MULTI-ELEMENT ANALYSIS ON RIPARIAN WETLANDS AND RIVER SEDIMENT IN NORTH DAKOTA

A Thesis
Submitted to the Graduate Faculty
of the
North Dakota State University
of Agriculture and Applied Science

By

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In Partial Fulfillment
for the Degree of
MASTER OF SCIENCE

Major Program:
Environmental Conservation Sciences

April 2013

Fargo, North Dakota

North Dakota State University
Graduate School

Title

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

MASTER OF SCIENCE

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ABSTRACT

River sediment, transfer metals, nutrients and pollutants from various sources and tributaries within a catchment, and deposit sediment whenever the flow rate of water is low. Multi-element fingerprinting technique could provide detailed information regarding the element concentrations in the sediment deposits and riparian soil.

During summer 2011 riparian soil and sediment samples were collected from the Red, Sheyenne, James, Missouri and Little Missouri Rivers in North Dakota to evaluate the suitability of multi-element fingerprinting method to assess the element variations.

During summer 2012, sediment deposits from the Red, Sheyenne and Turtle Rivers were collected to study the tributary contributions (Sheyenne and Turtle) to the elements with the emphasis on selenium and cadmium in the Red River. At the Little Missouri five tributaries were sampled to study the tributary contributions to the uranium concentrations. This study showed statistically significant variations in element concentrations between and within these rivers

ACKNOWLEDGMENT

I would like to thank my advisors Drs. Donna Jacob and Marinus Otte for their great amount of support and contribution both to my educational and my personal life. Working with Wet Ecosystem Research Group under your provision was such an incredible experience. Thanks to my committee members Drs. Larry Cihacek and Edward Shawn Dekeyser for their advice and for proofreading my dissertation. I would like to thank Mike Ell and North Dakota Department of Health.

This project was supported by EPA-DoH project FAR 0017348. Thanks to Drs. Craig Stockwell and Wendy Reed, the Environmental Conservation Sciences Program and the Department of Biological Sciences for their support.

I am very thankful to my colleagues and friends in Wet Ecosystem Research Group who assisted me with various aspects of my project: Post Doc: La Toya Kissoon. Graduate Students: Alex Yellick, Dimuthu Wijeyaratne, Alex Stalboerger, Carrie Werkmeister-Karki, Khurram Sheikh. I truly enjoyed every minute of lab work and field work, gatherings, meetings, and have learnt a lot from all of you. Undergraduate Students: Aude Monthean, John Schmidt, Emily Fischbach, Hannah Passolt, Candace Craft, Alex Hoehle, Ryan Sullivan, Nicholas Peterson, Yiqing Xu, Bryan Marquardt. Thanks to Larry Swenson in the Soil Testing Laboratory for letting me use his laboratory for loss-on-ignition analysis.

Thanks to my family members and specially my mother, for her unconditional love and support and encouragement that is always with me even though we are thousands of miles away. Thanks to my husband Arash, for believing in me and for being such an amazing friend and partner and for his endless support during all these years.

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CHAPTER 1. GENERAL INTRODUCTION

1.1. Abstract

Riparian wetlands are unique and important ecosystems that trap sediment, improve water quality, and provide habitat for many species of plants and animals. Riparian wetlands act as sources, sinks, or filters for sediments. Sediments in moving waters transfer nutrients, metals, and contaminants from different locations within the catchment and deposit whenever the flow rate of water is slow. Interactions between plants and sediment and element uptake by riparian plants are controlled by factors such as element composition and concentrations, particle size, and organic matter content of the sediments.

Geology and land use significantly varies in North Dakota, with bedrock in the west consisting of clay, sand stone, and uranium-bearing lignite, and in the east silty clay remaining from Lake Agassiz. These two regions consist of two very different catchment areas for rivers and riparian wetlands. Geochemistry is also impacted by geology and land use, and element patterns reflect these changes and impact the riparian wetlands flora and fauna (Moyle 1945; Newton et al. 1987; Nilsson and Håkanson 1992; Fraterrigo and Downing 2008). One of the first steps to monitor the riparian ecosystems in North Dakota is to study the element concentrations in riparian sediment, since 1) elements could be exchanged and transported along the rivers through sediment-water reactions (Jaynes and Carpenter 1986; Weis and Weis 2004; Nurminen and Horppila 2009), and they 2) represent a variety of sources and activities related to each region.

Currently techniques such as the three-tiered approach tested for Prairie Potholes in North Dakota (Hargiss 2009) and the methods used in the National Wetland Condition Assessment

(NWCA) are approved and being applied for wetland condition assessment. These methods have demonstrated that significant links and correlations exist between element composition of wetlands, plant communities and wetland conditions. For example, Hargiss (2009) investigated the condition of wetlands based on an Index of Plant Community Integrity (IPCI). IPCI is the method for quantitative assessment of wetland quality and categorizing them into five groups (Very good, Good, Fair, Poor, and Very poor) in the Prairie Pothole Region.

Following by these studies, Otte et al. (2010) sampled 20 in wetlands in the PPR, and these wetlands were previously sampled and studied for the Index of Plant Community Integrity (IPCI) (Hargiss 2009). Also the number of wetlands sampled was relatively small, Otte et al. (2010) discovered that wetlands in very good condition usually had significantly higher concentrations of uranium and lower concentrations of arsenic (Yellick 2013).

Study of the element composition of riparian sediments in North Dakota with the multi-element fingerprinting method (concentrations of different elements and metals in soil/sediment/plant samples even at very small amounts are measured with the multi-element analysis) will provide important results and knowledge: 1) for monitoring riparian wetland characteristics and 2) about the variation in properties that could be due to different land use and geology. Sediment fingerprinting also 3) could give us valuable information regarding possible tributaries and sources within a catchment that contribute to the concentrations of particulate elements or pollutants, 4) support the design and implementation of sediment control strategies in a relatively fast and cost effective way and 5) help us in development of a technique for condition assessment of riparian wetlands in North Dakota.

1.2. Multi-element analysis and sediment fingerprinting

Researchers have carried out studies on sediment chemistry of rivers (Wall and Wilding 1976; Peart and Walling 1986). In particular to the studies on riparian wetlands and rivers multi-element analysis has been used to study the element accumulation in wetland plants and riparian sediments (Bonanno and Giudice 2010; Wijeyaratne 2011; Wang et al. 2009). Sediment fingerprinting could give us valuable information regarding possible sources within a catchment that contribute to contaminants or elements with exceeding levels, and also support the design and implementation of sediment control strategies.

1.3. Riparian wetlands: functions and primary productivity

Riparian wetlands are wetlands adjacent to rivers and streams, and they usually occur as an ecotone between aquatic and non-aquatic ecosystems with distinct soil characteristics and vegetation communities (Mitsch et al. 2009). Riparian wetlands are some of the most diverse and dynamic parts of the landscape (Swanson et al. 1988). The abundance of water and fertile soils are characteristics that make riparian ecosystems different from other ecosystems (Brinson et al. 1981).

Periodic flooding usually results in a higher productivity in number of ways, including:

1. Provides enough water for the vegetation, and results in productivity in riparian ecosystems.
2. Supplies nutrients and results in changes in soil chemistry of riparian wetlands. These changes include sulfate reduction, nitrification, and iron plaque formation.
3. The flooding and flushing also results in transformation and translocation of many contaminants like methane, litter and roots in riparian wetlands, (Mitsch et al. 2009).

Stream riparian zones have a potential to regulate energy and material fluxes between dry land and aquatic ecosystems (Gregory et al.1991; Naiman and Decamps 1997). Riparian wetlands play many important roles, including stream stabilization (Osborne and Kovacic 1993), temperature regulation of streams (Gray and Eddington 1969), retention and filtration of nutrients (Vought et al. 1994), provision of different habitats (Sparks 1995), and adjustment of ecosystem (Wiens et al. 1985). Mostly the proof for effectiveness of riparian wetlands in improving water quality and removing chemicals been based on the sediment and chemical concentrations in the sediment (Kitchens et al. 1975; Knight et al. 1987; Phillips 1989; Hupp et al. 1993; Mitsch et al. 2009). Both natural and constructed wetlands are used for treatment of wastewater and rehabilitation of mine wastes (McCabe and Otte 2000). The role of riparian zones in the removal of nitrates from subsurface flows contaminated by agriculture and other human activities has received particular attention (Gilliam 1994; Hill 1996; Casey and Klaine 2001). Many studies have shown high reduction in NO3 concentrations along groundwater flow paths beneath riparian wetlands (Lowrance et al. 1984; Peterjohn and Correll 1984; Haycock and Burt 1993; Hill 1996).

1.4. Importance of sediment deposition

Most rivers have three main zones: 1) erosion, 2) storage and transport, 3) sediment deposition. In the deposition zone, sediment deposition is greater than erosion. The sediment deposition zone usually begins to support plant communities. After being stabilized a riparian wetland could be formed in the sediment deposition zone, and riparian vegetation constantly interacts with the elements and nutrients present in the sediment (Mitsch et al. 2009). Riparian plants acquire most of their nutrients from the sediment and the water column (Barko and Smart

1980; Barko et al. 1991; Clarke and Wharton 2001). Wetland ecosystems are important sediment traps. Riparian wetlands are known to be sinks for sediment, metals, and nutrients (Gorham et al. 1984).

The importance of suspended sediment in the transport of contaminants and nutrients, such as phosphorus, metals, and pesticides, through aquatic systems is known (Shear and Watson 1977; UNESCO 1983; Allan 1986; Collins et al. 1996; Warren et al. 2003; Dirszowsky 2004). As a result of the persistence and low solubility of almost all the contaminants in water they are adsorbed on clay particles and finally accumulate in sediments (Kang et al. 2000; Wiberg and Harris 2002). Sediment deposition in riparian wetlands concentrates many nutrient, pollutants and toxic metals through sorption mechanisms (Hart 1982; Bastian and Benforado 1987; Clausen and Johnson 1990). Riparian and River sediment usually consists of various aluminum and irons oxides and hydroxides which might increase the ability of sediments to carry and release variety of chemicals (Skopp and Daniel 1987). Therefore sediments other than being the carriers and accepters of contaminants when deposited could act as another contamination sources (Lee et al. 2003; Simpson et al. 2004; Atkinson et al. 2007).

1.5. Studies on element accumulation in river sediments and riparian wetlands

A number of studies on the accumulation of different elements and mostly metals in deposited or suspended sediment of natural riparian wetlands, and water of the rivers and lakes were carried out (Table 1.1).

They found and supported the fact that riparian wetlands have a large capacity to retain heavy metals and other contaminants from upland and river water. These studies also demonstrated that in order to understand and address different conditions in riparian ecosystems, one of the first steps is to assess the element composition in the sediment or water.

Table 1.1. Evidence of the element accumulation by riparian sediment and plants.

Summary of Studies on element accumulation in riparian sediments/plant, and river waters/suspended sediment		
Author	Elements	Sample/Location
Rybicka et al. 2005	As, Cd, Cr, Cu, Hg, Fe, Mn, Ni Pb, Zn	Suspended particulate matter and sediments/Odra river
Diagomanolin et al. 2004	Cr, Cu, Ni	Water/Karoon River (Iran)
Overesch 2007	As, Cd. Cr, Ni, Pb, Zn	Sediment and plant/ Central Elbe River (Germany)
Galicki et al. 2008	As, P, Pb	open water during remobilization events/ Sky Lake Mississippi River (USA)
Liu et al. 2008	Cr, Cu, Ni, P, Zn	Riparian sediment/Moshui lake (China)
Reczynski et al. 2010	As, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Pb, Zn	Dobczyce Reservoir (South Poland)
Wang et al. 2011	Ce, Dy, Er, Gd, Ho, La, Lu Nd, Pr, Sm, Tb,Tm, Yb, Y	Riparian sediment/Xianghai (China)
Zhang et al. 2012	Cd, Cr, Cu, Ni, Pb, Zn	Soil, water and plants/Pearl River (South China)

1.6. Sediment source tracing

Sediments act as both carriers and potential sources of pollutants in rivers and streams (Förstner and Müller 1974). The suspended sediment transported by a stream or a river represents a mixture of sediment derived from different locations and sources that contribute to the concentrations in the catchment. Different sources such as a small area of a catchment with a particular rock type or land use could be the main source for a particular element or the suspended sediment. Or in some catchments, sheet and rill erosion or gully erosion are the main sources for the suspended sediment (Collins and Walling 2002).

Source tracing and fingerprinting techniques (ICP-MS and ICP-OES) have now been used in many studies (Table 1.2) to provide accurate and reliable information on suspended sediment sources. Their application is becoming more and more accepted as a cost effective and unique method for providing information on catchment suspended sediment sources. Many different physical and chemical properties have been successfully used to discriminate potential sediment sources in drainage basins, including mineralogy (Klages and Hsieh1975; Johnson and Kelley 1984), sediment chemistry (Wall and Wilding 1976; Peart and Walling, 1986), mineral magnetism (Oldfield et al. 1979) and environmental radionuclides (Walling and Woodward 1992; He and Owen and Otton 1995).

The approach has been applied in both small and large river basins (Russell et al. 2001) and for understanding the contribution of possible sources, such as tributaries.

1.7. Aims, hypothesis and objectives of the project

Field studies and laboratory experiments were designed to assess each of our hypotheses and the specific objectives of this project were to:

a. To assess the biogeochemical behavior of elements in sediments of the selected areas of the Red, Sheyenne, James, Missouri and Little Missouri rivers.

b. To assess the spatial variation in element concentrations and link them to the geology and land use patterns.

c. To study and investigate the contributions of the tributaries to the element concentrations.

d. The suitability of multi-element fingerprinting method to study the riparian wetlands and their condition.

In this study it was hypothesized that:

1. Element composition of the river sediments would reflect the geology and land use of the study area.
2. Fingerprints would be significantly different between the rivers, especially major rivers such as Red and Little Missouri.
3. Fingerprints would differ and might show interesting patterns, at each river between upstream to downstream.
4. Tributaries passing through different areas, contribute to the concentrations of certain elements in the rivers.
5. The element concentrations depend on the properties of the sediments, such as particle size and organic matter content.
6. The fingerprints of the tributaries, upstream and downstream areas of the tributary-river confluence would be different from each other.

Table 1.2. Studies on wetlands and rivers with the application of sediment source tracing.

Authors	Technique	Description of the study
Bai et al. 2010	ICP-OES	Concentrations of elements in samples collected from three different sampling sites in China (uncultivated wetland, cultivated wetland and cultivated wetland after abandonment) were measured. It was concluded that some metal concentrations were impacted by land use changes in the area and some metals will be released after reclamation while for cultivated wetlands metal concentrations will increase and wetland becomes a sink after abandonment.
Botes and Staden 2007	ICP-OES	Trace metal content in river sediments and water samples was measured using ICP-OES analysis for the Olifants River and the Crocodile River (Gauteng Province). Results showed that some trace elements present in sediments had high concentrations. Results for both rivers demonstrated that a significant number of elements were present in water samples in different concentrations.
Collins et al. 1996	ICP-MS	Suitability of multi-element fingerprinting to address the possible sources for the suspended sediments in the Exe and Severn rivers in UK was assessed. Different sections of the catchment were sampled as a possible source; A mixing model has then been successfully used to calculate the relative contributions from the various sub-basin type spatial sources, using the composite signatures identified.

Table 1.2. Studies on wetlands and rivers with the application of sediment source tracing (Continued).

Authors	Technique	Description of the study
Collins et al. 1997	ICP-MS	In the Dart and Plynlimon catchments, UK, sediment source types were evaluated using the mean contributions and variations in the relative contributions of surface erosion. Many sources were identified for different land use categories and channel erosion. This study also demonstrated that sediment source tracing techniques could be applied for identifying sources within the catchment.
Dirszowsky 2004	ICP-MS	Bed material was examined in the upper Fraser River drainage basin to address the sources of sediments in the river. It was concluded that conservative mixing estimates based on composite fingerprints show that the Moose River sub-basin contributes disproportionately to the <63 µm and coarser grained bed material load of the upper Fraser River near Moose Lake, also glaciers were important in generating fine and stream sediments that explain the bedrock distribution.
N'guessan et al. 2009	ICP-MS	Major and trace elements in the Gascogne region (France) were collected from three main river basins. Eight elements that might be harmful (As, Cd, Co, Cr, Cu, Ni, Pb and Zn), four reference elements for normalization (Al, Cs, Fe and Sc) and four major elements (CA, Mg, Mn and P) were considered to study the influence of agricultural activities on the element concentrations.

Table 1.2. Studies on wetlands and rivers with the application of sediment source tracing (Continued).

Authors	Technique	Description of the study
Stutter et al. 2009	ICP-MS	The goal of this study was to assess the accuracy and convenience of sediment fingerprinting as a method to identify the possible sources in the catchment. Samples were collected from stream suspended particulate matter, bed sediments and soils in a small agricultural catchment in Scotland and major elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti) and trace elements (Ba, Be, Ce, Co, Cr, Mo, Nd, Pb, Sr, Th, V, Y, Zn). Results demonstrated that fingerprinting could be applied as a tool to investigate the sources for sediment in the catchment. It also showed that elements such as P influence the water quality when bed sediments are interacting with lower flowing waters.
Wijeyaratne. 2011	ICP-MS	In this study sediments from the turtle and Souris rivers (North Dakota) were collected from the river and its tributaries to investigate the sources of the sediments within the catchment. Results demonstrated that there was a significant variation in element concentration at Turtle River and sediment fingerprinting could be successfully used to identify the possible sources of sediments in these rivers

1.8. Thesis outline

The first chapter consists of a general introduction (Chapter 1) to review the literature relevant to the study. The three chapters following the introduction include the methods and results of my field and lab work. The final chapter is a general discussion (Chapter 5) and conclusions with regards to the findings in this research.

1.8.1. Chapter 2- Multi–element concentrations in riparian wetlands of North Dakota

The lab and field work studies were conducted to investigate the use of concentrations of multiple elements in riparian soil/sediments to develop multi-element fingerprints for monitoring the element compositions in rivers and riparian wetlands in North Dakota. Four sampling sites each were selected along the Red, James, Sheyenne, Missouri and Little Missouri rivers and the samples collected from riparian sediment were analyzed for multi-element concentrations to study the variations in the multi-element fingerprints between the rivers and within each river, pH, LOI and particle size (f<63µm).

1.8.2. Chapter 3- Sediment source tracing at the Red River using multi-element fingerprinting approach

In this chapter the aim was to identify the possible sources and tributaries that contribute the most to the cadmium and selenium concentrations at the Red River using the sediment fingerprinting method and a sediment source tracing technique which was based on the linear mixing assumption. Five sites and two tributaries along the Red River were sampled and the samples collected from sediment deposits were analyzed for multi-element concentrations to study the element variations along the Red River and pH, LOI and particle size (f<63µm).

Percentage contributions from tributaries to the element concentrations at the Rivers were calculated using a linear mixing model.

1.8.3. Chapter 4- Sediment source tracing at the Little Missouri River, using the multi-element fingerprinting approach

In this chapter the aim was to identify the possible sources and tributaries that contribute the most to the uranium concentrations at the Little Missouri River. Little Missouri River and its tributaries are known to intercept uranium-rich lignite (Murphy, 2007; Denson and Gill 1955; Denson et al. 1954). Five tributaries and two sites along the Little Missouri River and the samples collected from sediment deposits were analyzed for multi-element concentrations, pH, LOI and particle size (f<63μm). Percentage contributions from tributaries to the element concentrations at the Rivers were calculated using a linear mixing model.

CHAPTER 2. MULTI-ELEMENT CONCENTRATIONS IN RIPARIAN WETLANDS OF NORTH DAKOTA

2.1. Abstract

As they flow through the landscape, rivers in North Dakota, U.S.A., encounter a diverse geology and landscape. River sediments represent different sources within the catchment, and make up the substrate for riparian wetlands. In this study, sediment deposits from the Red, James, Sheyenne, Missouri, and Little Missouri rivers were sampled in order to investigate the element concentrations and their distribution in sediments that interact with riparian vegetation using the multi-element fingerprinting method. Four locations were sampled along each of the rivers, and sediment was analyzed for multiple elements using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). This study showed there was significant variation in element concentrations in the sediments between and within these rivers. Organic matter and pH did not correlate significantly with element concentrations. Particle size, on the other hand, played an important role in element distribution for the Red, James, and Sheyenne rivers. The Red River had the highest and the Little Missouri had the lowest proportion of particles smaller than 63 µm. This study showed the multi-element fingerprinting method could be applied to study element distributions and concentrations.

2.2. Introduction

Riparian wetlands are wetlands adjacent to rivers and streams, and they usually occur as an ecotone between aquatic and dry land ecosystems with distinct soil characteristics and vegetation communities (Mitsch et al. 2009) and are some of the most diverse and dynamic parts of the landscape (Swanson et al. 1988). Variation, richness, and abundance of species tend to be greater in riparian wetlands than in adjacent ecosystems (Odum 1979). Riparian wetlands act as important sinks for metals from river water or from the greater watershed by the process of element uptake by plants, deposition, and sedimentation (Gorham et al. 1984; Du Laing et al. 2009; Niu et al. 2009). Mitsch (1995) presented that a riparian wetland's ability to accumulate metals depends on many factors including water, sediment, and plants via chemical, physical, and biological processes A number of studies have shown accumulation of metals in natural riparian wetlands (Johns 1995; Diagomanolin et al. 2004; Helios et al. 2005; Overesch et al. 2007; Galicki et al. 2008; Liu et al. 2008; Reczynski 2010; Bai et al. 2011; Wang et al. 2011; Zhang et al. 2012). Although they are such diverse, productive and important environments only a little is known about riparian sediments and questions exist regarding the impacts of urbanization, mining, and other human-related activities on riparian wetland conditions, element compositions in riparian sediment, and their adaptations to different geology and landscape.

Sediments are an important source of information regarding the geology of the region and the magnitude of human-associated environmental contaminants. Urban riparian sediments are influenced mostly by human and urban related activities varying from metal contamination to agricultural amendments producing runoff waters loaded with fertilizers. In rivers, metals and many elements are predominantly transported while sorbed to sediments (Elder 1987). Moreover, once deposited in overbank systems, sediments provide long-term storage for metals in the environment (Spencer and MacLeod 2002) and usually physical and chemical characteristics of the sediment reflect the source. Few studies focus on riparian and river sediments in order to assess the concentrations of metals or nutrients (Johns 1995; Diagomanolin et al. 2004; Overesch 2007; Galicki et al. 2008; Wang et al. 2011).

