2	1.4932E-09	1.4869E-09	-8.828

Table 11b (continued).

Cr+2	1.0404E-12	1.036E-12	-11.985
CrOH+	1.3452E-09	1.3438E-09	-8.872
Cu(OH)2 (aq)	3.306E-20	3.306E-20	-19.481
Cu(OH)3-	2.0406E-22	2.0384E-22	-21.691
Cu(OH)4-2	2.6371E-27	2.6259E-27	-26.581
Cu+2	2.2448E-20	2.2353E-20	-19.651
Cu2(OH)2+2	4.0409E-34	4.0237E-34	-33.395
Cu2OH+3	1.5589E-38	1.544E-38	-37.811
Cu3(OH)4+2	1.1529E-47	1.148E-47	-46.94
CuOH+	1.1292E-19	1.128E-19	-18.948
DOC (NICA-Donnan)	0.0013917	0.0013917	-2.856
FA1-Al(6)(aq)	5.1743E-09	5.1743E-09	-8.286
FA1-Cd(6)(aq)	2.2386E-11	2.2386E-11	-10.65
FA1-Cu(6)(aq)	1.0155E-08	1.0155E-08	-7.993
FA1-Fe(II)(6)(aq)	7.0147E-07	7.0147E-07	-6.154
FA1-H(6)(aq)	0.00011053	0.00011053	-3.957
FA1-Mn(6)(aq)	5.0808E-10	5.0808E-10	-9.294
FA1-Ni(6)(aq)	2.2744E-10	2.2744E-10	-9.643
FA1-Pb(6)(aq)	6.3558E-11	6.3558E-11	-10.197
FA1-UO2(6)(aq)	1.0744E-09	1.0744E-09	-8.969
FA1-Zn(6)(aq)	7.1038E-12	7.1038E-12	-11.149
FA2-Al(6)(aq)	3.5822E-08	3.5822E-08	-7.446
FA2-Cd(6)(aq)	3.733E-14	3.733E-14	-13.428
FA2-Cu(6)(aq)	6.5604E-10	6.5604E-10	-9.183
FA2-Fe(II)(6)(aq)	6.0116E-13	6.0116E-13	-12.221
FA2-H(6)(aq)	0.000062015	0.000062015	-4.208
FA2-Mn(6)(aq)	7.8946E-14	7.8946E-14	-13.103
FA2-Ni(6)(aq)	2.2466E-12	2.2466E-12	-11.648
FA2-Pb(6)(aq)	2.7483E-11	2.7483E-11	-10.561
FA2-UO2(6)(aq)	3.6387E-11	3.6387E-11	-10.439
FA2-Zn(6)(aq)	1.7121E-14	1.7121E-14	-13.766
Fe(OH)2 (aq)	1.2114E-21	1.2114E-21	-20.917
Fe(OH)3-	6.1196E-24	6.1131E-24	-23.214
Fe+2	1.5106E-17	1.5042E-17	-16.823
FeOH+	9.5665E-19	9.5563E-19	-18.02
H+1	6.3163E-09	6.3096E-09	-8.2
H2AsO4-	2.0836E-10	2.0814E-10	-9.682
H2Mo6O21-4	6.7839E-66	6.6693E-66	-65.176
H2V10O28-4	1.8126E-79	1.782E-79	-78.749

Table 11b (continued).