North Dakota has diverse riparian wetland habitats, from the flat land of the Red River valley in the East to the steep gradients and narrow channels of the Little Missouri in the West. Riparian wetlands in North Dakota are found in a variety of landscapes and geologic conditions, but only a few studies address their characteristics and differences. In order to understand these systems, one of the first steps is to assess the element composition at each river. Multi-element fingerprinting is a technique that identifies the specific patterns of chemical element distribution and provides a sediment profile specific to each site and river. Other researchers have carried out studies on sediment chemistry of rivers (Wall and Wilding 1976; Peart and Walling 1986). Sediment profiles could be used for sediment source tracing and further studies on control and management strategies within a catchment. This information could also lead to valuable results for assessing and monitoring riparian wetland condition.

This study was carried out to evaluate the concentrations and distribution of multi-elements in riparian wetlands of the Red, Sheyenne, James, Missouri, and Little Missouri rivers in large scale for the first time in North Dakota, USA, to use and to evaluate the suitability of the multi-element fingerprinting method for monitoring riparian wetlands. It was hypothesized that 1) element fingerprints would significantly vary between the rivers due to the variation in geology in North Dakota, and 2) at each river element fingerprints would reflect the land use in the area. For example, the Red and Sheyenne rivers flow through agricultural lands and runoff waters entering these rivers were expected to show high concentrations of nutrients and elements found in fertilizers, such as cadmium. At the Little Missouri and Missouri rivers mining activities such as coal mining are dominant and the concentrations of metals such as uranium and lead were expected to be higher compared to the other rivers.

2.3. Materials and methods

2.3.1. Study area

The Red River, a relatively flat lake plain of the former Lake Agassiz (formed from melt waters of an ice sheet), flows through many agricultural and urban areas in the United States and Canada. The Red is about 885 km long and flows northward. The river spreads into the deltaic wetland named Netley Marsh after passing through Lake Winnipeg in Canada. When Lake Agassiz drained 9,500 years ago, the Red River was formed with the parent material from lacustrine soils precipitated at the bottom of the former Lake Agassiz (Anderson et al., 1984).

The Sheyenne River is 951 km long, and is one of the major tributaries of the Red River in eastern North Dakota. The River starts its journey north of McClusky, North Dakota and generally flows to the east, near McVille it turns south, and after passing through Griggs and Barnes counties the river turns northeastward again. Sheyenne River picks up the clay and silty-clay soil of the Red River Valley after Lisbon, and passes through the Sheyenne National Grassland (USGS 2012).

The James River is 1,143 km long and is one of the tributaries of the Missouri River in North Dakota, draining from the states of South Dakota and North Dakota. The river begins in northwestern North Dakota and flows to northeastern South Dakota and enters the Missouri River (USGS 2013).

The Missouri River is a major waterway of the central United States and the longest river in North America. The Rocky Mountains of western Montana are where the river begins and from there the Missouri River flows east and south for 4, 090 km and passes through states of Montana, North and South Dakota, Nebraska and Missouri before joining the Mississippi River.

The Little Missouri River is 901 km long and is a tributary of the Missouri River in the Northern Great Plains in western North Dakota. The Little Missouri starts in western Crook County, Wyoming, and flows northeastward through the southeastern corner of Montana and the northwestern corner of South Dakota. From the Badlands in South Dakota, the Little Missouri flows north into North Dakota. In North Dakota the river passes through both units of Theodore Roosevelt National Park, and in north unit flows east to Lake Sakakawea, and finally enters the Missouri River in the town of Killdeer. The Little Missouri flows through many different sedimentary deposits from the Paleocene, including sandstone and lignite coal (Murphy 2007).

2.3.2. Sample collection

Using topographic maps and satellite images of North Dakota, four depositional sites with vegetation were selected at each river (Figure 2.1). Further investigation was done on site to verify each site represents a natural riparian wetland. Indicators of wetlands, including hydric soil and hydrophyte vegetation were noted and the coordinates were recorded. The site was selected for even distribution within North Dakota so that along each river it was possible to study the changes in sediment element composition. At each river, the four sampling sites were designated A, B, C, and D, with the site A always the most upstream and site D always the most downstream (Table 2.1).

Sediment samples were collected (June through September 2011) so that they 1) represented the soil interacting with the riparian vegetation, and 2) were close enough to the river to represent the sediments carried by the water. Samples of the top soil (maximum depth 15 cm) among the riparian vegetation were collected along a transect perpendicular to the river. The first sample was collected 5 m from the water’s edge, and then the other four samples were collected at additional 2 m intervals.

The five samples, considered replicates along this transect, represent sediments deposited recently and wetland soils sample were collected by inverting a plastic zip-lock bag to grab the sample that was dug using a spade, then folding it back over the sample to prevent any contamination. The sealed bags were stored in a cooler with ice until they were brought to the laboratory.

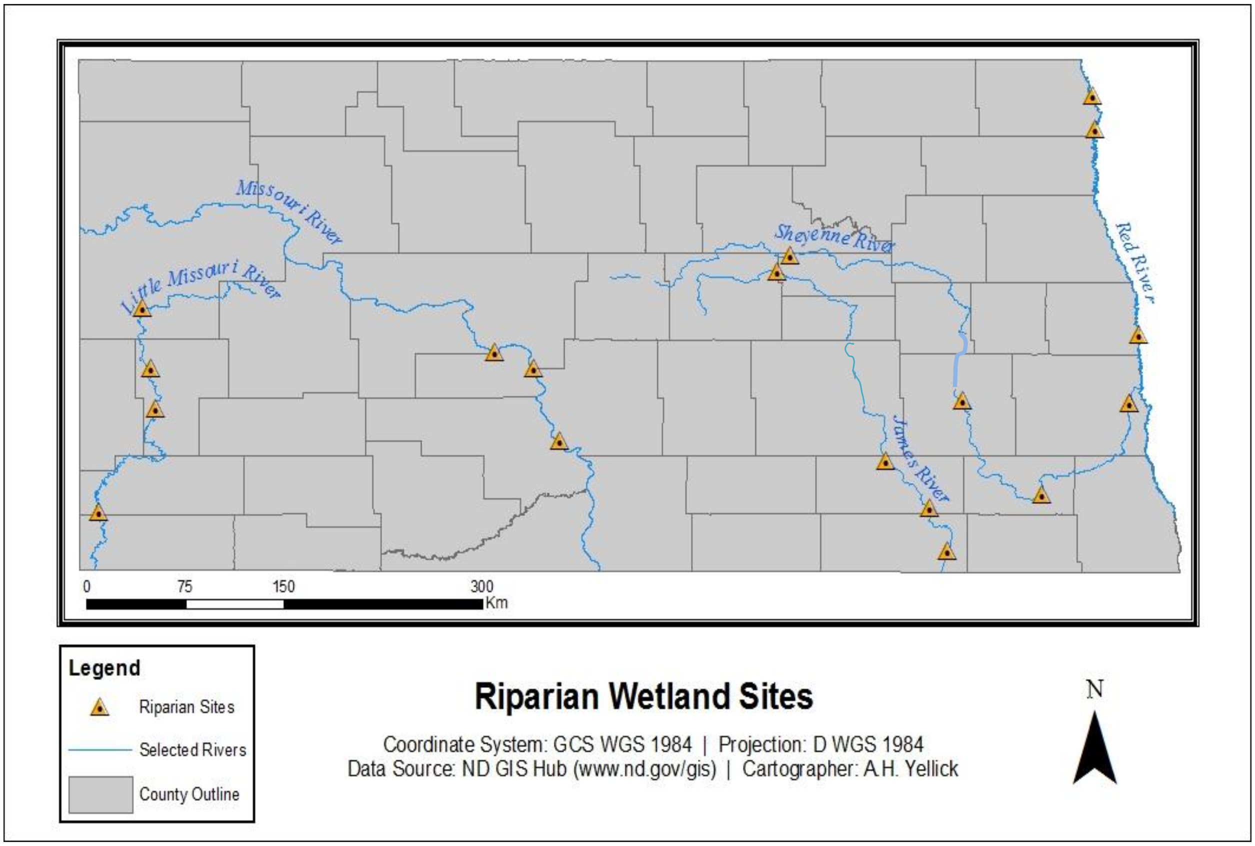


Figure 2.1. Map showing the general location of the rivers in North Dakota, USA. Sampling sites along the Red, Sheyenne, James, Missouri, and Little Missouri rivers are shown as A (furthest upstream), B, C, D (furthest downstream) (*n*=4 at each river).

At the Red and Sheyenne rivers all of the sampling sites were flooded, however the edge of the river, at normal river height, and the riparian zone by the river was identified and then samples were collected under the water at these flooded sites.

2.3.3. Sampling preparation

To preclude contamination during sample collection and transport, the clump of soil was cut and the interior was saved. At the flooded sites also the same procedure was applied and the soil under the water was taken out using a spade and the interior was saved. Samples were dried at 60 °C until they reached a constant weight, then homogenized with a mortar and pestle, first passed through a 2 mm mesh and afterwards sieved through a 63 µm sieve.

Table 2.1. Coordinates of the sampling sites along the Red, Sheyenne, James, Missouri and Little Missouri Rivers. The sampling sites along each river were named A, B, C, and D. Site A is always furthest upstream and site D is furthest downstream**.**

River	Site	Coordinates
Red	**A**	(47°21'6.18''N, 96° 50'31.98''W)
	B	(47°16'1.03''N, 96° 50'7.40''W)
	C	(48°35'15.99''N, 97° 8'28.46''W)
	D	(48°47'17.69''N, 97° 9'19.03''W)
Sheyenne	**A**	(47°49'39.85''N, 99°12'53.77''W)
	B	(46°57'49.66''N, 98°2'28.45''W)
	C	(46°56'55.10''N, 96°54'34.35''W)
	D	(46°24'3.19''N, 97°29'56.38''W)
James	**A**	(47°43'55.60''N, 99°17'55.86''W)
	B	(46°36'5.84''N, 98°33'34.77''W)
	C	(46°19'15.52''N ,98°15'54.83''W)
	D	(46° 3'46.54''N, 98° 8'45.05''W)
Missouri	**A**	(47°14'54.91''N, 101°13'23.84''W)
	B	(47° 9'11.02''N, 100°57'25.24''W)
	C	(47°17'28.34''N, 101° 3'12.18''W)
	D	(46°43'26.41''N, 100°46'49.13''W)
Little Missouri	**A**	(46°18'13.52''N, 103°54'48.27''W)
	B	(46°54'53.56''N, 103°31'53.20''W)
	C	(47° 9'25.77''N, 103°33'40.80''W)
	D	(47°31'4.75''N, 103°37'1.02''W)

2.3.4. Loss-on-ignition

Loss-on-ignition (LOI) was used to measure organic matter content of the sediments. After the crushed samples were passed through the 2 mm mesh, a subsample of approximately 15 g was dried at 105 °C in ceramic crucibles for two hours. The dry weight (Wd) of these samples was recorded, and then the samples were combusted to ash at 360 °C for another two hours in a Sybron Thermolyne muffle furnace (Sparks 1995). The weight of the remaining ash (Wa) was also recorded. The percentage of LOI, or percentage organic matter content, was calculated as [(Wd-Wa)/Wd]*100].

2.3.5. Particle size analysis

The ash remaining after measurement of LOI was used for determination of the fraction of particles smaller than 63 µm (f<63 µm), because this fraction is an important indicator for trace element-sediment chemistry in river sediments (Horowitz and Elrick 1987). The ash was used in order to avoid overestimation due to presence of organic matter. The initial dry weight of the ash was recorded (Wi) and then the samples were wet sieved through a 63 µm sieve using the tap water. The material remaining on the sieve was collected onto a pre-weighed Whatman No.1 filter paper, then oven dried at 60 °C and the dry weight was recorded (Wr). The percentage of particles smaller than 63 µm was calculated as [(Wi-Wr)/Wi]*100].

2.3.6. Soil pH

After samples were passed through a 2 mm mesh, pH was measured using a VWR Symphony SP90M5 Handheld Multimeter. Approximately 5 g of soil sample was used to determine the soil pH in a 1:2 soil: water ratio (Gavlak et al. 2003). The pH meter was calibrated at the beginning of the measurements and after every 25 samples to reduce errors.

2.3.7. Multi-element analysis

The samples (-63 µm sieved) were sent to Activation Laboratories Ltd., Ontario, Canada, to be analyzed for multiple elements using the group UT-2 Analytical Package. At Activation labs a 500 mg sample was digested at 90 °C in aqua regia in a microprocessor-controlled digestion block for two hours. The solution was then diluted and analyzed by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) with very low detection limits. Detection limits as reported by Activation Laboratories Ltd in µmol/g: Ag 0.00002, Al 3.70, As 0.001, Au 0.000003, B 0.09, Ba 0.0007, Be.0 01, Bi 0.0004, Ca 2.45, Cd 0.0004, Ce 0.0006, Co 0.001, Cr 0.009, Cs 0.2, Cu 0.001, Dy 0.0006, Er 0.0006, Eu 0.0007, Fe 1.79, Ga 0.0003, Gd 0.0006, Ge 0.001, Hf 0.0006, Ho 0.0006, In 0.0002, K 2.55, La 0.0036, Li 0.014, Lu 0.0006, Mg 4.11, Mn 0.018, Mo 0.0001, Na 0.43, Nb 0.0011, Nd 0.14, Ni 0.0017, P 0.32, Pb 0.0009, Pr 0.0007, Rb 0.001, Re 0.005, S 0.30, Sb 0.0001, Sc 0.002, Se 0.001, Sm 0.0006, Sn 0.0001, Sr 0.0057, Ta 0.0005, Tb 0.0006, Te 0.003, Th 0.0004, Ti 2.08, Tl 0.00009, Tm 0.0006, U 0.0004, V 0.019, W 0.005, Y 0.0001, Yb 0.0005, Zn 0.0015, Zr 0.0011.

2.3.8. Data analysis

The sediment element concentrations for Au, Ge, Hf, Ta, Te, and W were below detection limits for all rivers, therefore those elements will not be discussed further. Minitab® 16 statistical software was used for data analysis. All data were log-transformed prior to analysis in order to obtain homogeneity of variance. Pearson’s correlation analysis was performed to test the relationships between element concentrations, LOI, and pH. A one-way ANOVA (p-value<0.05) (General Linear Model) was used for comparison between the rivers and also and a one-way ANOVA for each river separately was used for comparison of sites along each river.. Pearson’s correlations were considered statistically significant if r ≥ 0.707. These correlations explain 50% or more variation (McClave and Sincich 2006).

2.4. Results

2.4.1. Variations in LOI, particle size (f<63 µm), and pH at each of the rivers

Results for LOI, particle size, and pH are given in Table 2.2. LOI and pH did not show significant variation within or between the rivers. Particle size (*f*<63 µm) varied significantly within each river except for the Little Missouri River.

Except for the James River, the average proportion of small particles (*f*<63 µm) showed an increasing trend from west to east in North Dakota in the order Red<James<Sheyenne<Missouri <Little Missouri (Figure 2.2). LOI, pH and elements did not show significant correlations for any sites or rivers.

Table 2.2. Range, Mean and *p*-value for LOI, percentage particle size (*f*<63 µm (%)) and pH within the Red, Sheyenne, James, Missouri and Little Missouri rivers (n=20) and between all of the rivers in North Dakota (n=100)**.**

River	LOI (% OM)			Particle size *f*<63 µm (%)			pH		
	range	mean	*p*- value	range	mean	*p*- value	range	mean	*p* value
Red	0.7- 9.2	3.3	0.63	38.1-99.4	73.6	0	6.6-8.2	7.6	0.81
Sheyenne	0-10.4	3.1	0.25	27.7- 100	64.5	0	6.6-7.9	7.4	0.12
James	1.0- 8.2	2.8	0.2	34.1-75	70	0	7.0-8.1	7.5	0.26
Missouri	0.1-10.1	3.1	0.8	21.5- 100	55.3	0	7.0-8.2	7.6	0.06
Little Missouri	3.1-5.6	2.3	0.16	21.6-100	51.5	0.33	6.6-8.4	7.4	0.13
All rivers	0-10.4	2.9	0.59	21.5-100	63	0.01	6.6-8.4	7.5	0.09

2.4.2. Analysis for multiple elements and development of fingerprints

Based on the results from the ANOVA analysis on the element concentrations rivers, Al, B, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Ga, Ho, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pr, Rb, Re, S, Sm, Sn, Sr, Th, Ti, U, V, Y, Yb, and Zn showed statistically significant variation between the rivers ($p<0.05$).

Among the elements which showed significant variation between the rivers, elements B, Bi, Ca, Cd, Cr, Ga, K, Li, Mn, Sn, V and Zn showed highest mean ($n=20$ at each river) concentrations at the Red, Sheyenne and James Rivers in eastern North Dakota, and elements Ba, Ce, Cs, Eu, La, Mo, Sm and Th showed highest concentrations at the Little Missouri and Missouri Rivers in western North Dakota.

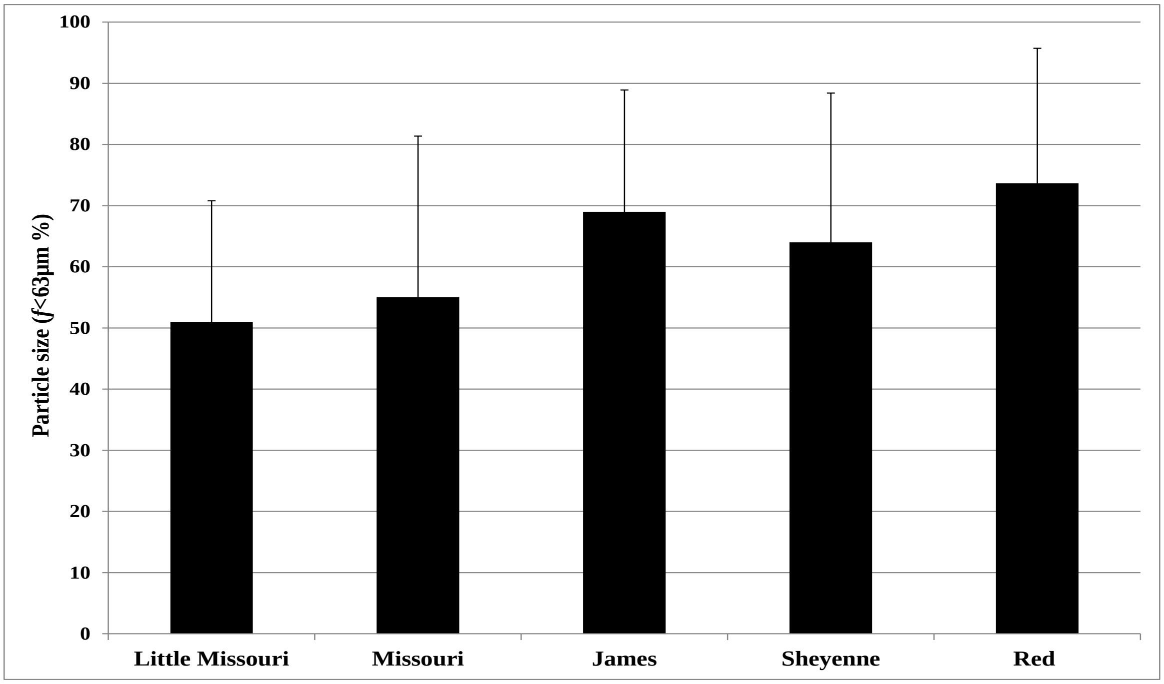


Figure 2.2. Mean particle size ($f<63$ μm) at the Red, James, Sheyenne, Missouri and Little Missouri rivers ($n=20$ at each river).

Many elements showed significant correlations with each other (e.g. Al and Li, Be and Ba, Cr and Al, Fe and Al, Ca and Mg…) over all of the rivers) ($r \geq 0.707$). As an example Ca and Mg ($n=100$) are shown in Figure 2.3.

A higher range of concentrations for both elements was recorded at the Red and James in eastern North Dakota while there was a lower range for both at the Missouri and Little Missouri rivers.

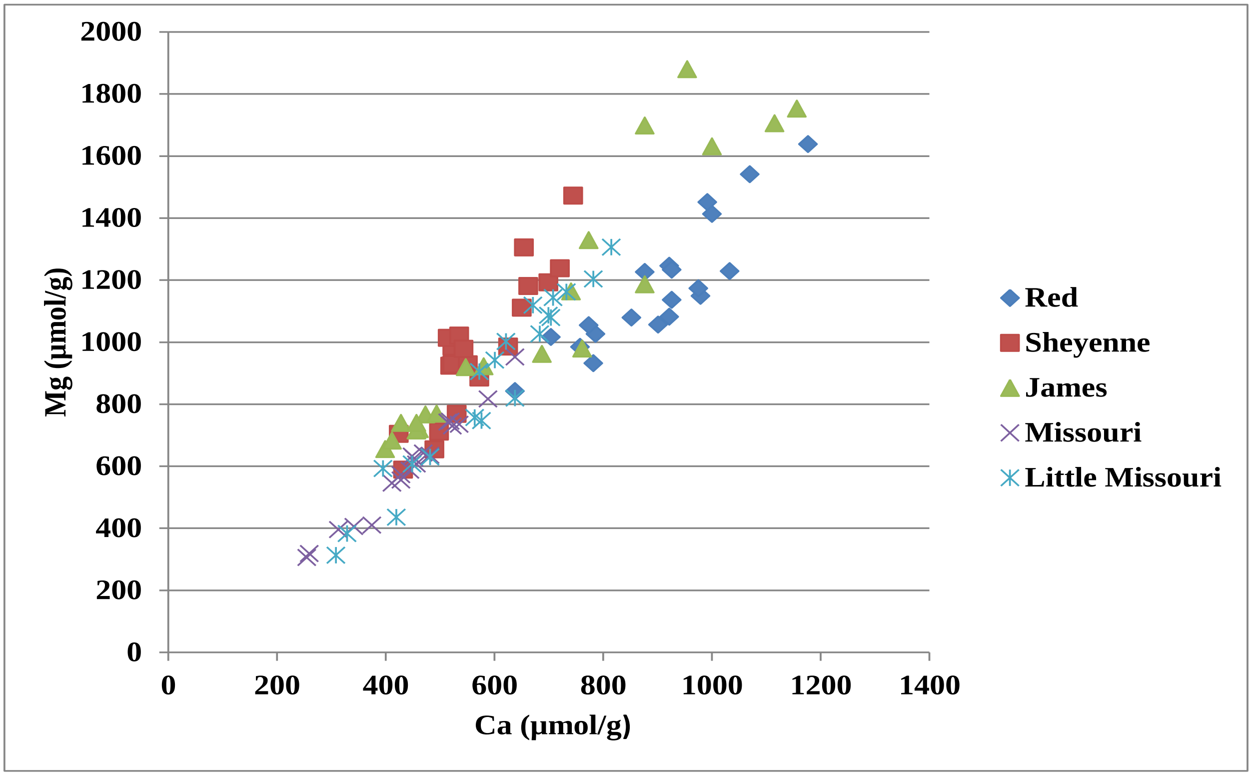


Figure 2.3. Relationships between Ca and Mg in riparian floodplain soils of the Red, Sheyenne, James, Missouri and Little Missouri rivers (*n*=100) in North Dakota.

2.4.3. Element variation at each of the rivers

2.4.3.1. Red River

An example of a fingerprint prepared for Red River site A is given in Figure 2.4. Similar fingerprints were prepared for all of the other sites at the Red River. The mean concentrations of elements ± standard deviation at the four sampling sites along the Red River are given in Table 2.3. For elements Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mn, Ni, P, Pb, Rb, S, Sc, Se, Sn, Ti, V, Zn and Zr concentrations significantly varied ($p < 0.05$) between the four sampling sites.

Of these elements, Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Ni, Pb, Rb, Sc, Se, Zn, and Zr showed an increasing pattern as the river flows from upstream (site A, south) to downstream (site D, north) in Pembina where the Red River enters Canada.

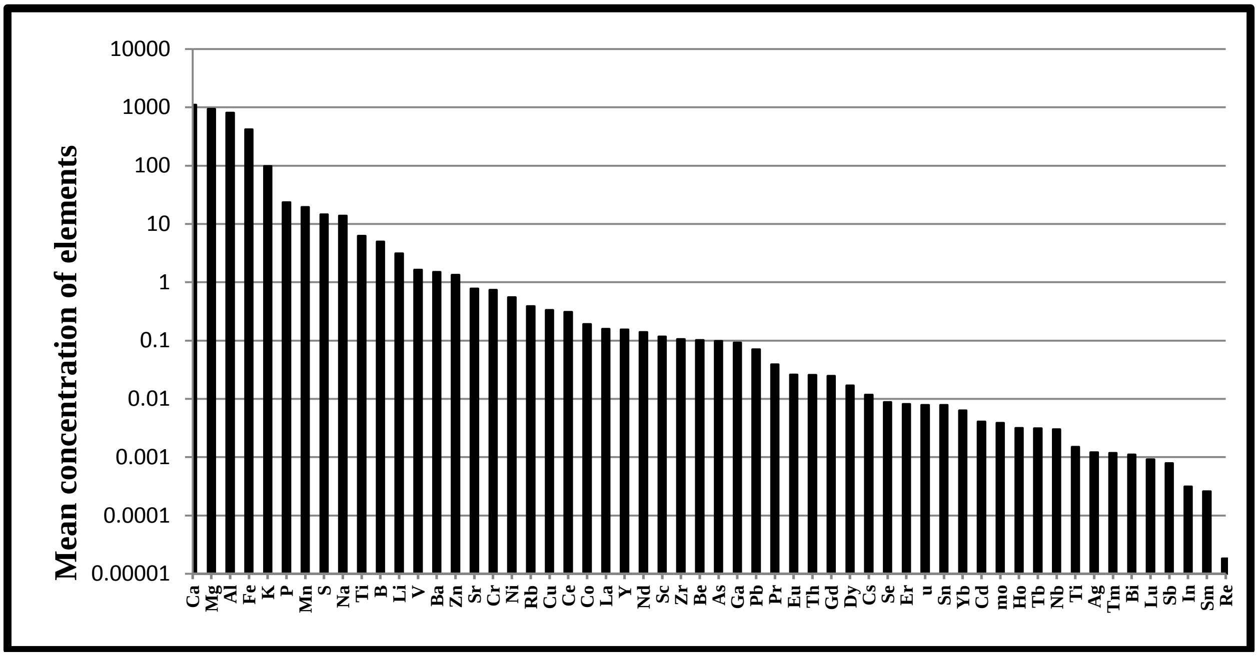


Figure 2.4 Multi-element fingerprints of sediment from the Red River site A (south). Elements are ordered from high to low mean concentrations (*n*=20).

Table 2.3. Mean concentration ± standard deviation of elements (µmolg^{-1} of dry sediment) in the sites (A (furthest upstream), B, C, D (furthest downstream)) of the Red River (*n*=5 at each site). Elements that significantly ($p < 0.05$) vary between the sites are in bold.

Element	Site A		Site B		Site C		Site D	
Ag	0.0007 ±	0.0005	0.0009 ±	0.0004	0.0011 ±	0.0003	0.0010 ±	0.0007
Al	**465 ±**	**35**	**552 ±**	**95**	**688 ±**	**70**	**815 ±**	**138**
As	**0.068 ±**	**0.007**	**0.079 ±**	**0.020**	**0.069 ±**	**0.011**	**0.098 ±**	**0.021**
B	4.31 ±	0.7	4.74 ±	0.9	4.59 ±	0.4	4.98 ±	0.6
Ba	**1.171 ±**	**0.1**	**1.320 ±**	**0.3**	**1.481 ±**	**0.1**	**1.499 ±**	**0.2**
Be	**0.064 ±**	**0.00**	**0.073 ±**	**0.01**	**0.093 ±**	**0.01**	**0.102 ±**	**0.01**
Bi	0.001 ±	0.005	0.001 ±	0.0001	0.001 ±	0.0001	0.001 ±	0.0001
Ca	1244 ±	250	1275 ±	256	1067 ±	142	1112 ±	114
Cd	**0.003 ±**	**0.0002**	**0.003 ±**	**0.0006**	**0.004 ±**	**0.0003**	**0.004 ±**	**0.0007**
Ce	0.327 ±	0.05	0.307 ±	0.04	0.295 ±	0.02	0.311 ±	0.03
Co	**0.145 ±**	**0.01**	**0.155 ±**	**0.03**	**0.165 ±**	**0.01**	**0.193 ±**	**0.03**
Cr	**0.48 ±**	**0.04**	**0.53 ±**	**0.1**	**0.63 ±**	**0.1**	**0.74 ±**	**0.1**
Cs	**0.007 ±**	**0.002**	**0.008 ±**	**0.002**	**0.009 ±**	**0.003**	**0.012 ±**	**0.003**
Cu	**0.225 ±**	**0.02**	**0.249 ±**	**0.03**	**0.334 ±**	**0.05**	**0.335 ±**	**0.03**
Dy	0.016 ±	0.002	0.016 ±	0.002	0.016 ±	0.001	0.017 ±	0.002
Er	0.007 ±	0.0007	0.008 ±	0.0011	0.008 ±	0.0005	0.008 ±	0.0010
Eu	0.026 ±	0.003	0.025 ±	0.004	0.025 ±	0.002	0.026 ±	0.003

Table 2.3. Mean concentration ± standard deviation of elements (μmolg^{-1} of dry sediment) in the sites (A (furthest upstream), B, C, D (furthest downstream)) of the Red River (n=5 at each site) (continued).

Element	**Site A**		**Site B**		**Site C**		**Site D**	
Fe	**306 ±**	**18**	**346 ±**	**55**	**380 ±**	**35**	**421 ±**	**59**
Ga	**0.052 ±**	**0.003**	**0.063 ±**	**0.010**	**0.079 ±**	**0.009**	**0.092 ±**	**0.01**
Gd	0.024 ±	0.003	0.023 ±	0.004	0.023 ±	0.003	0.025 ±	0.004
Ho	0.003 ±	0.0003	0.003 ±	0.0005	0.003 ±	0.0000	0.003 ±	0.0005
In	**0.174 ±**	**0.000**	**0.209 ±**	**0.048**	**0.261 ±**	**0.000**	**0.314 ±**	**0.048**
K	**54.7 ±**	**7**	**65.0 ±**	**13**	**84.9 ±**	**12**	**98.7 ±**	**17**
La	0.165 ±	0.03	0.157 ±	0.02	0.151 ±	0.01	0.158 ±	0.02
Li	**1.90 ±**	**0.10**	**2.24 ±**	**0.23**	**2.84 ±**	**0.20**	**3.13 ±**	**0.38**
Lu	0.001 ±	0	0.001 ±	0.0003	0.001 ±	0.0003	0.001 ±	0.0003
Mg	890 ±	155	932 ±	167	839 ±	116	938 ±	96
Mn	**11.62 ±**	**2**	**15.26 ±**	**4**	**14.14 ±**	**1**	**19.55 ±**	**2**
Mo	0.002 ±	0.002	0.002 ±	0.002	0.002 ±	0.002	0.004 ±	0.004
Na	12.8 ±	4	13.7 ±	4	12.9 ±	2	13.9 ±	3
Nb	0.005 ±	0.001	0.004 ±	0.002	0.005 ±	0.003	0.003 ±	0.001
Nd	0.145 ±	0.02	0.138 ±	0.02	0.134 ±	0.01	0.140 ±	0.02
Ni	**0.357 ±**	**0.03**	**0.382 ±**	**0.06**	**0.472 ±**	**0.03**	**0.554 ±**	**0.07**
P	**24.9 ±**	**1.142**	**25.4 ±**	**1.748**	**23.6 ±**	**0.604**	**23.6 ±**	**0.604**
Pb	**0.050 ±**	**0.005**	**0.053 ±**	**0.006**	**0.079 ±**	**0.01**	**0.070 ±**	**0.006**
Pr	0.041 ±	0.007	0.039 ±	0.006	0.038 ±	0.003	0.039 ±	0.004
Rb	**0.220 ±**	**0.02**	**0.271 ±**	**0.05**	**0.343 ±**	**0.05**	**0.387 ±**	**0.06**
Re	0.008 ±	0.003	0.015 ±	4.49E-03	0.010 ±	0.004	0.018 ±	0.005
S	**20.6 ±**	**4**	**21.6 ±**	**4**	**13.1 ±**	**1**	**14.7 ±**	**4**
Sb	0.001 ±	0.0005	0.001 ±	0.0006	0.001 ±	0.0004	0.001 ±	0.0004
Sc	**0.073 ±**	**0.01**	**0.088 ±**	**0.02**	**0.099 ±**	**0.01**	**0.117 ±**	**0.02**
Se	**0.006 ±**	**0.002**	**0.008 ±**	**0.001**	**0.009 ±**	**0.002**	**0.009 ±**	**0.002**
Sm	0.260 ±	0.03	0.250 ±	0.04	0.250 ±	0.02	0.260 ±	0.03
Sn	**0.006 ±**	**0.0003**	**0.007 ±**	**0.002**	**0.009 ±**	**0.001**	**0.008 ±**	**0.001**
Sr	0.772 ±	0.08	0.834 ±	0.15	0.791 ±	0.05	0.784 ±	0.10
Tb	0.0030 ±	0.001	0.0030 ±	0.001	0.0030 ±	0.0003	0.0031 ±	0.0004
Th	0.026 ±	0.005	0.024 ±	0.003	0.021 ±	0.003	0.026 ±	0.003
Ti	**7.10 ±**	**1.1**	**7.10 ±**	**1.1**	**6.27 ±**	**0**	**6.27 ±**	**0**
Tl	0.0009 ±	0.0001	0.0010 ±	0.0002	0.0013 ±	0.0003	0.002 ±	0.0003
Tm	0.0011 ±	0.0003	0.0011 ±	0.0003	0.0012 ±	0	0.001 ±	0
U	0.007 ±	0.001	0.007 ±	0.001	0.008 ±	0.001	0.008 ±	0.001
V	**1.01 ±**	**0.1**	**1.18 ±**	**0.2**	**1.39 ±**	**0.1**	**1.65 ±**	**0.2**
Y	0.145 ±	0.01	0.150 ±	0.02	0.151 ±	0.01	0.154 ±	0.01
Yb	0.005 ±	0.001	0.006 ±	0.001	0.006 ±	0.001	0.006 ±	0.001
Zn	**0.934 ±**	**0.05**	**1.11 ±**	**0.14**	**1.36 ±**	**0.16**	**1.34 ±**	**0.15**
Zr	**0.073 ±**	**0.02**	**0.077 ±**	**0.02**	**0.091 ±**	**0.03**	**0.106 ±**	**0.03**

Figure 2.5 shows an example of the increasing concentration of elements along the Red River. Concentrations of Fe significantly vary (p<0.05) along the four sampling sites at the Red River, and upstream (site A) has the lowest concentration and downstream (site D) has the highest concentrations.

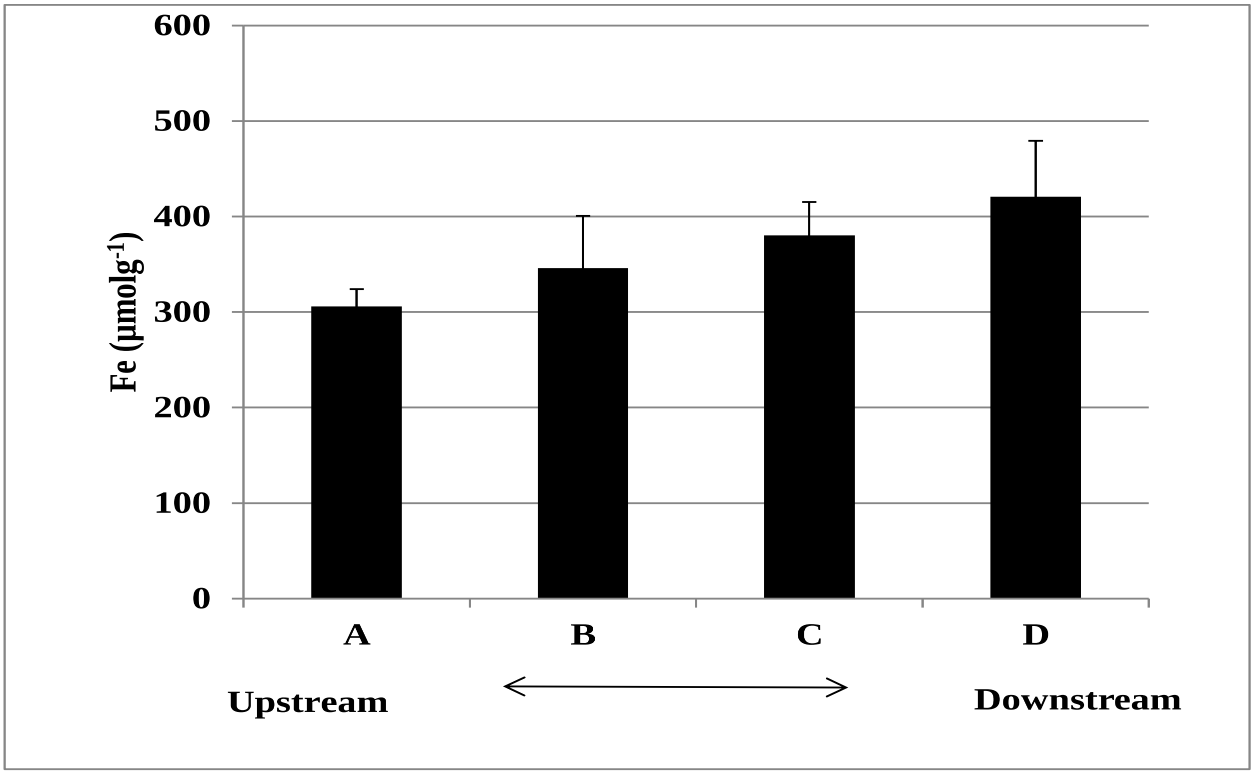


Figure 2.5. Mean concentration of Fe in the sediments at the sampling sites (*n*=5 at each site) of the Red River. The concentrations significantly increase (p<0.05) from Upstream (site A) to Downstream (Site D).

2.4.3.2. Sheyenne River

The mean concentrations of elements ± standard deviation at the four sampling sites along the Sheyenne River are given in Table 2.4. The mean concentrations of As, Ca, Cd, Co, Er, Eu, Gd, Ho, La, Li, Mg, Mn, Na, Nb, Nd, Ni, P, Pr, S, Sb, Sm, Th, Ti, U, V, Y showed statistically significant variation between the four sampling sites of the Sheyenne River (p <0.05).

Table 2.4. Mean concentration ± standard deviation of elements (µmolg^{-1} of dry sediment) in the sites (A (furthest upstream), B, C, D (furthest downstream) of the Sheyenne River (*n*=5 at each site). Elements that significantly (p< 0.05) vary between the sites are in bold.

Element	**Site A**		**Site B**		**Site C**		**Site D**	
Ag	0.0005 ±	0.00003	0.001 ±	0.0001	0.001 ±	0.0004	0.001 ±	0.0003
Al	582 ±	76	582 ±	64	566 ±	50	503 ±	80
As	**0.050 ±**	**0.005**	**0.068 ±**	**0.015**	**0.088 ±**	**0.013**	**0.107 ±**	**0.018**
B	5.64 ±	0.4	5.35 ±	0.4	4.66 ±	0.7	4.98 ±	1.0

Table 2.4. Mean concentration ± standard deviation of elements (µmolg^{-1} of dry sediment) in the sites (A (furthest upstream), B, C, D (furthest downstream) of the Sheyenne River (*n*=5 at each site) (continued).

Element	**Site A**		**Site B**		**Site C**		**Site D**	
Ba	1.146 ±	0.6	1.758 ±	0.1	1.438 ±	0.2	1.435 ±	0.2
Be	0.080 ±	0.01	0.071 ±	0.01	0.080 ±	0.00	0.073 ±	0.01
Bi	0.001 ±	0.010	0.001 ±	0.0001	0.001 ±	0.0001	0.001 ±	0.0001
Ca	**685 ±**	**68**	**974 ±**	**46**	**1046 ±**	**159**	**1209 ±**	**189**
Cd	**0.003 ±**	**0.0005**	**0.002 ±**	**0.0004**	**0.004 ±**	**0.0005**	**0.004 ±**	**0.0006**
Ce	0.253 ±	0.04	0.345 ±	0.02	0.298 ±	0.03	0.359 ±	0.05
Co	**0.138 ±**	**0.02**	**0.195 ±**	**0.03**	**0.175 ±**	**0.02**	**0.201 ±**	**0.03**
Cr	0.49 ±	0.03	0.48 ±	0.04	0.53 ±	0.04	0.50 ±	0.1
Cs	0.007 ±	0.001	0.009 ±	0.001	0.009 ±	0.002	0.009 ±	0.002
Cu	0.240 ±	0.02	0.245 ±	0.03	0.259 ±	0.03	0.251 ±	0.04
Dy	0.015 ±	0.002	0.019 ±	0.001	0.017 ±	0.002	0.018 ±	0.002
Er	**0.007 ±**	**0.0007**	**0.009 ±**	**0.0003**	**0.008 ±**	**0.0009**	**0.009 ±**	**0.0012**
Eu	**0.022 ±**	**0.003**	**0.029 ±**	**0.002**	**0.025 ±**	**0.002**	**0.030 ±**	**0.004**
Fe	347 ±	41	321 ±	29	330 ±	34	321 ±	51
Ga	0.063 ±	0.005	0.058 ±	0.008	0.063 ±	0.006	0.054 ±	0.008
Gd	**0.021 ±**	**0.003**	**0.028 ±**	**0.001**	**0.024 ±**	**0.003**	**0.028 ±**	**0.004**
Ho	**0.003 ±**	**0.0003**	**0.004 ±**	**0.0000**	**0.003 ±**	**0.0003**	**0.003 ±**	**0.0003**
In	0.226 ±	0.048	0.226 ±	0.048	0.226 ±	0.048	0.209 ±	0.048
K	78.8 ±	12	82.4 ±	6	73.7 ±	12	72.1 ±	15
La	**0.129 ±**	**0.02**	**0.172 ±**	**0.01**	**0.151 ±**	**0.02**	**0.184 ±**	**0.03**
Li	**2.44 ±**	**0.12**	**2.02 ±**	**0.17**	**2.26 ±**	**0.17**	**1.80 ±**	**0.29**
Lu	0.001 ±	0.0003	0.001 ±	0	0.001 ±	0.0003	0.001 ±	0.0003
Mg	**475 ±**	**46**	**523 ±**	**8**	**634 ±**	**75**	**651 ±**	**72**
Mn	**12.8 ±**	**3**	**72.3 ±**	**13**	**34.0 ±**	**7**	**46.6 ±**	**7**
Mo	0.002 ±	0.002	0.000 ±	0.000	0.001 ±	0.001	0.002 ±	0.001
Na	**36.5 ±**	**6**	**30.9 ±**	**5**	**19.3 ±**	**3**	**13.8 ±**	**3**
Nb	**0.009 ±**	**0.001**	**0.004 ±**	**0.001**	**0.003 ±**	**0.001**	**0.003 ±**	**0.001**
Nd	**0.117 ±**	**0.01**	**0.155 ±**	**0.01**	**0.134 ±**	**0.01**	**0.162 ±**	**0.02**
Ni	**0.336 ±**	**0.04**	**0.583 ±**	**0.08**	**0.532 ±**	**0.07**	**0.647 ±**	**0.11**
P	**26.8 ±**	**0.995**	**33.5 ±**	**1.104**	**27.8 ±**	**0.823**	**29.5 ±**	**0.587**
Pb	0.056 ±	0.007	0.060 ±	0.009	0.054 ±	0.004	0.056 ±	0.006
Pr	**0.033 ±**	**0.004**	**0.044 ±**	**0.003**	**0.038 ±**	**0.004**	**0.046 ±**	**0.007**
Rb	0.300 ±	0.05	0.274 ±	0.02	0.276 ±	0.04	0.246 ±	0.05
Re	0.014 ±	0.005	0.011 ±	0.004	0.012 ±	0.004	0.008 ±	0.003
S	**94.8 ±**	**75**	**42.4 ±**	**12**	**21.9 ±**	**1**	**14.4 ±**	**2**
Sb	**0.001 ±**	**0.0003**	**0.001 ±**	**0.0003**	**0.001 ±**	**0.0005**	**0.001 ±**	**0.0006**
Sc	0.076 ±	0.01	0.074 ±	0.01	0.083 ±	0.01	0.074 ±	0.02
Se	0.0098 ±	0.001	0.0095 ±	0.002	0.010 ±	0.003	0.0095 ±	0.002
Sm	**0.221 ±**	**0.03**	**0.290 ±**	**0.02**	**0.253 ±**	**0.02**	**0.297 ±**	**0.04**
Sn	0.005 ±	0.0004	0.005 ±	0.001	0.006 ±	0.001	0.005 ±	0.001
Sr	0.968 ±	0.09	1.184 ±	0.06	1.027 ±	0.13	1.149 ±	0.18
Tb	0.003 ±	0.000	0.004 ±	0.000	0.003 ±	0.001	0.004 ±	0.001
Th	**0.015 ±**	**0.002**	**0.023 ±**	**0.002**	**0.023 ±**	**0.002**	**0.027 ±**	**0.004**
Ti	**6.27 ±**	**0**	**7.10 ±**	**1.1**	**6.27 ±**	**0**	**6.27 ±**	**0**
Tl	0.0010 ±	0.07	0.0010 ±	0.0002	0.0011 ±	0.0001	0.0012 ±	0.0002

Table 2.4. Mean concentration ± standard deviation of elements (µmolg^{-1} of dry sediment) in the sites (A (furthest upstream), B, C, D (furthest downstream) of the Sheyenne River (*n*=5 at each site) (continued).