H2V2O7-2	5.6495E-16	5.6255E-16	-15.25
H2VO4-	1.6809E-09	1.6791E-09	-8.775
H3AsO4	2.6203E-16	2.6203E-16	-15.582
H3Mo8O28-5	7.7685E-89	7.5644E-89	-88.121
H3V10O28-3	5.4335E-83	5.3817E-83	-82.269
HAsO4-2	3.39E-09	3.3756E-09	-8.472
HFA1-(6)(aq)	0.00019639	0.00019639	-3.707
HFA1-(6)(aq)	0.000085144	0.000085144	-4.07
HFA2-(6)(aq)	7.8834E-08	7.8834E-08	-7.103
HFA2-(6)(aq)	0.000062124	0.000062124	-4.207
HMo7O24-5	3.8726E-75	3.7709E-75	-74.424
HMoO4-	3.8265E-13	3.8224E-13	-12.418
HV10O28-5	1.8301E-75	1.782E-75	-74.749
HV2O7-3	2.2611E-17	2.2396E-17	-16.65
HV3O10-4	3.9142E-24	3.8481E-24	-23.415
HV4O13-5	2.7663E-31	2.6936E-31	-30.57
HVO4-2	4.7525E-10	4.7323E-10	-9.325
Mn(OH)4-2	3.4898E-34	3.4749E-34	-33.459
Mn+2	1.0736E-18	1.0691E-18	-17.971
Mn2(OH)3+	5.8536E-36	5.8474E-36	-35.233
Mn2OH+3	4.6254E-39	4.5813E-39	-38.339
MnOH+	4.2899E-21	4.2854E-21	-20.368
Mo7O24-6	1.1833E-72	1.1388E-72	-71.944
Mo8O26-4	2.1193E-92	2.0836E-92	-91.681
MoO3(H2O)3(aq)	2.4118E-17	2.4118E-17	-16.618
MoO4-2	3.501E-09	3.4861E-09	-8.458
Ni(OH)2 (aq)	5.1612E-22	5.1612E-22	-21.287
Ni(OH)3-	8.2452E-25	8.2364E-25	-24.084
Ni+2	2.0353E-19	2.0267E-19	-18.693
NiOH+	4.0759E-21	4.0716E-21	-20.39
OH-	1.5975E-06	1.5958E-06	-5.797
Pb(OH)2 (aq)	1.367E-22	1.367E-22	-21.864
Pb(OH)3-	2.1838E-25	2.1815E-25	-24.661
Pb+2	6.7865E-22	6.7577E-22	-21.17
Pb2OH+3	2.9292E-41	2.9012E-41	-40.537
Pb3(OH)4+2	2.5304E-55	2.5196E-55	-54.599
Pb4(OH)4+4	1.7319E-73	1.7027E-73	-72.769
PbOH+	2.7117E-21	2.7088E-21	-20.567
Tl+1	1.4679E-11	1.4663E-11	-10.834
TlOH (aq)	1.4429E-16	1.4429E-16	-15.841

Table 11b (continued).

UO2(H2AsO4)2 (aq)	8.7114E-40	8.7114E-40	-39.06
UO2(OH)2 (aq)	4.012E-20	4.012E-20	-19.397
UO2(OH)3-	5.0561E-20	5.0507E-20	-19.297
UO2(OH)4-2	5.691E-24	5.6668E-24	-23.247
UO2+2	2.2659E-24	2.2563E-24	-23.647
UO2H2AsO4+	6.9535E-31	6.9461E-31	-30.158
UO2HAsO4 (aq)	6.9461E-26	6.9461E-26	-25.158
UO2OH+	2.013E-21	2.0108E-21	-20.697
V10O28-6	1.281E-74	1.2329E-74	-73.909
V2O7-4	1.8095E-20	1.7789E-20	-19.75
V4O12-4	3.2192E-28	3.1648E-28	-27.5
V4O13-6	7.3618E-34	7.085E-34	-33.15
V5O15-5	2.5527E-36	2.4857E-36	-35.605
V6O18-6	4.5413E-45	4.3705E-45	-44.359
VO2+	9.2377E-19	9.2279E-19	-18.035
VO4-3	2.4504E-15	2.427E-15	-14.615
Z-(6)(aq)	-0.00034294	-0.00034294	0
Zn(OH)2 (aq)	3.6964E-20	3.6964E-20	-19.432
Zn(OH)3-	1.8673E-23	1.8653E-23	-22.729
Zn(OH)4-2	4.738E-28	4.7179E-28	-27.326
Zn+2	1.1578E-19	1.1529E-19	-18.938
Zn2OH+3	2.1417E-39	2.1212E-39	-38.673
ZnOH+	1.8418E-20	1.8399E-20	-19.735

3 CHAPTER 3

CONCLUSIONS AND ENGINEERING SIGNIFICANCE

3.1 **Conclusions**

The goal of this study was to evaluate the spatial changes in the concentrations of trace elements in the Athabasca River. To do so, water samples were collected from upstream to downstream of industry, along five transects across the river. Water samples were gathered in the fall of 2017, using metal-free sampling methods. The spatial variation in the concentrations of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Re, Sb, Tl, Th, U, V, and Zn, were measured in the total, dissolved, and colloidal fractions. All of these measurements enabled us to test the hypotheses and answer the questions related to these study which were as follow:

1. To determine the physical forms of trace elements,
2. To find out whether concentrations of trace elements in their various forms are more abundant downstream of industry compared to upstream,
3. To determine whether these trace elements change across the river, from side to side,
4. To compare the concentrations of trace elements along and across the Athabasca River with the surface water quality guidelines,
5. To find out if the industrial activities of the Athabasca bituminous sands region are an important source of these elements to the lower Athabasca River,
6. To determine the contribution of tributaries.