Element	**Site A**		**Site B**		**Site C**		**Site D**	
Tm	0.0009 ±	0.0003	0.0012 ±	0.0000	0.0012 ±	0.0000	0.0012 ±	0.0000
U	**0.006 ±**	**0.000**	**0.007 ±**	**0.001**	**0.007 ±**	**0.001**	**0.008 ±**	**0.001**
V	**0.96 ±**	**0.1**	**1.22 ±**	**0.1**	**1.26 ±**	**0.1**	**1.26 ±**	**0.2**
Y	**0.141 ±**	**0.01**	**0.176 ±**	**0.01**	**0.156 ±**	**0.01**	**0.171 ±**	**0.02**
Yb	0.006 ±	0.001	0.007 ±	0.000	0.006 ±	0.001	0.006 ±	0.001
Zn	1.26 ±	0.11	1.27 ±	0.16	1.22 ±	0.12	1.20 ±	0.18
Zr	0.079 ±	0.03	0.084	0.01	0.070 ±	0.02	0.064 ±	0.02

2.4.3.3. James River

The mean concentrations of elements ± standard deviation at the four sampling sites along the James River are given in Table 2.5. The concentration of Ba, Be, Ca, Cd, Cu, Ga, Li, Mg, Mn, Mo, Ni, P, Pb, Re, S, Sn, Th, Ti, U, Zn showed statistically significant variation between the four sampling sites of the James River (*p* <0.05).

Table 2.5. Mean concentration ± standard deviation of elements (µmolg^{-1} of dry sediment in the sites (A (furthest upstream), B, C, D (furthest downstream)) of the James River (*n*=5 at each site). Elements that significantly (*p*<0.05) vary between the sites are in bold.

Element	**Site A**		**Site B**		**Site C**		**Site D**	
Ag	0.001 ±	0.0005	0.001 ±	0.0003	0.001 ±	0.0004	0.0004 ±	0.0002
Al	573 ±	108	500 ±	35	563 ±	109	470 ±	50
As	0.077 ±	0.03	0.051 ±	0.01	0.051 ±	0.01	0.074 ±	0.02
B	4.37 ±	0.6	4.77 ±	0.4	4.75 ±	0.5	4.22 ±	0.6
Ba	**1.506 ±**	**0.2**	**0.940 ±**	**0.4**	**1.185 ±**	**0.4**	**1.656 ±**	**0.2**
Be	**0.071 ±**	**0.01**	**0.078 ±**	**0.01**	**0.091 ±**	**0.01**	**0.068 ±**	**0.01**
Bi	0.001 ±	0.009	0.001 ±	0.007	0.001 ±	0.016	0.001 ±	0.007
Ca	**1539 ±**	**289**	**712 ±**	**45**	**790 ±**	**100**	**1220 ±**	**387**
Cd	**0.003 ±**	**0.0003**	**0.002 ±**	**0.0002**	**0.003 ±**	**0.0004**	**0.002 ±**	**0.0003**
Ce	0.288 ±	0.03	0.254 ±	0.02	0.257 ±	0.04	0.279 ±	0.03
Co	0.146 ±	0.02	0.120 ±	0.01	0.137 ±	0.02	0.146 ±	0.01
Cr	0.55 ±	0.1	0.47 ±	0.0	0.51 ±	0.1	0.45 ±	0.0
Cs	0.008 ±	0.002	0.007 ±	0.002	0.008 ±	0.003	0.006 ±	0.002
Cu	**0.262 ±**	**0.04**	**0.194 ±**	**0.02**	**0.222 ±**	**0.03**	**0.207 ±**	**0.02**
Dy	0.015 ±	0.001	0.014 ±	0.001	0.015 ±	0.002	0.015 ±	0.001
Er	0.007 ±	0.0007	0.006 ±	0.0003	0.007 ±	0.0010	0.007 ±	0.0003
Eu	0.024 ±	0.002	0.022 ±	0.001	0.023 ±	0.003	0.023 ±	0.002
Fe	357 ±	51	317 ±	27	354 ±	63	335 ±	43
Ga	**0.060 ±**	**0.01**	**0.057 ±**	**0.01**	**0.062 ±**	**0.01**	**0.049 ±**	**0.01**
Gd	0.022 ±	0.003	0.020 ±	0.002	0.021 ±	0.004	0.021 ±	0.002
Ho	0.003 ±	0.0003	0.002 ±	0.0000	0.003 ±	0.0003	0.003 ±	0.0003

Table 2.5. Mean concentration ± standard deviation of elements (µmolg^{-1} of dry sediment in the sites (A (furthest upstream), B, C, D (furthest downstream)) of the James River (*n*=5 at each site) (continued).

Element	**Site A**		**Site B**		**Site C**		**Site D**	
In	0.209 ±	0.048	0.174 ±	0.000	0.203 ±	0.048	0.174 ±	0.000
K	71.1 ±	16	69.1 ±	7	79.3 ±	19	64.0 ±	11
La	0.146 ±	0.02	0.129 ±	0.01	0.131 ±	0.02	0.144 ±	0.02
Li	**2.51 ±**	**0.33**	**1.82 ±**	**0.19**	**2.30 ±**	**0.22**	**1.88 ±**	**0.13**
Lu	0.001 ±	0	0.001 ±	0	0.001 ±	0.0003	0.001 ±	0
Mg	**869 ±**	**112**	**435 ±**	**32**	**507 ±**	**55**	**919 ±**	**209**
Mn	**10.3 ±**	**1.7**	**40.1 ±**	**6.2**	**26.4 ±**	**4.9**	**21.1 ±**	**8.4**
Mo	**0.002 ±**	**0.002**	**0.001 ±**	**0.001**	**0.001 ±**	**0.001**	**0.004 ±**	**0.001**
Na	18.0 ±	3	21.2 ±	2	19.7 ±	4	15.7 ±	4
Nb	0.005 ±	0.003	0.006 ±	0.001	0.007 ±	0.001	0.006 ±	0.004
Nd	0.128 ±	0.01	0.115 ±	0.01	0.119 ±	0.02	0.125 ±	0.01
Ni	**0.444 ±**	**0.07**	**0.315 ±**	**0.03**	**0.377 ±**	**0.06**	**0.416 ±**	**0.03**
P	**19.5 ±**	**1**	**27.1 ±**	**2**	**28.5 ±**	**2**	**23.4 ±**	**1**
Pb	**0.049 ±**	**0.004**	**0.060 ±**	**0.002**	**0.052 ±**	**0.006**	**0.049 ±**	**0.002**
Pr	0.036 ±	0.004	0.033 ±	0.002	0.033 ±	0.005	0.035 ±	0.004
Rb	0.252 ±	0.05	0.241 ±	0.02	0.284 ±	0.06	0.212 ±	0.03
Re	**0.006 ±**	**2.40E-03**	**0.013 ±**	**2.00E-03**	**0.017 ±**	**0.004**	**0.005 ±**	**0**
S	**18.3 ±**	**10**	**100.3 ±**	**13**	**64.1 ±**	**17**	**22.6 ±**	**13**
Sb	0.001 ±	0.0005	0.001 ±	0.0004	0.001 ±	0.0002	0.001 ±	0.0006
Sc	0.086 ±	0.02	0.062 ±	0.00	0.076 ±	0.02	0.074 ±	0.01
Se	0.006 ±	0.002	0.008 ±	0.001	0.009 ±	0.002	0.007 ±	0.002
Sm	0.235 ±	0.02	0.217 ±	0.01	0.224 ±	0.03	0.228 ±	0.02
Sn	**0.005 ±**	**0.001**	**0.007 ±**	**0.001**	**0.005 ±**	**0.001**	**0.004 ±**	**0.0004**
Sr	0.972 ±	0.08	0.824 ±	0.05	0.899 ±	0.1	0.823 ±	0.1
Tb	0.003 ±	0.000	0.003 ±	0.000	0.003 ±	0.000	0.003 ±	0.000
Th	**0.023 ±**	**0.002**	**0.015 ±**	**0.001**	**0.016 ±**	**0.002**	**0.021 ±**	**0.002**
Ti	**9.19 ±**	**1.1**	**6.27 ±**	**0.0**	**7.10 ±**	**1.1**	**7.94 ±**	**0.9**
Tl	0.0013 ±	0.0002	0.0008 ±	0.0001	0.0011 ±	0.0003	0.0011 ±	0.0438
Tm	0.001 ±	0.0003	0.001 ±	0.0003	0.001 ±	0.0003	0.001 ±	0.0003
U	**0.006 ±**	**0.000**	**0.005 ±**	**0.000**	**0.005 ±**	**0.001**	**0.006 ±**	**0.000**
V	1.14 ±	0.2	1.13 ±	0.1	1.12 ±	0.2	0.96 ±	0.1
Y	0.135 ±	0.01	0.126 ±	0.00	0.137 ±	0.01	0.136 ±	0.01
Yb	0.0052 ±	0.001	0.0050 ±	0.000	0.0052 ±	0.001	0.0052 ±	0.001
Zn	**0.878 ±**	**0.07**	**1.18 ±**	**0.09**	**1.23 ±**	**0.16**	**1.02 ±**	**0.08**
Zr	0.070 ±	0.02	0.068 ±	0.01	0.065 ±	0.03	0.063 ±	0.02

2.4.3.4. Missouri River

The mean concentrations of elements ± standard deviation at the four sampling sites along the Missouri River are given in Table 2.6. The concentration of Al, As, Ba, Be, Bi, Ca, Co, Cr, Cu, Fe, Ga, K, Li, Lu, Mg, Na, Nb, Ni, Pb, Rb, Sc, Se, V, Zn showed statistically significant variation between the four sampling sites of the Missouri River (*p* <0.05). Particle size showed statistically significant variation along the Missouri River.

Table 2.6. Mean concentration ± standard deviation of elements (μmolg^{-1} of dry sediment) in the sites (A (furthest upstream), B, C, D (furthest downstream)) of the Missouri River (*n*=5 at each site). Elements that significantly (*p*<0.05) vary between the sites are in bold.

Element	**Site A**			**Site B**			**Site C**			**Site D**		
Ag	0.0004	±	0.00004	0.0008	±	0.00007	0.0005	±	0.00001	0.0006	±	0.00003
Al	**405**	**±**	**81**	**400**	**±**	**65**	**484**	**±**	**53**	**672**	**±**	**132**
As	**0.08**	**±**	**0.02**	**0.08**	**±**	**0.01**	**0.10**	**±**	**0.01**	**0.13**	**±**	**0.02**
B	4.1	±	0.79	3.2	±	0.45	3.3	±	0.43	4.1	±	0.67
Ba	**3.0**	**±**	**0.69**	**3.0**	**±**	**0.60**	**3.1**	**±**	**0.27**	**2.3**	**±**	**0.31**
Be	**0.07**	**±**	**0.0099**	**0.06**	**±**	**0.0050**	**0.07**	**±**	**0.0127**	**0.09**	**±**	**0.0149**
Bi	**0.0005**	**±**	**0.0001**	**0.0005**	**±**	**0.0001**	**0.0007**	**±**	**0.0001**	**0.0009**	**±**	**0.0002**
Ca	**731**	**±**	**147**	**635**	**±**	**95**	**655**	**±**	**80**	**427**	**±**	**51**
Cd	0.002	±	0.0002	0.002	±	0.0002	0.002	±	0.0003	0.002	±	0.0005
Ce	0.29	±	0.04	0.33	±	0.04	0.31	±	0.03	0.36	±	0.05
Co	**0.11**	**±**	**0.020**	**0.12**	**±**	**0.018**	**0.13**	**±**	**0.016**	**0.16**	**±**	**0.024**
Cr	**0.42**	**±**	**0.06**	**0.45**	**±**	**0.06**	**0.46**	**±**	**0.05**	**0.59**	**±**	**0.10**
Cs	0.009	±	0.002	0.008	±	0.002	0.010	±	0.001	0.013	±	0.004
Cu	**0.21**	**±**	**0.04**	**0.20**	**±**	**0.01**	**0.24**	**±**	**0.03**	**0.28**	**±**	**0.04**
Dy	0.014	±	0.0021	0.015	±	0.0018	0.015	±	0.0015	0.017	±	0.0022
Er	0.006	±	0.0011	0.007	±	0.0007	0.007	±	0.0008	0.008	±	0.0012
Eu	0.025	±	0.004	0.026	±	0.003	0.026	±	0.002	0.030	±	0.005
Fe	**287**	**±**	**53**	**296**	**±**	**37**	**337**	**±**	**39**	**417**	**±**	**66**
Ga	**0.042**	**±**	**0.0093**	**0.039**	**±**	**0.0037**	**0.050**	**±**	**0.0087**	**0.073**	**±**	**0.0123**
Gd	0.021	±	0.0037	0.023	±	0.0040	0.024	±	0.0025	0.026	±	0.0049
Ho	0.0025	±	0.0003	0.0027	±	0.0003	0.0027	±	0.0003	0.0030	±	0.0004
In	0.0002	±	3.9E-05	0.0002	±	0.0E+00	0.0002	±	4.8E-05	0.0002	±	4.8E-05
K	**42**	**±**	**9**	**42**	**±**	**10**	**51**	**±**	**8**	**72**	**±**	**16**
La	0.15	±	0.02	0.17	±	0.03	0.16	±	0.02	0.18	±	0.03
Li	**1.70**	**±**	**0.18**	**1.63**	**±**	**0.09**	**1.84**	**±**	**0.28**	**2.27**	**±**	**0.24**
Lu	**0.0009**	**±**	**0**	**0.0006**	**±**	**0**	**0.0006**	**±**	**0**	**0.0009**	**±**	**0**
Mg	**522**	**±**	**86**	**467**	**±**	**51**	**478**	**±**	**45**	**346**	**±**	**52**
Mn	5	±	1.4	5	±	0.8	6	±	0.9	7	±	2.1
Mo	0.0033	±	0.002	0.0029	±	0.002	0.0016	±	0.003	0.0030	±	0.001
Na	**15**	**±**	**4**	**11**	**±**	**2**	**15**	**±**	**2**	**23**	**±**	**7**
Nb	**0.003**	**±**	**0.001**	**0.006**	**±**	**0.002**	**0.003**	**±**	**0.002**	**0.007**	**±**	**0.001**
Nd	0.13	±	0.02	0.15	±	0.02	0.14	±	0.01	0.16	±	0.03
Ni	**0.31**	**±**	**0.06**	**0.32**	**±**	**0.04**	**0.37**	**±**	**0.04**	**0.42**	**±**	**0.07**
P	24	±	0.37	26	±	1.58	25	±	0.35	25	±	1.43
Pb	**0.05**	**±**	**0.005**	**0.04**	**±**	**0.004**	**0.05**	**±**	**0.005**	**0.06**	**±**	**0.007**
Pr	0.04	±	0.005	0.04	±	0.005	0.04	±	0.004	0.05	±	0.007
Rb	**0.17**	**±**	**0.03**	**0.18**	**±**	**0.03**	**0.21**	**±**	**0.03**	**0.27**	**±**	**0.05**
Re	5.4E-06	±	0	7.5E-06	±	2.941E-06	5.4E-06	±	0	5.4E-06	±	0
S	17	±	3	21	±	5	19	±	1	18	±	2

Table 2.6. Mean concentration ± standard deviation of elements (µmolg^{-1} of dry sediment) in the sites (A (furthest upstream), B, C, D (furthest downstream)) of the Missouri River (*n*=5 at each site) **(**continued).

Element	Site A	Site B	Site C	Site D
Sb	0.0012 ± 0.0005	0.0011 ± 0.0005	0.0008 ± 0.0007	0.0013 ± 0.0004
Sc	**0.061 ± 0.018**	**0.059 ± 0.013**	**0.075 ± 0.015**	**0.098 ± 0.020**
Se	**0.005 ± 0.0010**	**0.006 ± 0.0016**	**0.006 ± 0.0014**	**0.008 ± 0.0007**
Sm	0.0002 ± 3.6E-05	0.0003 ± 3.1E-05	0.0003 ± 2.1E-05	0.0003 ± 4.7E-05
Sn	0.003 ± 0.00063	0.005 ± 0.0028	0.004 ± 0.00044	0.005 ± 0.00088
Sr	1.01 ± 0.354	0.73 ± 0.087	0.85 ± 0.095	1.11 ± 0.184
Tb	0.0028 ± 0.00034	0.0029 ± 0.00056	0.0029 ± 0.00034	0.0035 ± 0.00056
Th	0.025 ± 0.0034	0.028 ± 0.0040	0.028 ± 0.0023	0.026 ± 0.0032
Ti	7.9 ± 0.9	8.4 ± 1.5	8.8 ± 0.9	8.7 ± 1.7
Ti	0.0006 ± 0.0001	0.0007 ± 0.0001	0.0007 ± 0.0001	0.0011 ± 0.0003
Tm	0.0008 ± 0.00032	0.0008 ± 0.00032	0.0009 ± 0.00032	0.0012 ± 0.00000
U	0.0048 ± 0.0009	0.0053 ± 0.0008	0.0050 ± 0.0005	0.0054 ± 0.0008
V	**0.69 ± 0.12**	**0.73 ± 0.09**	**0.79 ± 0.10**	**0.98 ± 0.16**
Y	0.13 ± 0.02	0.13 ± 0.01	0.14 ± 0.02	0.16 ± 0.02
Yb	0.0046 ± 0.0008	0.0045 ± 0.0005	0.0050 ± 0.0005	0.0060 ± 0.0008
Zn	**0.83 ± 0.13**	**0.85 ± 0.08**	**0.94 ± 0.10**	**1.2 ± 0.16**
Zr	0.062 ± 0.03	0.057 ± 0.01	0.085 ± 0.01	0.093 ± 0.04

2.4.3.5. Little Missouri River

The mean concentrations of elements ± standard deviation at the four sampling sites along the Missouri River are given in Table 2.7. The concentration of Ca, Mg, and S showed significant variation between the sites along the river (p <0.05).

Table 2.7. Mean concentration ± standard deviation of elements (µmolg^{-1} of dry sediment) in the sites (A (furthest upstream), B, C, D (furthest downstream)) of the Little Missouri River (*n*=5 at each site). Elements that significantly (p<0.05) vary between the sites are in bold.

Element	Site A	Site B	Site C	Site D
Ag	0.0011 ± 0.0010	0.0009 ± 0.0003	0.0007 ± 0.0003	0.0008 ± 0.0001
Al	452 ± 75	505 ± 104	510 ± 102	526 ± 94
As	0.096 ± 0.03	0.093 ± 0.01	0.096 ± 0.01	0.118 ± 0.08
B	3.44 ± 0.5	3.48 ± 0.8	3.76 ± 0.6	3.57 ± 0.5
Ba	2.980 ± 0.7	2.563 ± 0.7	2.884 ± 0.5	2.549 ± 0.8
Be	0.064 ± 0.01	0.075 ± 0.01	0.080 ± 0.02	0.084 ± 0.01
Bi	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.002	0.001 ± 0.001
Ca	**1139 ± 136**	**1049 ± 97**	**765 ± 169**	**495 ± 179**
Cd	0.002 ± 0.0003	0.003 ± 0.0006	0.002 ± 0.0003	0.002 ± 0.0006
Ce	0.320 ± 0.04	0.319 ± 0.03	0.329 ± 0.05	0.335 ± 0.05
Co	0.143 ± 0.02	0.156 ± 0.02	0.153 ± 0.02	0.182 ± 0.05
Cr	0.42 ± 0.0	0.46 ± 0.1	0.45 ± 0.1	0.53 ± 0.1
Cs	0.009 ± 0.002	0.009 ± 0.002	0.011 ± 0.003	0.010 ± 0.003
Cu	0.246 ± 0.03	0.270 ± 0.03	0.238 ± 0.03	0.256 ± 0.06

Table 2.7. Mean concentration ± standard deviation of elements (μmolg^{-1} of dry sediment) in the sites (A (furthest upstream), B, C, D (furthest downstream)) of the Little Missouri River (*n*=5 at each site) (continued).