Having investigated all of these objectives the following were found:

1. The majority of the investigated trace elements were predominantly (54.8 to 99.7%) in the particulate fraction (> 0.45 μm). In the dissolved fraction (< 0.45 μm), the size-based distribution of trace elements revealed that Fe and Pb were mainly found in the primarily inorganic colloidal fraction, whereas the ionic fraction (< 1 kDa) was the dominant (> 50%)

form of the rest of the elements. The results of the chemical speciation of trace elements in the dissolved form, and the findings predicted by the Visual MINTEQ software were consistent.

2. We found that the total concentrations of Al, As, Co, Cu, Fe, Mn, Ni, Pb, Th, Tl, and V were significantly ($p < 0.05$) more abundant downstream, compared to upstream of industry. In the dissolved fraction, the concentrations of As, Co, Cu, Ni, Pb, Re, and V were significantly ($p < 0.05$) more abundant downstream of industry.
3. In terms of the spatial changes of trace elements across the river, we found that the variations in the total concentration of these elements were not significant ($p < 0.05$) across the transects. In the dissolved form, however, significant ($p < 0.05$) spatial variations were observed in the concentrations of Fe, Mo, Ni, Re, Sb, and U across the river.
4. Our findings show that none of the average concentration of the investigated trace elements (for which the guideline is available and defined) in the Athabasca River were higher than the available surface water guidelines.
5. Our normalization analysis revealed no significant ($p < 0.05$) enrichment of any of these elements along or across the river, relative to crustal composition.
6. The results of the PCA and correlation analyses showed meaningful contributions of tributaries, to the Athabasca River, in the both total and dissolved fractions.

3.2 Engineering Significance

For several years, our understanding of water quality of the Athabasca River was limited by lack of high quality sampling and analysis. The cutting-edge sampling and analyzing methods that were used in this research enabled us to overcome this shortcoming and boost our understanding of trace element inputs to the Athabasca River.

For engineers and scientists, having a firm understanding of the sources of trace elements and the impact of their different forms on aquatic life is critical. In this study we were able to measure the concentrations of trace elements among various forms, which has been a challenging task for decades. The bioavailability, bioaccessibility and forms of trace elements in this complex aquatic system will help engineers predict whether any elements in water could pose a health risk to people and aquatic life.

According to our findings, in the Athabasca River, none of the average concentrations of the investigated trace elements exceeded the surface water guidelines. Additionally, the results of the PCA and correlation analyses indicated the important contribution of tributaries. These findings are important when planning future industrial activities and while appropriately protecting human and ecological health, supporting communities such as Fort McKay and Fort Chip with their water needs.

3.3 **Future work and recommendations**

In this study, the sample sites and transect locations were selected in a way to document natural inputs (T1 and T2), as well as potential industrial inputs (T3 at the midstream, in front of tailings ponds and bitumen upgrading facilities, and T4 and T5 downstream of industry). Increasing the transect numbers and sampling sites along the river in the future studies could provide additional insight and confirm these initial findings.

The same recommendation could also be applied for the sample depths. Our results were based on the average concentration of elements in the samples, gathered from surface and middle layers. Looking forward, collecting more samples from different depths and investigation elements behavior at discrete levels could be an area of productive scientific research.

Moreover, according to previous studies, pH and aquatic inputs to rivers affect the behavior and distribution of trace elements and may change tremendously by season (Porcelli et al., 1997; Pokrovsky et al., 2006, 2012; Dahlqvist et al., 2007; Stolpe et al., 2013; Gaillardet et al., 2014; Marttila et al., 2016). Therefore, future research should consider the potential importance of temporal and seasonal variations more carefully, to validate the kinds of conclusions that can be drawn from this study. This could also be so helpful to further evaluate and identify possible anthropogenic inputs to the river.

To better understand the natural impact of tributaries on trace element behavior in the Athabasca River and on water quality in the river, and to consider the assumption of the tributary contributions, future research could conduct a comparison of the distribution of trace elements in the colloidal fraction of the Athabasca River with the corresponding results for the tributaries and the mixing zones, where tributaries flow into the Athabasca River.