Element	**Site A**		**Site B**		**Site C**		**Site D**	
Dy	0.016 ±	0.002	0.016 ±	0.002	0.016 ±	0.002	0.017 ±	0.003
Er	0.007 ±	0.0009	0.008 ±	0.0010	0.008 ±	0.0010	0.008 ±	0.0017
Eu	0.027 ±	0.003	0.027 ±	0.003	0.028 ±	0.004	0.028 ±	0.004
Fe	311 ±	41	333 ±	44	340 ±	51	438 ±	240
Ga	0.044 ±	0.01	0.055 ±	0.01	0.049 ±	0.01	0.059 ±	0.02
Gd	0.025 ±	0.004	0.025 ±	0.004	0.025 ±	0.005	0.025 ±	0.004
Ho	0.003 ±	0.0003	0.003 ±	0.0005	0.003 ±	0.0003	0.003 ±	0.0005
In	0.192 ±	0.039	0.209 ±	0.048	0.209 ±	0.048	0.209 ±	0.048
K	48.1 ±	8	57.3 ±	17	50.7 ±	11	50.7 ±	11
La	0.162 ±	0.02	0.161 ±	0.02	0.165 ±	0.03	0.168 ±	0.03
Li	1.83 ±	0.23	1.97 ±	0.26	2.03 ±	0.21	2.02 ±	0.32
Lu	0.001 ±	0	0.001 ±	0.0003	0.001 ±	0.0003	0.001 ±	0.0003
Mg	**726 ±**	**83**	**655 ±**	**58**	**565 ±**	**100**	**403 ±**	**101**
Mn	8.3 ±	1.1	13.4 ±	10.9	7.7 ±	1.2	11.8 ±	9.6
Mo	0.006 ±	0.004	0.004 ±	0.005	0.005 ±	0.002	0.007 ±	0.007
Na	22.3 ±	7	17.3 ±	2	20.5 ±	4	26.5 ±	12
Nb	0.003 ±	0.001	0.003 ±	0.001	0.002 ±	0.001	0.003 ±	0.002
Nd	0.146 ±	0.02	0.144 ±	0.02	0.149 ±	0.02	0.150 ±	0.02
Ni	0.411 ±	0.04	0.444 ±	0.07	0.401 ±	0.05	0.476 ±	0.13
P	24.7 ±	1	24.7 ±	2	21.5 ±	1	22.8 ±	3
Pb	0.053 ±	0.01	0.058 ±	0.01	0.057 ±	0.006	0.061 ±	0.007
Pr	0.041 ±	0.005	0.040 ±	0.004	0.042 ±	0.006	0.042 ±	0.006
Rb	0.172 ±	0.03	0.208 ±	0.06	0.194 ±	0.04	0.200 ±	0.04
Re	0.005 ±	0	0.006 ±	0.002	0.008 ±	0.003	0.005 ±	0
S	**11.8 ±**	**1**	**14.4 ±**	**3**	**18.3 ±**	**2**	**27.4 ±**	**12**
Sb	0.0013 ±	0.0006	0.0011 ±	0.0007	0.0014 ±	0.0008	0.0013 ±	0.0007
Sc	0.077 ±	0.01	0.083 ±	0.02	0.080 ±	0.02	0.087 ±	0.02
Se	0.006 ±	0.001	0.006 ±	0.002	0.006 ±	0.001	0.008 ±	0.003
Sm	0.274 ±	0.03	0.271 ±	0.03	0.281 ±	0.04	0.281 ±	0.04
Sn	0.003 ±	0.0005	0.004 ±	0.001	0.004 ±	0.000	0.004 ±	0.001
Sr	0.926 ±	0.11	0.943 ±	0.08	0.811 ±	0.12	0.808 ±	0.22
Tb	0.003 ±	0.000	0.003 ±	0.001	0.003 ±	0.001	0.003 ±	0.001
Th	0.027 ±	0.003	0.028 ±	0.004	0.028 ±	0.004	0.028 ±	0.004
Ti	6.27 ±	0.0	6.27 ±	0.0	5.85 ±	0.9	7.10 ±	1.1
Ti	0.0007 ±	0.0001	0.0008 ±	0.0003	0.0007 ±	0.0002	0.0008 ±	0.0001
Tm	0.0011 ±	0.0003	0.0011 ±	0.0003	0.0009 ±	0.0003	0.0011 ±	0.0003
U	0.006 ±	0.001	0.007 ±	0.001	0.007 ±	0.002	0.006 ±	0.001
Y	0.143 ±	0.01	0.148 ±	0.02	0.149 ±	0.02	0.160 ±	0.03
Yb	0.005 ±	0.001	0.006 ±	0.001	0.006 ±	0.001	0.006 ±	0.001
Zn	0.889 ±	0.10	1.046 ±	0.20	0.955 ±	0.11	1.078 ±	0.21
Zr	0.088 ±	0.03	0.088 ±	0.02	0.088 ±	0.03	0.086 ±	0.03

2.5. Discussion

2.5.1. Particle size, organic matter and pH variations between and within the rivers

In this study particle size (*f*<63 µm) significantly varied between the sampling sites and the rivers (Figure 2.2). Particle size ranged between 2.75%- 100%. The Red River had the highest average proportion of small particles (*f*<63 µm) and the Little Missouri showed the lowest average. In fact, particle size (*f*<63 µm) showed a generally decreasing order from the Red River in the east to the Little Missouri River in the west. In a study by Blanchard et al. (2011) sediment samples collected from the Sheyenne River contained 90% fine-grained particles (less than 63 µm). Many other factors such as geology and clay soils of the Red River vally, size of watershed, flooding, and wind erosion could result in smaller particles at the Red, James, and Sheyenne rivers. Elements As, Al, Ba, Be, Bi, Cr, Cu, Cs, Cd, Dy, Fe, Ga, K, Li, Ni, Pb, Rb, Sc, Se, Ti, Zn, Zr, and V concentrations increase as the Red River flows from upstream to downstream (Table 2.3). The binding area of particles is known to show a negative correlation with the size of particle and smaller particles (clays and silts) tend to bind more elements (Håkanson and Jansson 2002). It also could be that the Turtle River, which is a tributary of the Red River in the northeastern North Dakota, is partly fed by the Dakota aquifer, and this water is rich in solids, mainly carbonates and sulfates (Kelly and Paulson 1970; Rowden 2008).

Organic matter content in sediments is one of the important factors impacting the concentration of elements (Otte et al. 1991; Coquery and Welbourn 1995; Rognerud and Fjeld 2001).There were no significant correlations between element concentrations and organic matter content (LOI) across or between sites along the five rivers in North Dakota .

The pH is an important factor controlling the behavior of elements especially metals in sediments through many different processes. A change in pH results in an increase or decrease in solubility of sediment consisting metals because the capacity and ability of metal-binding by organic matter, clay minerals and different oxides such as Al and Fe oxides is related to pH (Förstner and Müller 1974; Tipping et al. 2003). There were no significant correlations between element concentrations and pH across or between sites along the rivers, and pH did not correlate with LOI or particle size. The pH range among the rivers was very narrow (6.1-8.4) and thus may not influence significant differences in the element concentrations in the soil

2.5.2. Differences between the rivers based on the multi-element variations within the rivers, ND

This study showed that as expected, there was considerable variation in element concentrations in the sediments of the Red, Sheyenne, James, Missouri and Little Missouri rivers. Out of 56 elements that were detectable, 40 showed statistically significant variations between the rivers (p-value<0.05). Red and Sheyenne rivers flow through agricultural lands and runoff waters entering these rivers were expected to show high concentrations of nutrients and elements found in fertilizers, such as cadmium. The results supported the initial hypothesis and mean concentration ($\mu molg^{-1}$**)** of Cd at the Red (0.0034) and Sheyenne (0.0029) Rivers was higher than James (0.0025), Missouri (0.0022) and Little Missouri (0.0018) Rivers. Also nutrients such as K and Ca showed their highest concentrations ($\mu molg^{-1}$**)** at Red (73 and 1159), Sheyenne (76 and 953) and James Rivers (70 and 1026) in comparison to the Missouri (50 and 804) and Little Missouri (50 and 573) Rivers (n=20 at each river). The high concentrations of cadmium could be explained by the fact that it is present naturally and locally in high concentrations in the Northern Plains because of shale-derived material such as the Pierre shale formation (Holmgren et al. 1993, Hopkins et al. 1999). Metals could originate from natural processes such as rock weathering or from anthropogenic activities such as industrial emissions, domestic effluents, and agriculture (Hutchinson and Rothwell 2008). Also generally, elements such as K, Zn and Cd are associated with clay particles (Vital and Stattegger 2000), and natural processes such as wind erosion and flooding in eastern North Dakota may result in the deposition of clay particles containing these elements. This shows that riparian plants in eastern North Dakota might be exposed to different elements than the plants in western North Dakota. This may impact the uptake of various elements in plant tissue becasue and studies have shown that wetlands plants accumulate high concentrations of elements in their tissue (Szymanowska et al. 1999; Samecka-Cymerman and Kempers 2001; Matthews et al. 2004).

The biogeochemistry of wetlands and riverine systems is dramatically changed by land use and geology as proved in many studies (Moyle 1945; Stewart and Kantrud 1972; Barko and Smart 1986; Koch 2001; Lougheed et al. 2001; Hansel-Welch et al. 2003; Bayley et al. 2007; Del Pozo et al. 2011). At the Little Missouri and Missouri rivers, considering the fact that coal and lignite mining is one of the dominant activities in the area, it was hypothesised that concentrations of metals associated with these activities such as uranium and lead will be higher in comparison with other rivers. However, the results showed that the highest mean concentrations (n=20 at each river) for both lead and uranium was observed at the Red River (Figure 2.6). It is possible that these elements were mostly present in a dissolved or suspended form in the water at the Little Missouri and Missouri Rivers, and because of that, these elements did not show high concentrations in the sediment at these rivers.

Many elements showed significant correlations with each other across the rivers, such as correlations between Fe and Al, and Fe and Cr. Iron oxides play an important role and act as carriers of metals with sorption sites for many elements (McBride 1994; Shuman et al 2005). Wijeyaratne 2011 found similar results in their study in which phosphorus and aluminum concentrations showed significant positive correlations with iron in the sediment deposits of the Souris River in North Dakota. The correlations of elements with iron showed that their concentrations in North Dakota are influenced by the iron behavior in the sediment

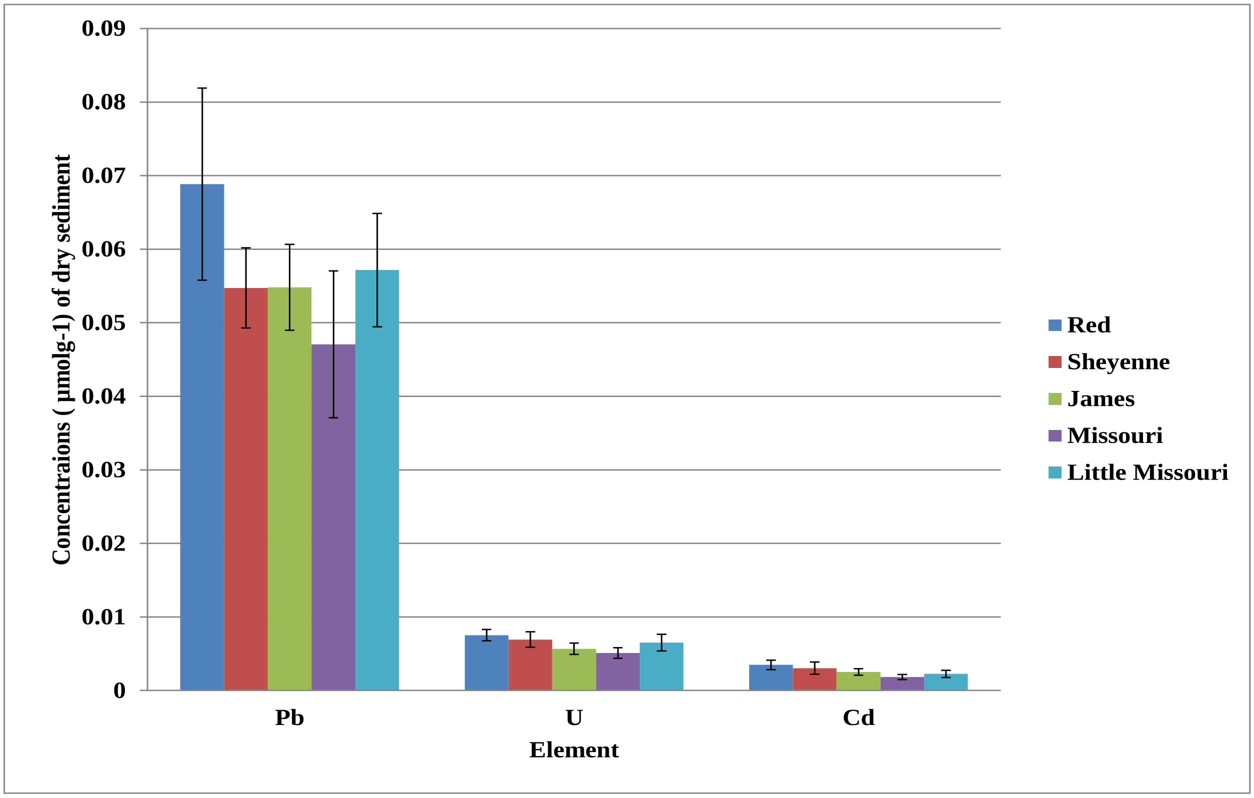


Figure 2.6. Mean concentration ± standard deviation (*n*=20 at each river) of Pb, U and Cd at the Red, Sheyenne, James, Missouri and Little Missouri rivers in North Dakota.

2.6. Conclusion

In conclusion, the results of multi-element fingerprinting method showed there was significant variation in element concentrations in sediments along the Red, Sheyenne, James, Missouri, and Little Missouri rivers. The organic matter content and pH did not play an important role in the variation in element concentrations. Variations in element concentrations were indeed sufficient to continue investigation on the distribution and pattern of elements in sediment between the rivers or along a river.

CHAPTER 3. SEDIMENT SOURCE TRACING AT THE RED RIVER USING THE MULTI-ELEMENT FINGERPRINTING APPROACH

3.1. Abstract

For the Red River of the North, North Dakota, it has been reported that fine sediment contains high concentrations of Cd and Se. High concentrations of these elements can cause environmental issues and impact riparian wetland flora and fauna through element cycling and translocation by riparian vegetation. River sediments play an important role for 1) identification of different element sources within a catchment, and 2) investigation of tributary contribution to the element concentration in the rivers.

In this study the possibility for tracing sources and tributaries contributing to element concentrations in the Red River was assessed using the multi-element fingerprinting technique. The Turtle and Sheyenne rivers were selected as two main tributaries. Riverbank depositional sediments were sampled from three locations, (1) erosional sediment in the main channel upstream and (2) depositional sediment downstream of the confluence of the tributaries, and (3) erosional sediment inside the tributaries. These samples were analyzed using ICP-MS for multi-element concentrations. Results demonstrated that element concentrations and particle size vary significantly at the sites along the Red River, and the Turtle and Sheyenne rivers both contribute to the cadmium and selenium concentrations in the sediment deposits of the Red River and concentrations of these elements increased in downstream.

3.2. Introduction

Sediments act as both carriers and potential sources of pollutants in rivers and streams (Förstner and Müller 1974). The importance of suspended sediment in the transport of contaminants and nutrients, such as phosphorus, metals, and pesticides, through aquatic systems is known (Shear and Watson 1977; UNESCO 1983; Allan 1986; Collins et al. 1996; Warren et al. 2003; Dirszowsky 2004).

Se and Cd are naturally present in the environment; high concentrations of Cd and Se originate from both natural and anthropogenic sources (Arimoto et al. 1992) and they enter streams and rivers through runoff and erosion of bedrock. Studies have been done to assess the concentrations of Cd and Se and other trace metals in river and riparian sediments around the world (Johns 1995; Reczynski et al. 2010; Bai et al. 2011; Zhang et al. 2012). Cadmium and selenium concentrations are usually very low and often below detection limits, however in some locations in the Northern Plains cadmium concentrations are high mainly because of the existence of shale-derived soils (Holmgren et al. 1993). That being said, only few studies have been done to study these elements in North Dakota, in a study by Martin and Harman (1984) sediment samples from 13 riverine and pothole-type wetlands in Iowa, Montana, Nebraska, North Dakota, and South Dakota were collected and analyzed for total concentrations of arsenic, cadmium, lead, mercury, and selenium.

The Red River of the North, North Dakota, USA, consists mostly of silty-clay and very fine clay soils (USGS 2012). It has been reported that the fine sediment at the confluence of the Red and Turtle rivers contains high concentrations of As, Cd, and Se (Wijeyaratne 2011). Turtle River is classified as ‘impaired’ with regards to the Cd concentrations in water (US EPA, 2008). There is concern regarding metal contamination and the impacts on river organisms in North

Dakota, plus the consequences of elements transported across international borders into Canada. Also, Chapter 2 of this thesis for the Red River showed average concentrations of particular elements and metals in sediments, including cadmium and selenium, significantly increased as the river flowed downstream.

In this study, the multi–element fingerprinting technique was applied 1) to study the potential sources of cadmium and selenium concentrations in the sediment deposits of the Red River of the North, and 2) to evaluate the suitability of the multi-element fingerprinting method for measuring sediment contribution from tributaries and for sediment source tracing.

It was hypothesized that the Sheyenne and Turtle rivers, both major tributaries to the Red River, will contribute to selenium and cadmium in sediment. It was also expected that the Turtle River will show higher concentrations of cadmium in comparison to the Red River, mainly because it is partly fed by the Pierre aquifer, which is known to contain high concentrations of Cd from the Pierre Shale formation Kelly and Paulson 1970).

3.3. Materials and methods

3.3.1. Study area

The Red River flows through a relatively flat lake plain of the former Lake Agassiz (formed from melt waters of an ice sheet). This River flows approximately 885 km northward through many agricultural and urban areas in both United States and Canada. When Lake Agassiz drained 9,500 years ago the Red River Valley was formed with the material from lacustrine soils precipitated at the bottom of the Lake Agassiz.

The Turtle River, 120 km long, is a tributary of the Red River in northeastern North Dakota, and is considered to be in the watershed of Hudson Bay (USGS, 2011).

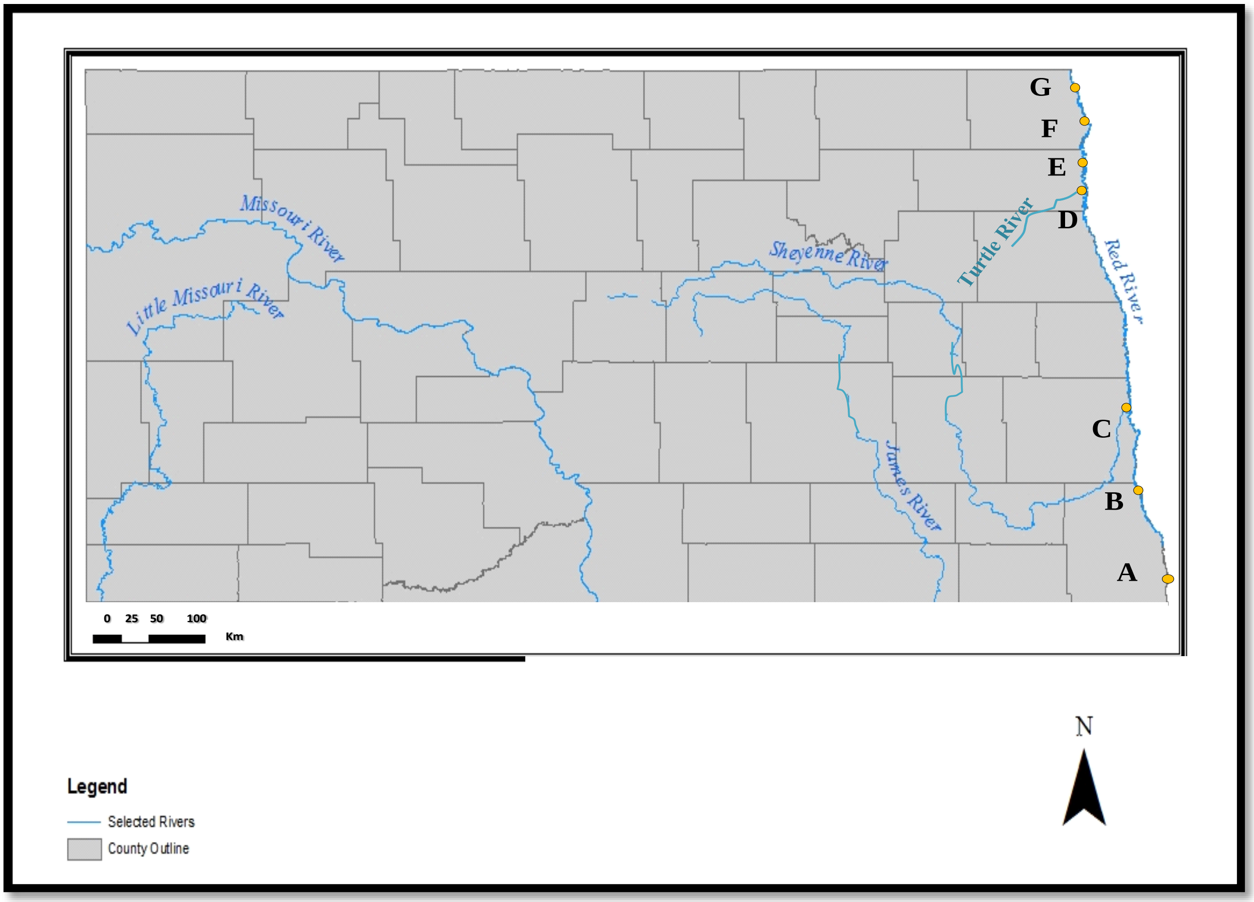


Figure 3.1. Map showing the general location of the Red, James, Missouri and Little Missouri Rivers, tributaries (Sheyenne and Turtle) and the sampling sites (A (furthest upstream), B, C, D, E, F, G (furthest downstream) along the Red River in North Dakota**.**

The river flows generally eastward and near the Red River turns northward and enters the Red just upstream of Oslo, Minnesota. The Sheyenne River, 951 km long, is another major tributary of the Red River in eastern North Dakota. The Sheyenne River picks up the clay and silty-clay soil of the Red River Valley after it passes through the Sheyenne National Grassland and enters the Red River near Harwood and West Fargo (USGS, 2011).

3.3.2. Sample collection

Two tributaries and five sites were selected along the Red River. Sites were selected for even distribution along the length of the river in North Dakota to study the concentration and pattern of selenium, cadmium, and other elements along the river (Table 3.1). The Sheyenne and Turtle rivers were chosen because they are two main tributaries of the Red River.

Table 3.1. Coordinates of the sampling sites along the Red River, ND (A (furthest upstream), B, C, D, E, F, G (furthest downstream)).

Sampling site	Coordinates
A	45°59'51.28"N, 96°34'27.41"W
B	46°9'8.57"N, 96°34'45.31"W
C (downstream from tributary: Sheyenne River)	47°1'49.87"N, 96°50'12.66"W
D (downstream from tributary: Turtle River)	48°9'51.16"N, 97° 9'32.38"W
E	48°24'49.71"N, 97° 8'12.55"W
F	48°47'11.86"N, 97° 9'25.92"W
G	48°58'25.15"N, 97°14'17.32"W

Sediment samples were collected in June 2012 in five replicates and in a transect parallel to the river with various distances between the replicates yet within the sediment deposition site. Sediment by the edge of the river (maximum distance of 2m from the river bank) was sampled for both main river and tributaries because they represent the most recent deposits. Samples were collected from the top layers of sediment (maximum depth of sampling 3 cm) so that they represent the suspended sediment transported and deposited by the river. For the tributaries, samples consisted of three locations sediments: 1) erosional sediment in the tributary maximum of 100 m upstream from the confluence (eroded sediment), 2) erosional sediment maximum of 100 m upstream along the main river (eroded sediment), and 3) depositional sediment maximum of 100 m downstream along the main river (deposited sediment) (Figure 3.2). The flow rate of water could result in sediment mixing at the confluence point, so the sample collection at 100 m distance was assumed to be far enough away to reduce the impact this mixing. Also it was expected that, depending on the size of the watershed and flow rate of water, sediment coming (eroded sediment) from the tributary and upstream locations of the Red River would become deposited within 100 m downstream as shown in Figure 3.2. A total of 55 samples were collected.