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5 Appendix 1: Supporting Information

Table S1. Mean concentrations of DOC measured in the samples from the upstream, midstream, and downstream and at different sides of the river.

Location			**DOC (mg/L)**	**Stdev**
up	**West**	**Top**	15.5	0.2
up	**West**	**Middle**	12.8	0.02
up	**Middle**	**Top**	15.4	0.12
up	**Middle**	**Middle**	16.1	0.04
up	**East**	**Middle**	18.2	0.15
up	**East**	**Top**	16.4	0.13
up	**West**	**Top**	28.2	0.04
up	**West**	**Middle**	13.6	0.01
up	**Middle**	**Middle**	17.1	0.27
up	**Middle**	**Top**	26.5	0.01
up	**East**	**Middle**	16.7	0.18
up	**East**	**Top**	14.7	0.04
mid	**West**	**Top**	16.9	0.07
mid	**West**	**Middle**	15.1	0.1
mid	**Middle**	**Middle**	15.1	0.1
mid	**Middle**	**Top**	17.2	0.11
mid	**East**	**Middle**	15.2	0.02
mid	**East**	**Top**	17.5	0.02
mid	**West**	**Middle**	15.5	0.05
mid	**West**	**Top**	15.6	0.13
mid	**Middle**	**Top**	29.2	0.02
mid	**East**	**Top**	16.3	0.03
mid	**East**	**Middle**	12.4	0.02
mid	**Middle**	**Middle**	13.5	0.01
down	**West**	**Top**	20.5	0.04
down	**West**	**Middle**	16.6	0.05
down	**Middle**	**Top**	14.4	0
down	**Middle**	**Middle**	14.6	0.03
down	**East**	**Middle**	9.97	0.18
down	**East**	**Top**	14.4	0.09

Table S2. Outlier detection methods, for the total and dissolved fractions of datasets. In this table, numbers are the concentrations of outliers detected by each method. The only purpose of presenting these concentrations here was to show the difference in the number of outliers each method detect.

Trace Elements	**Form**	**>3 scaled MAD[1]**	**Histogram**	**Grubbs' test (ESD, extreme studentized deviate)**	**>3 scaled MAD[2]**	**GESD[3]**
Al	Dissolved					0.4
	Total	2998.4, 4118.9, 3422.9, 3522.6, 3060.1				4118.94
V	Dissolved	4,				
	Total	7, 9.4, 7.6, 7.9, 7	9.4	9.4		9.4
Cr	Dissolved	0.17, 0.4, 0.18, 0.17, 0.16	0.4	0.4	0.4	0.17, 0.4, 0.18, 0.17, 0.16
	Total	3.8, 4.3, 7.3, 3.9, 5	7.3	7.3	7.3	7.3
Mn	Dissolved					9.95
	Total					81.3
Fe	Dissolved					
	Total	2982.8		2982.8	2982.8	2982.78
Co	Dissolved					
	Total	0.7, 1.1, 0.9, 0.8, 0.7, 0.8	1.1	1.1	1.1	1.1
Ni	Dissolved	0.7, 0.7, 1.2, 1.2, 1.2, 1.1, 1.2, 1.1, 1.2				
	Total	4.6, 3.4, 5.1, 3.9		4.6, 3.4, 5.1, 3.9	5.1	4.6, 5.1, 3.9
Cu	Dissolved	0.5, 0.5, 1, 1, 1.1, 1.1, 1, 1.1, 1,1, 1				
	Total	1.7, 1.9, 2.6, 2, 2.1, 2.1, 1.7	2.6	2.6	2.6	2.6
Zn	Dissolved	1.3		1.3, 1.2	1.3	1.3, 1.2
	Total	42.2	42.2	42.2	42.2	42.2,
As	Dissolved	0.6				
	Total	1.2, 0.9, 0.9, 0.9	1.2	1.2	1.2	1.21
Mo	Dissolved	0.4, 0.4, 0.5				
	Total	1.3	1.3	1.3	1.3	1.3
Cd	Dissolved	0.004, 0.004, 0.004,				
	Total	0.035				0.032, 0.035,
Sb	Dissolved					
	Total	0.12				0.1
Re	Dissolved					0.006
	Total					0.007
Tl	Dissolved	0.002, 0.004 (*7)				
	Total	0.035, 0.049, 0.036, 0.038, 0.035		0.049	0.049	0.049
Pb	Dissolved					
	Total	0.8, 1.2, 0.9, 0.8, 0.8, 0.8	1.231	1.231	1.231	1.231
Th	Dissolved	0.02 (*3)		0.02 (*3)	0.02 (*3)	0.02 (*3)
	Total	0.8, 0.6, 0.6	0.8	0.85	0.85	0.85

[1] median absolute deviations

[3] generalized extreme Studentized deviate

[2] mean absolute deviations

Table S3. The comparison between one sided t-test and MANOVA with the significance level of $p < 0.05$.