Table 3.1 shows the coordinates of the sampling sites (A, B, E, F, G) and downstream of Sheyenne (C) and Turtle (D) tributaries along the Red River. The locations downstream of tributaries (C and D) were considered as sites when evaluating the element variations along the Red River. The other comparison was for the contribution of each tributary and these samples consisted of the upstream sites, within the tributaries, and downstream.

3.3.3. Sample preparation, Loss-on-ignition, particle size analysis, and soil pH

All methods were the same as described in Chapter 2.2

3.3.4. Data analysis

Minitab 16 statistical software was used for statistical analysis. All data except pH were log-transformed to ensure normalized distribution. Pearson correlation analysis was performed on element concentrations, LOI and pH to investigate the possible relationships between them. Significance of differences (probability) and element variations betweenthe sampling sites and tributary locations was determined by General Linear Model (one-way ANOVA, $p<0.05$) and pairwise tests by the Tukey Method ($p<0.01$) using

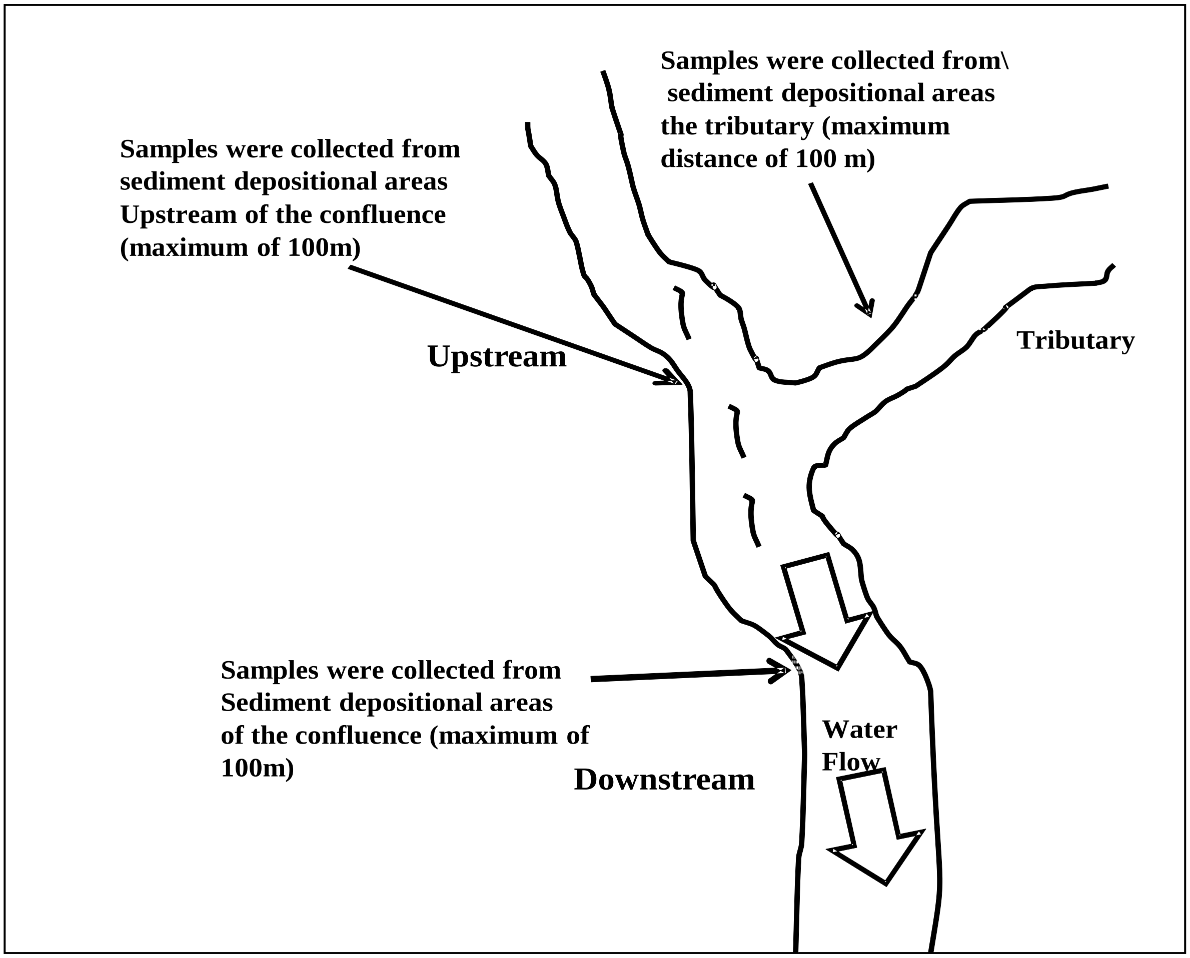


Figure 3.2. Sampling plan for the Red River. Tributaries were sampled at three locations and downstream of the confluence and inside tributary and from the first 100 m distance (five replicates at each location).

(Minitab®15©2006 Minitab Inc.). Correlations were considered statistically significant if r ≥ 0.707. These correlations explain 50% or more variation (McClave and Sincich 2006).

Calculations for Se and Cd contributions from the tributaries to the rivers were based on those used by Wijeyaratne (2011). First, element concentrations were measured for the three sampling sites (Figure 1.2) near the confluence of the main river and the tributary. These multi-element concentrations were used for a series of calculations.

In part (A) the percentage sediment contribution of the tributary and upstream to the elements was calculated. In part (B) then the **mean** percentage sediment contribution ± 95%

confidence interval from tributary and upstream was calculated from calculating the mean overall percentage sediment contribution of the tributary and upstream. After that the relative contribution of Se and Cd from each tributary was calculated from the sediment concentrations of these elements and the estimated relative **mean** percentage sediment contribution in part A (see calculations below).

3.3.4.1. Percentage sediment contribution of the tributary

The percentage sediment contribution of the tributary ($\boldsymbol{a_x}$) for all of the elements except cadmium and selenium in the Red River was calculated assuming linear mixing between upstream and tributary sediments, as follows:

(A)

$$\mathbf{[X]_D = \alpha_x\ [X]_T + b_x [X]_U}$$

$$\mathbf{\alpha_x + b_x = 1}$$

and therefore:

$$\mathbf{\alpha_x = [X]_D - [X]_U / [X]_T - [X]_U\ x100}$$

Where,

$\boldsymbol{a_x}$-Mean percentage contribution of tributary for element *x*

$\boldsymbol{b_x}$- Mean percentage contribution of upstream for element *x*

$[\boldsymbol{X}]_{\boldsymbol{D}}$- Mean concentration of element *x* at the downstream location

$[\boldsymbol{X}]_{\boldsymbol{U}}$- Mean concentration of element *x* at the upstream location

$[\boldsymbol{X}]_{\boldsymbol{T}}$- Mean concentration of element *x* at the tributary location

3.3.4.2. Contribution of Cd and Se from each tributary

In order for these calculations in part B to be valid for most of the elements percentage sediment contributions should be between 0-100%, otherwise the tributary does not follow linear mixing.

Elements with estimated contributions of > 1or <0 did not meet the assumptions of conservative, linear mixing and so were not used for the calculations. Elements which showed a tributary contribution between 0 and 1, or 0% and 100% were used to calculate the **mean** percentage sediment contributions from tributaries ± 95%.

The **mean** percentage sediment contributions ± 95% confidence interval could be calculated for each tributary from the following steps:

1. Separate the group of elements with percentage sediment contributions between 0 and 100% and calculate the average of them, this will be the mean percentage sediment contribution.
2. Obtain the standard deviation, number of elements for the same group of elements.
3. To calculate the 95% confidence interval use the formula below (the confidence coefficient for 95% confidence is 1.96 (fixed value)):

([confidence coefficient]x[standard deviation]/[number of elements with percentage contribution between 0 and 100%]^[0.5])

The calculated **mean** percentage sediment contributions from tributary (A_t) and upstream of the main river (A_u=1- A_t) were used to estimate the percentage contribution of Cd and Se from each tributary (**C** $_{\text{[Se or Cd]}}$), as follows: (B)

$$\mathbf{C_{\text{Se or /Cd}} = A_t\,[\text{Se or Cd}]_t / ((A_t[\text{Se or Cd}]_t) + (A_u\,[\text{Se or Cd}]_u))}$$

Where:

A_t – Mean sediment contribution from the tributary

A_u – Mean sediment contribution from upstream of the main river

$[Se\ or\ Cd]_t$ – Mean measured Cd or Se concentration in tributary sediments

$[Se\ or\ Cd]_u$ – Mean measured Cd or Se concentration in the upstream sediments

This linear mixing model yields the proportion of the tributary contribution relative to the total contributed by the river sources (main river and tributary) and indicates the impact of the tributary on element contribution, which is different than just the sediment element concentrations.

3.4. Results

3.4.1. Particle size (*f*<63 µm), pH, and LOI at the Red River

At the sites along the Red River, particle size (*f*<63 µm) ranged from 44.5-99.7 % with an average of 71%. LOI ranged from 3.1- 5.6% with an average of 3.7%. Particle size (*f*<63µm) and LOI showed statistically significant variation ($p<0.01$) between the sites along the river (Figure 3.3).

Proportion particle size (*f*<63µm) shows an increasing gradient from site A upstream to site G downstream. Results of Tukey's comparisons on *f*<63 showed that sites A (lowest %) and G (highest %) are significantly different from each other and all of the other sites, and for LOI site B is significantly different from the other sites along the Red River ($p<0.01$). No significant variations were detected for pH between the sampling sites along the Red River, pH ranged from 7.4-8.1 with an average of 7.8.

3.4.2. Analysis for multiple elements and development of fingerprints for the Red River

The element concentrations for Ag, Au, Ge, Hf, In, Nb, Re, Ta, and W were below detection limits (see Chapter 2 for detection limits) therefore those elements will not be further discussed.

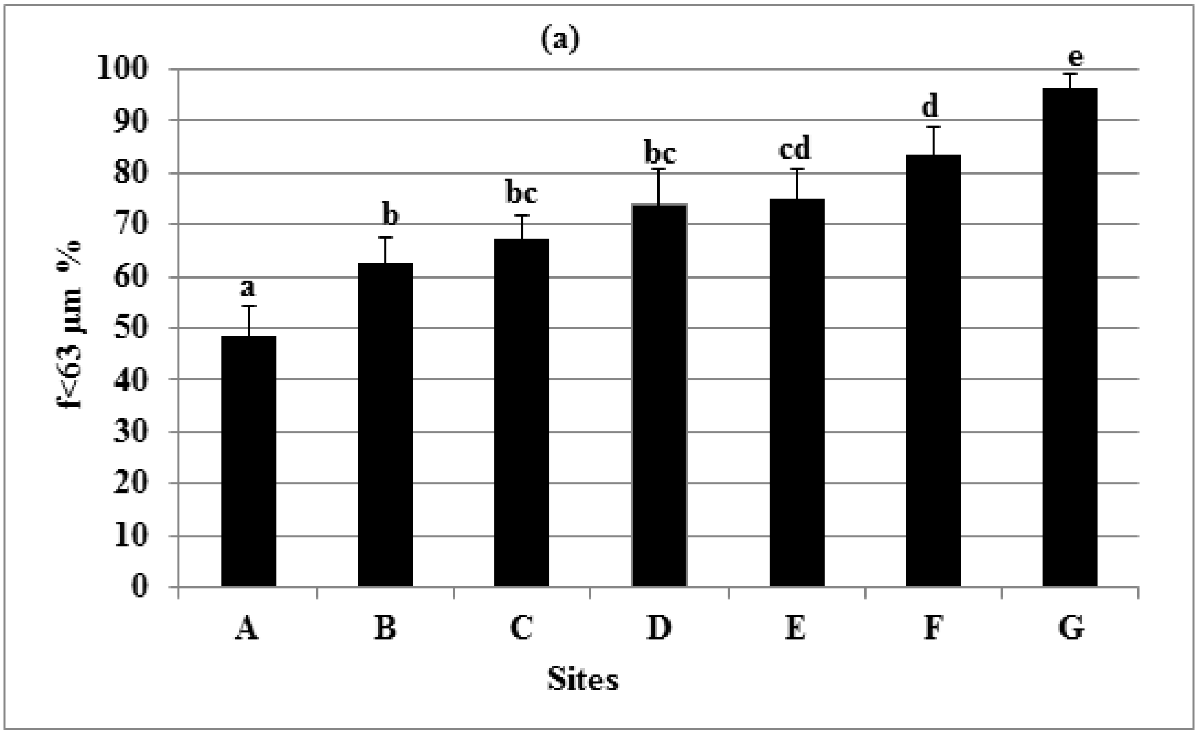
The results of ANOVA analysis showed that element (Al, As, B, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Rb, S, Sb, Sc, Sm, Sn, Sr, Tb, Te, Th, Ti, Tm, U, V, Y, Yb, Zn, Zr) concentrations significantly vary between the sampling sites along the Red River ($p < 0.05$) (Table 3.2). Cadmium concentrations in the sediments ranged from 0.002-0.006 µmol g^{-1} with an average of 0.003, and selenium concentrations ranged from 0.005-0.014 µmol g^{-1} with an average of 0.009 (Table 3.2).

3.4.3. Analysis for multiple elements at the Sheyenne tributary

Table 3.3 shows the mean element concentrations at the Sheyenne River and upstream and downstream of the confluence with the Red River (n=5 at each site).

ANOVA analysis showed that the mean concentrations of elements Al, Bi, Cr, Mg, Mn, Na, P, S, Sn, and Sr vary significantly between the Sheyenne River and upstream and downstream of the confluence with the Red River ($p<0.05$).

Based on the results of Tukey's pair-wise comparisons, downstream concentrations of Al, Bi, Cr and S were significantly higher than upstream, tributary concentrations of elements Sn and Mg were significantly lower than both upstream and downstream, and tributary concentrations of elements Mn and P were significantly higher than both upstream and downstream, for Na upstream concentration was significantly lower than tributary and downstream concentrations and for Sr upstream concentration was significantly lower than tributary ($p<0.01$).



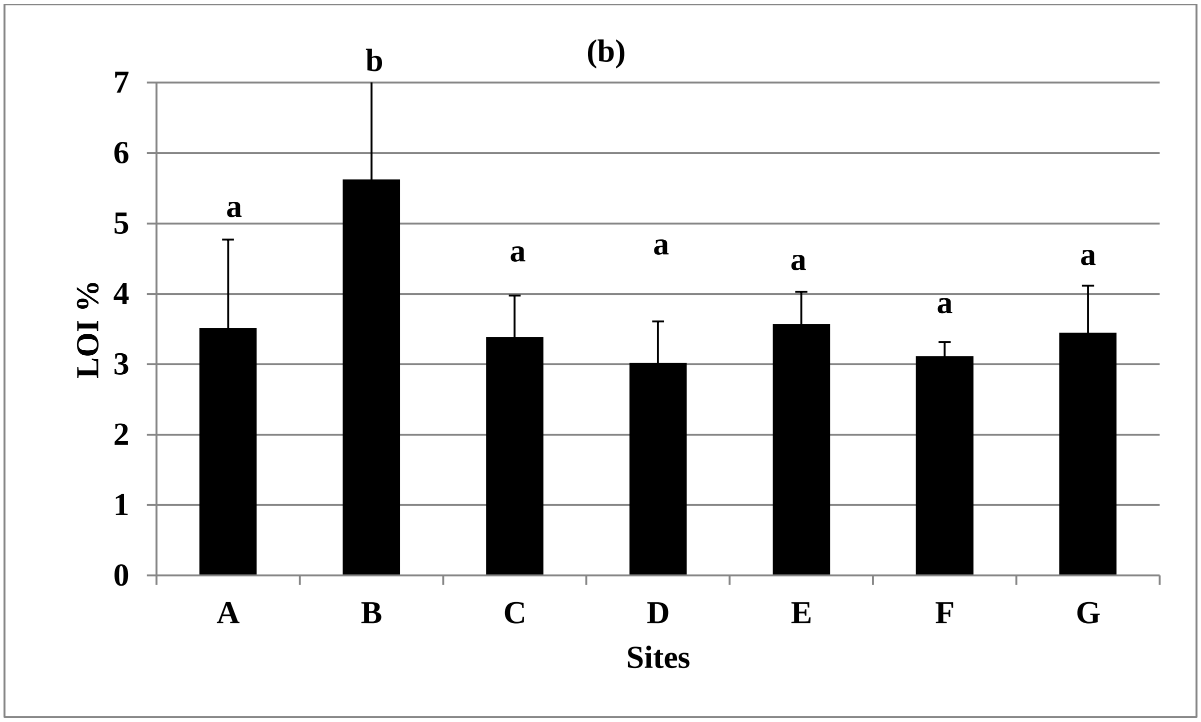


Figure 3.3. Mean and standard deviation of (a) particle size (*f*<63µm %) and (b) LOI (OM %) at the Red River sites (A (furthest upstream), B, C, D, E, F, G (furthest downstream)) (*n*=5). Different letters above the bars indicate significant differences between the sites (*p*<0.01).

Table 3.2. Mean concentration (μmol g^{-1}) ± standard deviation of elements at the sampling sites ((A (furthest upstream), B, C, D, E, F, G (furthest downstream)) (n=5) along the Red River.

Elements	**A**	**B**	**C**	**D**	**E**	**F**	**G**
Al	454 ± 64	456 ± 38	788 ± 170	549 ± 27	554 ± 80	622 ± 63	549 ± 83
As	0.073 ± 0.014	0.069 ± 0.010	0.085 ± 0.011	0.072 ± 0.005	0.085 ± 0.017	0.084 ± 0.008	0.101 ± 0.013
B	1.89 ± 0.18	1.72 ± 0.14	2.48 ± 0.63	1.91 ± 0.12	2.02 ± 0.33	1.83 ± 0.44	2.55 ± 0.33
Ba	0.0063 ± 0.0008	0.0062 ± 0.0004	1.41 ± 0.5623	0.008 ± 0.0006	0.0074 ± 0.0005	1.31 ± 0.09	0.008 ± 0.0004
Be	0.087 ± 0.01	0.089 ± 0.01	0.10 ± 0.03	0.10 ± 0.01	0.100 ± 0.01	0.080 ± 0.01	0.109 ± 0.01
Bi	0.00064 ± 0.0001	0.00061 ± 6.239E-05	0.0009 ± 0.000142	0.0008 ± 7.26E-05	0.00086 ± 8.29E-05	0.00078 ± 8.693E-05	0.001 ± 0.0001
Ca	1413 ± 130	1367 ± 73	1152 ± 135	1340 ± 93	1329 ± 79	1277 ± 85	917 ± 113
Cd	0.0033 ± 0.0004	0.0027 ± 0.0004	0.0032 ± 0.0008	0.0032 ± 0.0005	0.0032 ± 0.0007	0.0027 ± 0.0003	0.0060 ± 0.0010
Ce	0.11 ± 0.01	0.12 ± 0.00	0.254 ± 0.03	0.128 ± 0.01	0.12 ± 0.01	0.23 ± 0.01	0.18 ± 0.02
Co	0.092 ± 0.01	0.107 ± 0.01	0.168 ± 0.033	0.125 ± 0.005	0.135 ± 0.02	0.154 ± 0.01	0.166 ± 0.02
Cr	0.28 ± 0.05	0.31 ± 0.04	0.72 ± 0.17	0.39 ± 0.01	0.39 ± 0.08	0.54 ± 0.06	0.42 ± 0.04
Cs	0.0003 ± 8.931E-05	0.0004 ± 0.0002	0.009 ± 0.0022	0.001 ± 0.0003	0.0007 ± 0.0003	0.0076 ± 0.0003	0.0007 ± 0.0002
Cu	0.21 ± 0.03	0.20 ± 0.03	0.376 ± 0.08	0.230 ± 0.02	0.22 ± 0.05	0.27 ± 0.02	0.27 ± 0.04
Dy	0.011 ± 0.0007	0.012 ± 0.0003	0.015 ± 0.0020	0.012 ± 0.0004	0.012 ± 0.0011	0.013 ± 0.0003	0.020 ± 0.0012
Er	0.005 ± 0.0004	0.005 ± 0.0000	0.007 ± 0.0008	0.006 ± 0.0003	0.006 ± 0.0004	0.006 ± 0.0003	0.009 ± 0.0005
Eu	0.004 ± 0.0004	0.004 ± 0.0003	0.005 ± 0.000551	0.004 ± 0	0.004 ± 0.0003	0.004 ± 0.0004	0.006 ± 0.0004
Fe	251 ± 31	264 ± 21	399 ± 68	283 ± 13	284 ± 44	349 ± 22	302 ± 28
Ga	0.049 ± 0.006	0.051 ± 0.004	0.085 ± 0.017	0.059 ± 0.003	0.060 ± 0.008	0.063 ± 0.009	0.059 ± 0.008
Gd	0.017 ± 0.0013	0.018 ± 0	0.020 ± 0.0021	0.018 ± 0.0004	0.018 ± 0.001	0.019 ± 0.001	0.029 ± 0.0021
Ho	0.002 ± 0.0003	0.002 ± 0.0003	0.003 ± 0.000332	0.002 ± 0	0.002 ± 0.0003	0.002 ± 0	0.004 ± 0
K	56.79 ± 8.0	57.30 ± 4.3	101 ± 27.8	65 ± 4.3	66.51 ± 10.5	76.75 ± 6.5	72.65 ± 8.0
La	1.04 ± 0.08	0.99 ± 0.074	0.129 ± 0.02	0.945 ± 0.03	1.04 ± 0.116	0.11 ± 0.004	1.40 ± 0.083
Li	1.86 ± 0.22	1.98 ± 0.18	3.61 ± 1.09	2.32 ± 0.10	2.34 ± 0.42	2.60 ± 0.22	2.37 ± 0.22
Lu	0.0006 ± 0	0.0006 ± 0	0.0006 ± 0	0.0006 ± 0	0.0006 ± 0	0.0012 ± 0.001	0.0011 ± 0
Mg	886 ± 108	924 ± 45	768 ± 68	1035 ± 84	1052 ± 92	910 ± 57	666 ± 63

Table 3.2. Mean concentration (μmol g^{-1}) ± standard deviation of elements at the sampling sites ((A (furthest upstream), B, C, D, E, F, G (furthest downstream)) (*n*=5) along the Red River (continued).

Elements	A			B			C			D			E			F			G		
Mn	12.34	±	2.4	12.27	±	2.1	13.9	±	4	13.3	±	2	16.40	±	2.0	16.93	±	2.1	23.63	±	4.3
Mo	0.003	±	0.0012	0.002	±	0.0007	0.0051	±	0.002	0.0019	±	0.002	0.003	±	0.004	0.003	±	0.0009	0.006	±	0.001
Na	17.32	±	2.2	15.75	±	1.9	26.3	±	5.25	15.7	±	4.07	16.01	±	1.5	16.97	±	1.5	18.28	±	3.5
Nd	0.22	±	0.0138	0.24	±	0.0091	0.111	±	0.012	0.255	±	0.009	0.25	±	0.02	0.098	±	0.009	0.36	±	0.04
Ni	0.29	±	0.03	0.30	±	0.0	0.562	±	0.12	0.373	±	0.02	0.38	±	0.06	0.46	±	0.02	0.50	±	0.11
P	23.51	±	2.77	23.57	±	0.97	22.0	±	2.2	21.7	±	0.4	22.02	±	0.84	22.73	±	0.74	30.03	±	1.83
Pb	0.04	±	0.008	0.04	±	0.005	0.052	±	0.004	0.076	±	0.014	0.06	±	0.012	0.05	±	0.005	0.06	±	0.005
Pr	0.026	±	0.002	0.028	±	0.001	0.031	±	0.0039	0.030	±	0.0008	0.029	±	0.002	0.027	±	0.002	0.043	±	0.005
Rb	0.22	±	0.03	0.22	±	0.02	0.380	±	0.10	0.282	±	0.03	0.27	±	0.04	0.30	±	0.02	0.27	±	0.03
S	49.41	±	20.5	36.99	±	9.3	65	±	65.6	10	±	1.9	11.85	±	2.7	14.91	±	3.6	16.41	±	5.0
Sb	0.004	±	0.0007	0.005	±	0.0013	0.001	±	0.000	0.006	±	0.001	0.007	±	0.0024	0.001	±	0.0002	0.006	±	0.0008
Sc	0.069	±	0.008	0.075	±	0.004	0.130	±	0.03	0.085	±	0.01	0.086	±	0.012	0.099	±	0.007	0.088	±	0.008
Se	0.008	±	0.002	0.006	±	0.002	0.017	±	0.003	0.007	±	0.005	0.006	±	0.001	0.005	±	0.001	0.012	±	0.004
Sm	0.02	±	0.0011	0.02	±	0.0004	0.021	±	0.002	0.021	±	0.000	0.02	±	0.0012	0.02	±	0.0018	0.03	±	0.0030
Sn	0.0002	±	0	0.0002	±	0	0.0068	±	0.001185	0.0002	±	3.9E-05	0.0002	±	4.77E-05	0.0048	±	0.0005775	0.0002	±	4.771E-05
Sr	0.888	±	0.07	0.776	±	0.06	0.950	±	0.11	0.712	±	0.07	0.740	±	0.06	0.748	±	0.07	0.744	±	0.04
Tb	0.002	±	0.0003	0.003	±	0.0000	0.003	±	0.000526	0.003	±	0	0.002	±	0.0003	0.003	±	0.0000	0.004	±	0.0003
Te	0.002	±	0.0004	0.001	±	0.0001	0.000	±	0.0001	0.002	±	0.0002	0.001	±	0.0001	0.000	±	0.0004	0.004	±	0.0009
Th	0.018	±	0.001	0.021	±	0.001	0.026	±	0.006	0.024	±	0.001	0.023	±	0.002	0.021	±	0.002	0.034	±	0.006
Ti	5.85	±	0.9	6.69	±	0.9	5.43	±	1.14	6.69	±	0.93	6.27	±	0.0	5.43	±	1.1	7.10	±	1.1
Tl	0.0010	±	0.0001	0.0009	±	8.187E-05	0.001	±	9.54E-05	0.001	±	2.19E-05	0.0009	±	0.0001	0.0010	±	0.0001	0.0012	±	0.0001
Tm	0.001	±	0	0.001	±	0	0.0011	±	0.000265	0.0006	±	0	0.001	±	0	0.001	±	0.0003242	0.001	±	0
U	0.006	±	0.0005	0.005	±	0.0003	0.007	±	0.0014	0.005	±	0.0002	0.005	±	0.0005	0.005	±	0.0002	0.009	±	0.0011
V	0.96	±	0.12	0.95	±	0.07	1.92	±	0.58	1.18	±	0.08	1.19	±	0.17	1.39	±	0.13	1.57	±	0.25
Y	0.12	±	0.008	0.12	±	0.004	0.169	±	0.02	0.125	±	0.01	0.128	±	0.011	0.146	±	0.012	0.200	±	0.012
Yb	0.004	±	0.0003	0.004	±	0.0003	0.005	±	0.000517	0.005	±	0	0.005	±	0.0003	0.004	±	0.0007	0.007	±	0.0005
Zn	0.88	±	0.14	0.83	±	0.11	1.289	±	0.14	0.907	±	0.04	0.91	±	0.15	1.05	±	0.07	1.08	±	0.13
Zr	0.046	±	0.007	0.054	±	0.011	0.058	±	0.01	0.069	±	0.01	0.060	±	0.003	0.058	±	0.007	0.066	±	0.004

Table 3.3. Mean element concentration (µmol g^{-1}) ± standard deviation of elements at the Sheyenne River and upstream and downstream of the confluence of the Red River and Sheyenne River. For each row data presented by different superscripts are significantly different from each other (ANOVA, $p<0.05$; Tukey's pairwise comparisons, $p<0.01$). Elements that show significant variations between the sites are in bold.

Element	**Upstream**			**Tributary**			**Downstream**		
Al	664^{ab}	±	104	554^{a}	±	99	788^{b}	±	170
As	0.104	±	0.041	0.098	±	0.01	0.085	±	0.011
B	1.94	±	0.13	2.16	±	0.32	2.48	±	0.63
Ba	1.24	±	0.0615	1.26	±	0.042	1.41	±	0.5623
Be	0.08	±	0.017	0.08	±	0.01	0.1	±	0.03
Bi	0.0008^{ab}	±	0.0001	0.0006^{a}	±	0.0001	0.0009^{b}	±	0.0001
Ca	1241	±	164	1233	±	99	1152	±	135
Cd	0.003	±	0.0004	0.0029	±	0.0004	0.0032	±	0.0008
Ce	0.238	±	0.03	0.222	±	0.015	0.254	±	0.03
Co	0.141	±	0.014	0.148	±	0.008	0.168	±	0.033
Cr	0.59^{a}	±	0.12	0.49^{ab}	±	0.11	0.72^{b}	±	0.17
Cs	0.009	±	0.0027	0.008	±	0.0013	0.009	±	0.0022
Cu	0.331	±	0.05	0.286	±	0.03	0.376	±	0.08
Dy	0.014	±	0.0015	0.014	±	0.0003	0.015	±	0.0020
Er	0.007	±	0.0008	0.007	±	0.0003	0.007	±	0.0008
Eu	0.005	±	0.0004654	0.004	±	0.0003605	0.005	±	0.0006
Fe	380	±	68	328	±	26	399	±	68
Ga	0.07	±	0.015	0.058	±	0.016	0.085	±	0.017
Gd	0.02	±	0.002	0.019	±	0.0012	0.02	±	0.0021
Ho	0.003	±	0.0003	0.002	±	0	0.003	±	0.0003
K	81	±	10	75	±	9.6	101	±	27.8
La	0.125	±	0.01	0.113	±	0	0.129	±	0.02
Li	2.95	±	0.56	2.41	±	0.32	3.61	±	1.09
Lu	0.0006	±	0	0.0006	±	0	0.0006	±	0
Mg	835^{b}	±	29	589^{a}	±	0	768^{b}	±	0
Mn	10.9^{a}	±	1	31.7^{b}	±	50	13.9^{a}	±	68
Mo	0.0034	±	0.001	0.0028	±	3	0.0051	±	4
Na	19.5^{a}	±	3.61	29.2^{b}	±	0.001	26.3^{b}	±	0.002
Nd	0.102	±	0.01	0.1	±	7.93	0.111	±	5.25
Ni	0.468	±	0.07	0.509	±	0.01	0.562	±	0.012
P	20.3^{a}	±	1.7	27.8^{b}	±	0.04	22.0^{a}	±	0.12
Pb	0.053	±	0.008	0.047	±	0.4	0.052	±	2.2
Pr	0.029	±	0.003	0.027	±	0.005	0.031	±	0.004

Table 3.3. Mean element concentration (µmol g^{-1}) ± standard deviation of elements at the Sheyenne River and upstream and downstream of the confluence of the Red River and Sheyenne River (continued),

Element	**Upstream**			**Tributary**			**Downstream**		
Rb	0.329	±	0.05	0.278	±	0.03	0.38	±	0.1
S	11^{a}	±	0.7	30^{ab}	±	6	65^{b}	±	65.6
Sb	0.001	±	0	0.002	±	0	0.001	±	0
Sc	0.109	±	0.02	0.088	±	0.01	0.13	±	0.03
Se	0.014	±	0.01	0.017	±	0.01	0.017	±	0.003
Sm	0.019	±	0.001	0.019	±	0.002	0.021	±	0.002
Sn	0.0063^{b}	±	0.001	0.0040^{a}	±	0.0005	0.0068^{b}	±	0.001
Sr	0.776^{a}	±	0.11	1.145^{b}	±	0.14	0.950^{ab}	±	0.11
Tb	0.003	±	0.0003	0.003	±	0	0.003	±	0.0005
Te	0	±	0.0001	0	±	0.0001	0	±	0.0001
Th	0.023	±	0.006	0.019	±	0.002	0.026	±	0.006
Ti	6.69	±	0.93	5.01	±	1.14	5.43	±	1.14
Tl	0.001	±	0.0003	0.001	±	0.0001	0.001	±	0.00
Tm	0.0009	±	0.0003	0.0009	±	0.0003	0.0011	±	0.0003
U	0.005	±	0.0007	0.005	±	0.0004	0.007	±	0.0014
V	1.59	±	0.34	1.37	±	0.22	1.92	±	0.58
Y	0.155	±	0.01	0.158	±	0.01	0.169	±	0.02
Yb	0.004	±	0.0003	0.005	±	0.0005	0.005	±	0.0005
Zn	1.195	±	0.14	1.2	±	0.12	1.289	±	0.14
Zr	0.065	±	0.01	0.054	±	0.01	0.058	±	0.01

3.4.4. Percentage sediment contribution from the Sheyenne tributary

The percentage sediment contributions to the elements from the Sheyenne River to the Red River are shown in Figure 3.4. Percentage sediment contributions from tributary to the Red River for elements Mg, Mn, Na, P, Pb, Sb, Sr, Ti, and Zr were between 0-100%. For elements Al, B, Bi, Ce, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Gd, Ho, K, La, Li, Mo, Nd, Pr, Rb, Sc, Sm, Sn, Th, TI, U and V the percentage contributions were smaller than 0. For Tb the percentage contribution was 0 and for elements As, B, Ba, Ca, Co, Er, Ni, S, Te, Y, Yb and Zn the percentage contributions were greater than 100%.

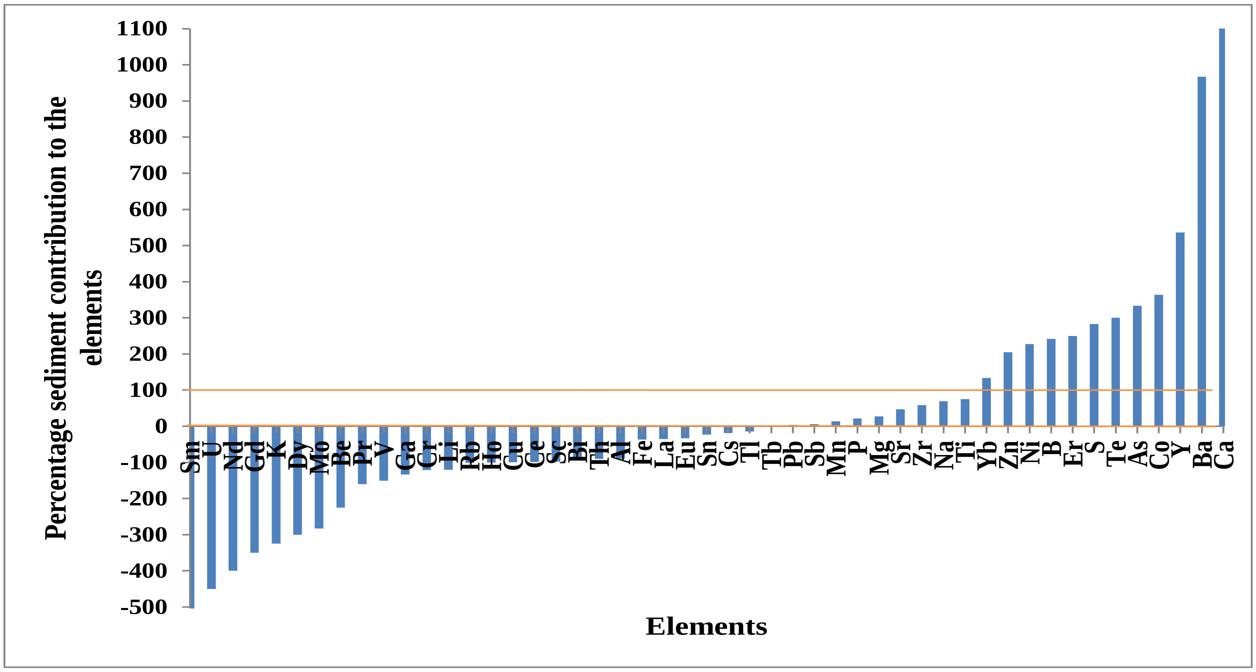


Figure 3.4. Percentage sediment contribution from the Sheyenne River to the Red River, the elements are ordered from low to high based on their percentage contribution. Red Lines show the percentage contributions between 0-100 percent.

3.4.5. Analysis for multiple elements at the Turtle tributary

Table 3.4 shows the mean element concentrations at the Turtle River and upstream and downstream of the confluence with the Red River (n=5 at each site). ANOVA analysis showed that mean concentrations of elements Al, As, B, Cd, Ce, Cu, Fe, Ga, Gd, La, Mg, Na, Nd, P, Pb, Pr, Rb, S, Sm, Sr, Th, V, Zn, and Zr significantly vary between the Turtle River and downstream and upstream locations of the Red River ($p < 0.05$). Based on the results of Tukey's pair-wise comparisons, tributary concentrations of elements Al, As, Cd, Cu, Fe, Ga,La, Na, Rb, S, Sr, V and Zn were significantly (p<0.01) higher than both upstream and downstream, or lower than both upstream and downstream (Mg, Zr). Upstream concentration of elements Ce, Gd, Nd, Pr, Sm and Th were significantly higher than both downstream and tributary, or lower than both downstream and tributary (B). Downstream concentrations of P were lower than both tributary and upstream, and for Pb downstream concentrations were significantly higher than both tributary and upstream.

Table 3.4. Mean element concentration (µmol g^{-1}) ± standard deviation at the Turtle River and upstream and downstream of the confluence of the Red River and Turtle River. Elements that show significant variation between the sites are in bold (ANOVA, $p<0.05$). For each row different letters are significantly different from each other Tukey's pairwise comparisons, $p<0.01$).

Element	Upstream			Tributary			Downstream		
Al	514^{a}	±	37	617^{b}	±	33	549^{a}	±	27
As	0.075^{a}	±	0.007	0.097^{b}	±	0.02	0.072^{a}	±	0.005
B	1.91^{a}	±	0.14	2.72^{b}	±	0.27	2.35^{b}	±	0.12
Ba	0.007	±	0.0004	0.008	±	0.001	0.008	±	0.0006
Be	0.0976	±	0.005	0.1065	±	0.01	0.1043	±	0.01
Bi	0.001	±	0.0001	0.0009	±	0.0001	0.0008	±	0.0001
Ca	1360	±	93	1234	±	76	1340	±	93
Cd	0.0032^{a}	±	0.0003	0.0043^{b}	±	0.0005	0.0031^{a}	±	0.0005
Ce	0.164^{b}	±	0.0003	0.125^{a}	±	0.0005	0.128^{a}	±	0.0005
Co	0.126	±	0.009	0.127	±	0.007	0.125	±	0.005
Cr	0.41	±	0.03	0.42	±	0.04	0.39	±	0.01
Cs	0.0004	±	0.0002	0.001	±	0.0003	0.001	±	0.0003
Cu	0.226^{a}	±	0.03	0.283^{b}	±	0.02	0.230^{a}	±	0.02
Dy	0.013	±	0.0008	0.014	±	0.0004	0.012	±	0.0004
Er	0.006	±	0.0003	0.006	±	0.0003	0.006	±	0.0003
Eu	0.004	±	0	0.004	±	0	0.004	±	0
Fe	284^{a}	±	10	318^{b}	±	11	283^{a}	±	13
Ga	0.059^{a}	±	0.005	0.067^{b}	±	0.004	0.059^{a}	±	0.003
Gd	0.021^{b}	±	0.002	0.019^{a}	±	0.0004	0.018^{a}	±	0.0004
Ho	0.002	±	0	0.003	±	0	0.003	±	0
K	62	±	5.9	78	±	5.3	65	±	4.3
La	0.925^{a}	±	0.05	1.05^{b}	±	0.05	0.945^{a}	±	0.03
Li	0.0006	±	0.11	0.0006	±	0.18	0.0006	±	0.10
Lu	0.0006	±	0	0.0006	±	0	0.0006	±	0
Mg	1069^{b}	±	65	853^{a}	±	94	1035^{b}	±	84
Mn	12.4	±	2	18.1	±	7	13.3	±	2
Mo	0.0011	±	0.001	0.0034	±	0.003	0.0019	±	0.002
Na	13.7^{a}	±	1.05	48.5^{b}	±	8.35	15.7^{a}	±	4.07
Nd	0.333^{b}	±	0.04	0.245^{a}	±	0.008	0.255^{a}	±	0.009
Ni	0.383	±	0.06	0.386	±	0.01	0.373	±	0.02
P	24.3^{b}	±	1.1	25.3^{b}	±	2.9	21.7^{a}	±	0.4

Table 3.4. Mean element concentration (µmol g^{-1}) ± standard deviation at the Turtle River and upstream and downstream of the confluence of the Red River and Turtle River (continued).

Element	Upstream			Tributary			Downstream		
Pb	0.058^{a}	±	0.004	0.050^{a}	±	0.003	0.076^{b}	±	0.014
Pr	0.039^{b}	±	0.004	0.030^{a}	±	0.001	0.030^{a}	±	0.0008
Rb	0.261^{a}	±	0.02	0.320^{b}	±	0.02	0.282^{a}	±	0.03
S	9^{a}	±	0.9	42^{b}	±	12.7	10^{a}	±	1.9
Se	0.007	±	0.002	0.007	±	0.002	0.005	±	0.001
Sb	0.01	±	0.01	0.008	±	0.01	0.006	±	0.01
Sc	0.084	±	0.002	0.089	±	0.002	0.085	±	0.005
Sm	0.025^{b}	±	0.002	0.021^{a}	±	0.001	0.021^{a}	±	0.000
Sn	0.0002	±	0	0.0002	±	0.00005	0.0002	±	0.00004
Sr	0.672^{a}	±	0.05	1.427^{b}	±	0.07	0.712^{a}	±	0.07
Te	0.001	±	0.0002	0.002	±	0.0004	0.002	±	0.0002
Th	0.034^{b}	±	0.006	0.020^{a}	±	0.001	0.024^{a}	±	0.001
Ti	7.52	±	1.14	5.85	±	0.93	6.69	±	0.93
Tl	0.001	±	0.00004	0.001	±	0.00006	0.001	±	0.00002
Tm	0.0006	±	0	0.0007	±	0	0.0006	±	0
U	0.006	±	0.0005	0.006	±	0.0004	0.005	±	0.0002
V	1.21^{a}	±	0.09	1.30^{b}	±	0.11	1.18^{a}	±	0.08
Y	0.134	±	0.01	0.138	±	0.01	0.125	±	0.01
Yb	0.005	±	0.0003	0.005	±	0	0.005	±	0
Zn	0.908^{a}	±	0.07	1.10^{b}	±	0.08	0.907^{a}	±	0.04
Zr	0.061^{b}	±	0.01	0.048^{a}	±	0.01	0.069^{b}	±	0.01

3.4.6. Percentage sediment contribution from the Turtle tributary

The percentage contributions from the Turtle River to the Red River are shown in Figure 3.5. Percentage sediment contributions from tributary to the Red River for elements Al, B, Be, Ca, Ce, Cs, Cu, Ga, K, La, Li, Mg, Mn, Mo, Na, Nd, Pr, Rb, S, Sc, Sn, Sr, Te, Th and Ti were between 0-100%.

For elements As, Co, Cr, Dy, Er, Fe, Li, Ni, P, Pb, Tl, U, V, Y, Yb, and Zn the percentage contributions were smaller or equal to zero. For elements Ba, Bi, Ce, Gd, Nd, Pr, Sb, and Sm the percentage contributions were greater than 100%.

3.4.7. Percentage contribution of cadmium and selenium from Turtle and Sheyenne Rivers

The calculated percentage sediment contributions of the tributaries to the elements were mostly higher than %100 or lower than 0, only for a few elements the percentage sediment contribution were between 0-%100.