Trace Elements	Form	Downstream>Upstream	
		one sided t-test	MANOVA
Al	Dissolved		
	Total	✓	✓
V	Dissolved	✓	✓
	Total	✓	✓
Cr	Dissolved		
	Total		
Mn	Dissolved		
	Total	✓	✓
Fe	Dissolved	✓	
	Total	✓	✓
Co	Dissolved	✓	✓
	Total	✓	✓
Ni	Dissolved	✓	✓
	Total	✓	✓
Cu	Dissolved	✓	✓
	Total	✓	✓
Zn	Dissolved		
	Total		
As	Dissolved	✓	✓
	Total	✓	✓
Mo	Dissolved		
	Total		
Cd	Dissolved		
	Total		
Sb	Dissolved		
	Total		
Re	Dissolved	✓	✓
	Total	✓	
Tl	Dissolved		
	Total	✓	✓
Pb	Dissolved	✓	✓
	Total	✓	✓
Th	Dissolved		
	Total	✓	✓
U	Dissolved		
	Total		

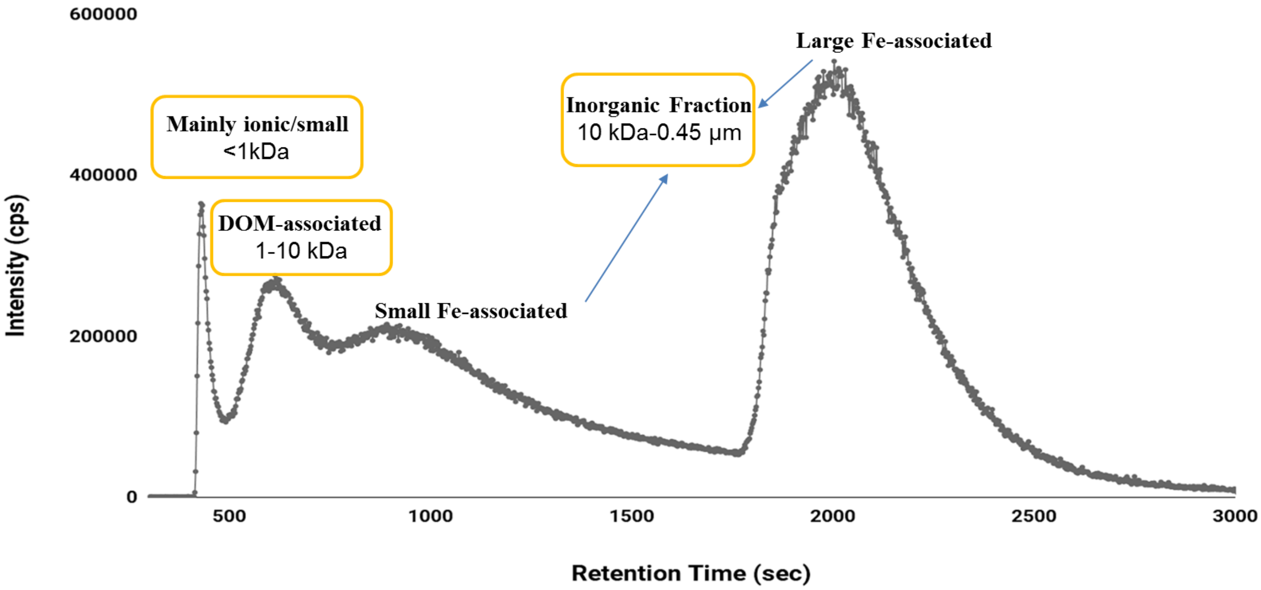


Figure S1- Distribution of trace elements amongst dissolved colloidal species.

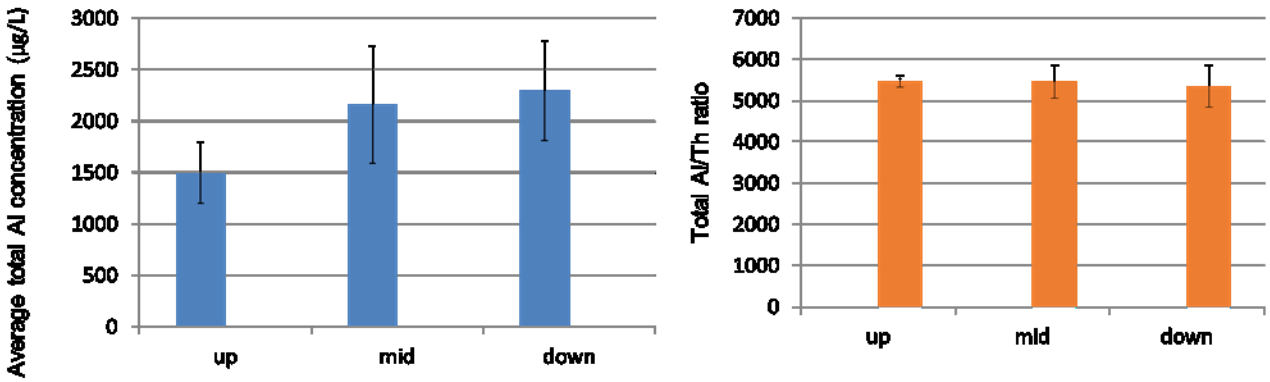


Figure S2- Spatial variation in the total concentration of Al (left) and the normalization graph for the average total Al to total Th concentrations(right) in the Athabasca River.

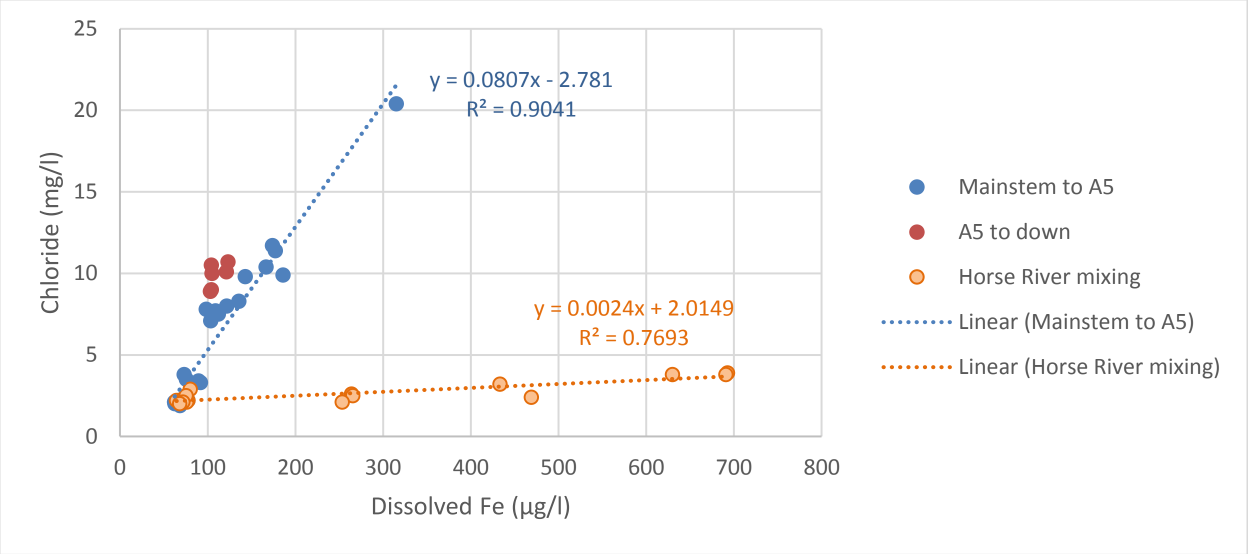
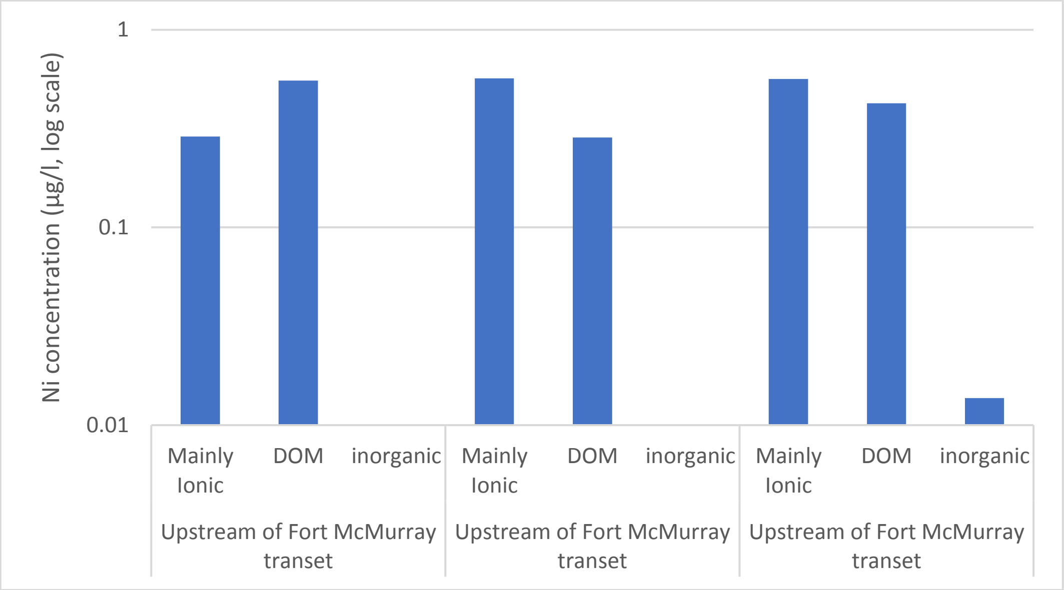


Figure S3. Fe-Cl^{-1} relationship in the Athabasca River. The blue dots describe the Fe-Cl^{-1} ratio from Upstream FMM to upstream of A9 (i.e. T4, not mainstem to A5). The red dots are from the site named "Downstream of A5" (i.e. T5, not A5 to down). The point with coordinates of ca. (300, 20) is the Clearwater River. The small clump of blue dots just below the red dots also correspond to the points at T4.



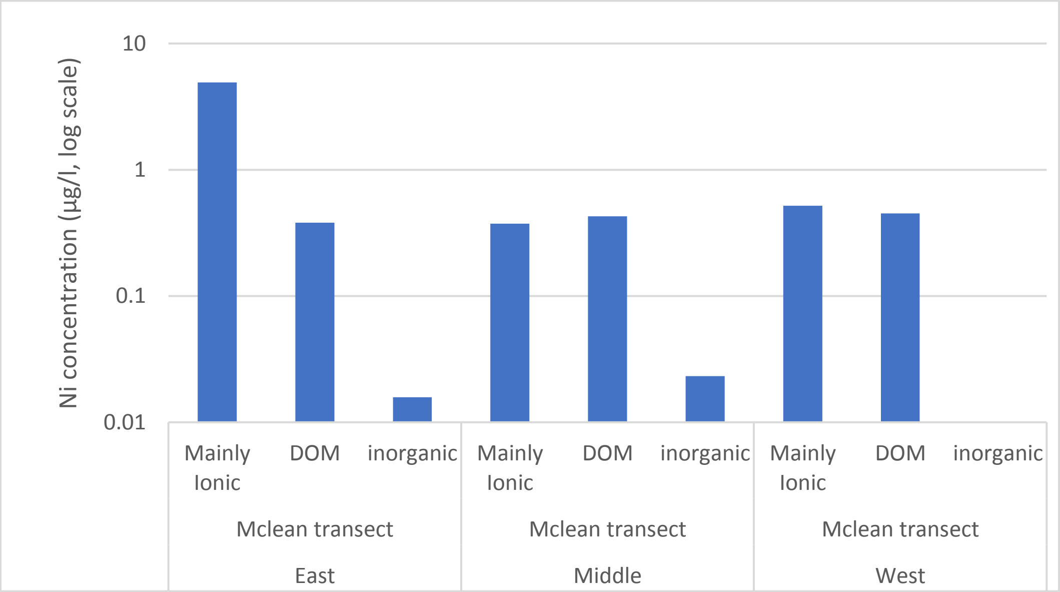


Figure S4. Spatial variation in the Ni colloidal fraction concentrations, for Upstream of Fort McMurray (T1) and Mclean transects (T2), upstream of industry.