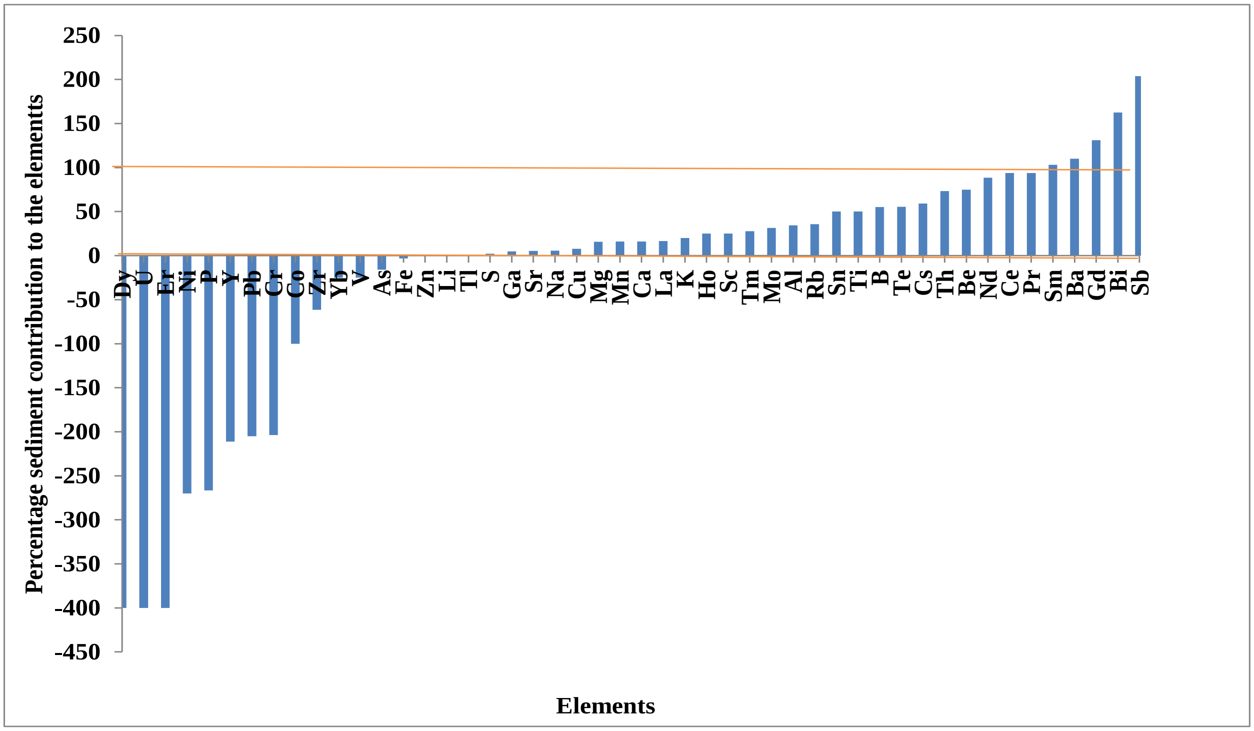
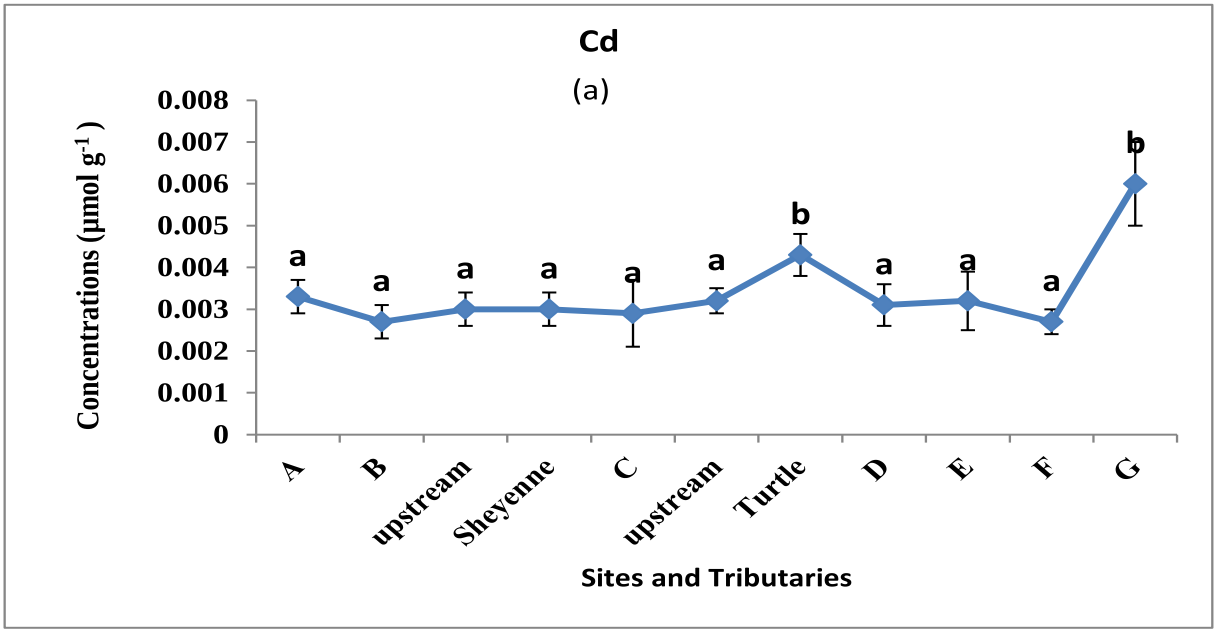


Figure 3.5. Percentage sediment contribution to the elements from Turtle tributary to the Red River, the elements are ordered from low to high based on their percentage contribution. Red Lines show the percentage contributions between 0-100 %.

This indicated that because the percentage sediment contribution did not meet the assumptions of linear mixing for many elements, further calculation, including mean percentage sediment contribution from tributaries, could not be used to calculate the relative percentage contribution of cadmium and selenium from the tributaries.

Figure 3.6 shows the Cd and Se concentration s (µmol g^{-1}) at the sampling sites (A, B, C, D, E, F, G) Sheyenne and Turtle Rivers, and downstream locations of the confluence with the tributaries. Results of ANOVA and Tukey's analysis showed that cadmium concentration (µmol g^{-1}) at the Turtle River (0.0043) and site G (0.006) was significantly higher than the Sheyenne

River and other sites, and for selenium mean concentrations at the Sheyenne tributary (0.017) and downstream location (0.017) was significantly higher than Turtle tributary (0.007) (Figure 1.7).



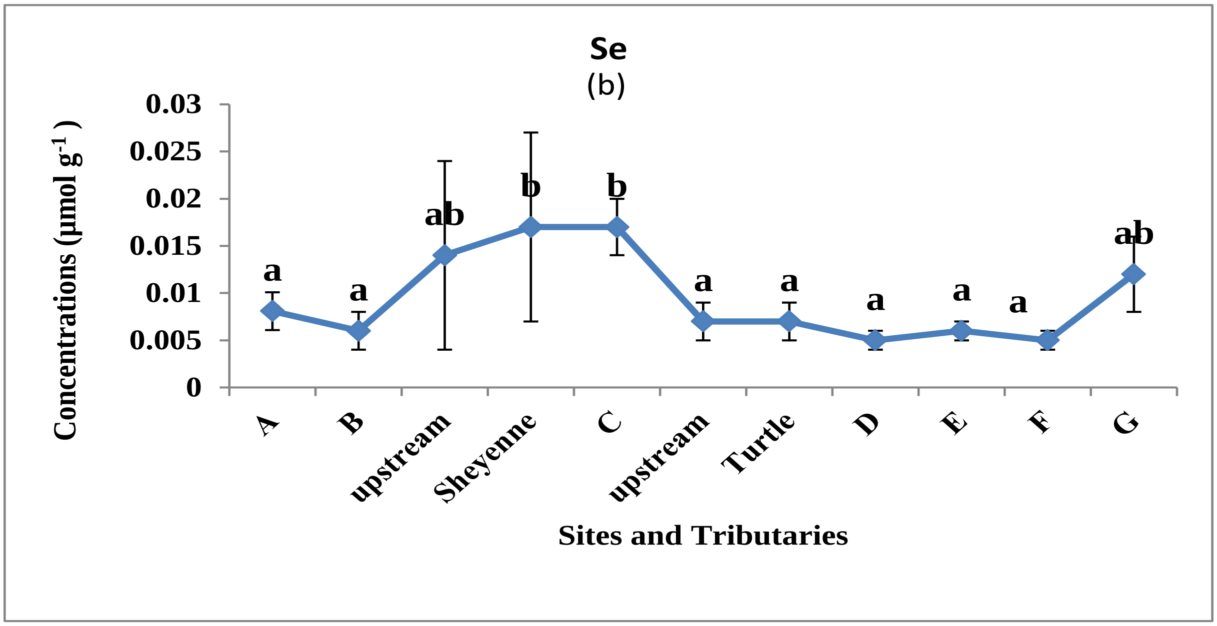


Figure 3.6. Mean element concentration (µmol g^{-1}) ± standard deviation of (a) Cd and (b) Se at the depositional sites (A (furthest upstream), B, C, D, E, F, G (furthest downstream)), Sheyenne and Turtle tributaries and downstream locations on the Red River (n=55).

3.5. Discussion

Sediments are important indicators of past and current events and in comparison to water analysis, sediments represent a longer time period (Håkanson and Jansson 2002). Elements, contaminants and nutrients can be transported or exchanged along the sediment-water interface (Jaynes and Carpenter 1986; Weis and Weis 2004; Nurminen and Horppila 2009). Multi-element concentrations in the sediments showed significant variations between the sampling sites (A (furthest upstream), B, C, D, E, F, and G (furthest downstream)) along the Red River (Table 3.2). The variations in the elements distribution in the sediment and water is influenced by factors such as organic matter, pH, particle size, nutrient concentrations, calcium carbonate concentrations (Guilizzoni 1991), sediment oxidation (Tessenow and Baynes 1975). In this study both LOI (estimate of organic matter) and particle size fraction smaller than 63 µm (estimate of clay and silt content) showed significant variation among sites and near confluence locations of the Red River (Figure 3.3). These variations therefore could be partly the reason for variation in element concentrations. Suspended sediment transported by a river presents different sources and geology within the catchment (Walling 2005) as result element concentrations in the sediment might show great variations between the sediment deposition sites. There were no significant correlations between LOI, pH and element concentrations, demonstrating that LOI and pH do not impact the element concentrations in the sediments. Also particle size showed a general increasing pattern as the river flows from upstream to downstream (Figure 3.3), which could be due to the fact that coarser particles deposit at the upstream location and finer would be in a suspended form and as the flows towards downstream finer particles such as clay and silt will deposit (Ciffroy et al. 2000; Wood and Armitage 1997).

3.5.1. Sediment contributions from tributaries to the Red River

3.5.1.1. Sheyenne

Element concentrations of Mn, Na, P, and Sr at the Sheyenne River were significantly higher than both upstream and downstream locations on the Red River (Table 3.3).The land use in the Sheyenne River watershed is dominated by agriculture (62 %) and elements such as P, N, K and Mg are known to be present in fertilizers (USGS 1995). Also high concentrations of phosphorus at the Sheyenne River could be a result of soil reduction. Phosphorus solubility is affected by reduction of sulfate to sulfide in flooded soils. When sulfate is being reduced to sulfide, various reaction occur which result in more availability of phosphorus.

Devils Lake in North Dakota is an endorheic (closed drainage basin lake) that has a diversion and flows into Sheyenne River. The Devils Lake has highly saline water and many questions exist regarding the impact of the water on downstream lakes and Rivers including Sheyenne River (Hollis 2007) and the high concentrations of elements Na, and Mg in the Sheyenne River could be the result of saline water of Devils Lake entering the Sheyenne River. Percentage sediment contribution for most of the elements was smaller than zero or higher than %100, with only a few elements (Mg, Mn, Na, P, Pb, Sr, Ti and Zr) between 0-%100 (Figure 3.5). This indicates that the assumption of linear mixing was not valid for this tributary. The percentage contribution of tributaries to the main river and the deposition of sediments in sink areas can be affected by variety of local factors, including increase in cross-sectional area, occurrence of obstructions to flow and flow separation (Fairbridge 1968; Rosgen and Silvery 1996). Dams that form the Lake Ashtabula control the flow rate and affect the quality and chemistry of water in the Sheyenne River (USGS 1995). One possible explanation is that the sediments tend to get suspended in the water near the confluence of the Sheyenne and Red River because the flow rate might be faster at the Red River in comparison to the Sheyenne and sediment tends to deposit further downstream, or diluted because of being mixed with an upwelling groundwater entering the water or small streams entering the Red River.

3.5.1.2. Turtle

At the Turtle River concentrations of Al, As, Cd, Cu, Fe, Ga, K, La, Na, Rb, S, Sr, V and Zn were significantly higher than both upstream and downstream in the Red River (Table 3.4). High concentrations of elements such as Al, As, Fe, K, Na and S could be explained by the fact that the Turtle River is partly fed by the Dakota Aquifer, which has a high total dissolved solids, salinity and contains high concentrations of iron, chlorides and sulfate (Kelly and Paulson 1970). The sulfates and carbonates form precipitates with metal ions and these metals could be deposited in sediments or released into the surface waters depending on the characteristics of environments such as reduced or oxidized conditions in the sediment (Gibbs 1973; Evans 2001; Förstner 1990; Ankley et al. 1992). The dominant form of iron (ferrous iron Fe^{2+}) and sulfur (sulfide S^{2-}) in hydric soils form different compounds with metals and these compounds are highly insoluble and immobile in reduced flooded soils in comparison to non-flooded oxidized soils (Kissoon et al. 2011; Jacob and Otte 2004). Sediment contribution of Turtle River to elements such as Al, Ca Mg, Mn, Na, S and Sr can be explained by the underlying geology. Carbonate minerals, sulfur bearing gypsum ($CaSO_4.2H_2O$), pyrite (FeS_2) and compounds such as hydrogen sulfide (H_2S) are all present in the underlying geology (Kelly and Paulson 1970). .

Percentage sediment contribution for As, Co, Cr, Dy, Er, Fe, Ni, P, Pb, U, V, Y, Yb was less than zero and for Ba, Bi, Ce, Gd, Nd, Pr, Sb and Sm was higher than % 100 (Figure 3.6). The percentage sediment contribution for elements Al, B, Be, Ca, Ce, Cs, Cu, Ga, K, La, Li, Mg, Mn, Mo, Na, Nd, Pr, Rb, S, Sc, Sn, Sr, Te, Th and Ti were between 0-100% (Figure 3.6).

Factors such as pH, type and concentration of ligands and oxidation states of the minerals in the sediments control the trace element mobility and speciation (Förstner 1990; Evans 2001). These factors could be different from place to place depending on the chemical, physical and biological properties of the environment; metals may become immobilized or released back to the water in response to the changes in environment (Li et al. 2001). The Turtle River has saline water chemistry of the Dakota Aquifer and the fact that percentage sediment contributions for metals such as As, Fe, Ni, Pb and Cr did not follow the linear mixing assumption could be the result of changes in water chemistry at the confluence of the Turtle and Red River.

3.5.2. Tributary contributions to the Se and Cd concentrations at the Red River

Relative percentage tributary contributions to Cd and Se could not be calculated, because especially at the Sheyenne River, the sediments did not show the assumption of linear mixing. Evidence of a tributary contribution following the linear mixing model would be a positive contribution (0-100 %) for most of the elements with an average contribution accompanied by a narrow standard deviation. The mobility and also concentrations of elements that are sorbed on to the sediments can be affected by flow rate of water. A lower flow rate could increase the ability of sediments to release the elements that bind with it to the water, because at low flow rate more time is available for contact between water and sediment (Evans 2001; Dhakal et al. 2005; Leopold 2006). Variations in water chemistry and flow rate of water at the confluences of the Turtle and Sheyenne Rivers might result in sediments to release some elements into the water or stay suspended in the water. Also snow melt and groundwater entering the Red River at downstream of the confluence will change the water chemistry.

Cadmium enters aquatic systems through natural sources, most of the Cd entering the rivers is absorbed to particulate matter and sediments are the major source of Cd (Wong et al.

2007, Rauf et al. 2009). As expected, mean cadmium concentrations in the tributary Turtle River and site G were significantly higher than the tributary Sheyenne River and all of the other sites along the Red River (Figure 3.6 (a)). The Pierre aquifer, which for a part feeds the Turtle River, intersects with Pierre Shale (Kelly and Paulson 1970, Jacob et al. 2013). This may explain higher concentrations of Cd at the Turtle River in comparison with the Sheyenne River. The high concentrations of Cd in site G might be because of the attachment to the clay particles, as mentioned in the beginning of the discussion particle size (f<63μm) shows an increasing pattern with the highest percentage at site G.

The results of studies on selenium concentrations in North Dakota in 1930 showed that the selenium content in soil ranged from 0.006-0.02 (μmol g^{-1}) (Williams et al. 1941). These results are similar to the range 0.005-0.014 we found in our study in sediment samples along the Red River. Mean concentrations of Se in Sheyenne tributary and downstream location of the confluence of the Sheyenne with the Red River were significantly higher than Turtle tributary (Figure 3.6 (b)). Se in water could exist in dissolved, particulate and colloidal forms. Sources of selenium in the soil are highly siliceous rocks such as sandstones; granites and limestone are parent material that adds to selenium content in soils. Atmospheric and anthropogenic sources also contribute to Se, such as industrial waste, nuclear waste, and agricultural practices. Most of the selenium, however, due to abiotic and biotic movements of dissolved ions from the water gets buried in the sediment (Ihnat 1989).

3.6. Conclusion

In conclusion, this research shows that there is a statistically significant variation of element concentrations in the Red River sediments. For the contribution from the Turtle River and Sheyenne River tributaries to the Red River, the percentage sediment contribution for most of the elements did not support the linear mixing model. The results also demonstrates that the variation in element concentrations is sufficient to use the multi-element fingerprinting technique to study the element variations and patterns along the River. However, to draw conclusions about the relative contributions of elements of concern, namely Cd and Se, more information is required such as flow rate of water at the confluences and data on sediment movement.

CHAPTER 4. SEDIMENT SOURCE TRACING AT THE LITTLE MISSOURI RIVER, USING THE MULTI-ELEMENT FINGERPRINTING APPROACH

4.1. Abstract

In southwestern North Dakota at least 21 uranium deposits exist. The Little Missouri River is known to cut through uranium-containing lignite in North Dakota. High concentrations of uranium can cause environmental issues due to toxicity and persistence in rivers. In this study, the possibility for tracing sources and the tributaries contributing to U and other element concentrations in the Little Missouri River was assessed using the multi-element fingerprinting technique. Five tributaries were selected based on nearby uranium deposits. Riverbank depositional sediments were sampled from three locations in each river, (1) in the main channel upstream and (2) downstream of the confluence with the tributaries, and (3) inside the tributaries. At the Little Missouri River, uranium concentrations were generally higher at the southern sites closer to uranium deposits. The largest tributary at the upstream of the Little Missouri River showed the highest contribution to uranium concentrations compared to other tributaries. The differences in uranium contributions may be due to factors such as the distance of tributary from uranium depositions, land use, underlying geology.

4.2. Introduction

Uranium naturally consists of gamma-emitting radioactive isotopes. In an aquifer, uranium as a toxic metal is a risk to the ecosystem and human health (Schöner et al. 2006). Rivers and streams are the major source of dissolved uranium to the ocean (Palmer and Edmond 1993; Dunk et al. 2002). The amount of metals that are released to the environment is increasing as a result of activities such as mining (Förstner 1990). Riparian vegetation and soil accumulate metals via chemical, physical and chemical processes, and natural wetlands are sinks for hazardous trace metals such as uranium (Schell et al. 1989; Owen and Otton 1995; Cole 1998).

A number of studies on the accumulation and abundance of metals in natural riparian wetlands were done and they demonstrated that wetland soils have great potential to retain metals and other elements from surrounding land and from the river itself (Arias et al. 2005; Prokisch et al. 2009). Studies on the function of vegetation in wetlands also reported that wetlands play a key role in decreasing metal concentration through uptake by plants and storing them in different compartments, including roots and shoots (Canário et al. 2010). Many studies focus on the distribution and accumulation of metals in the sediment deposits or sediment suspended in the river water (Jain and Sharma 2001; Diagomanolin et al. 2004; Helios et al. 2005; Wang et al. 2011).

The Little Missouri River, North Dakota, U.S.A., is known to cut through uranium lignite. Analysis of surface and core samples indicates that lignite contains a high percentage of uranium (Denson and Gill 1955). In North Dakota there are at least 21 areas in the western part of the state that contain uranium, mostly within lignite or sandstone (Murphy 2007; Denson 1959). Some of the tributaries, especially those located upstream, pass through these deposits.

Although different hypotheses exist regarding the various sources of uranium in western North Dakota, the uranium concentrations and behavior in the Little Missouri River and the adjacent riparian areas are poorly studied. The multi-element fingerprinting technique is currently being applied to study different mechanisms in wetlands, such as element uptake in plants and tracing suspended sediment sources in catchments and river systems. This technique is capable of identifying the distribution and low concentrations of 62 elements in soil, sediment, and plant materials.

In this study, the multi–element fingerprinting technique was applied 1) to evaluate the suitability of the multi-element fingerprinting method for measuring sediment contribution from tributaries and for sediment source tracing, and 2) to address the potential sources of uranium in depositional sediments of the Little Missouri River. It was hypothesized that at the Little Missouri River, tributaries near uranium-rich lignite will show higher concentrations of uranium in sediment, and were expected to contribute to the uranium concentrations at the Little Missouri River. Also element concentrations and patterns in the sediment would reflect the characteristics of the sources from which it originates.

4.3. Materials and methods

4.3.1. Study area

The Little Missouri River is 901 km long and is a tributary of the Missouri River in the Northern Great Plains in western North Dakota. The river starts in Wyoming and flows northeastward through the southeastern corner of Montana, the Badlands in South Dakota, and then into North Dakota. There the river passes through both units of Theodore Roosevelt National Park, east to Lake Sakakawea, and finally enters the Missouri River near the town of Killdeer. The Little Missouri flows through many different sedimentary deposits from the Paleocene, including sandstone and lignite coal (Figure 4.1) (USGS, 2011).

4.3.2. Sample collection

At the Little Missouri River, two riverbank sites and five tributaries were selected. Sites were selected to study the uranium and other element variations along the Little Missouri River. Major tributaries that pass through lignite deposits were chosen based on a map by Murphy, 2007 (Figure 4.1). Sediment from the top layers of sediment (maximum depth of sampling

=3cm) by the edge of the river were sampled for both main river and tributaries because they represent the most recent deposits and eroded sites. The samples were collected in five replicates along a transect parallel to the river (with various distances between the replicates yet within the sediment deposition site) by the river bank (maximum distance of 2m from the edge of the river) to be representative of the element concentrations in the latest sediments by the river

For tributaries, sampling consisted of three locations in depositional sediments: 1) erosional sediment in the tributary maximum of 50 m upstream from the confluence, 2) erosional sediment maximum of 50 m upstream along the main river, and 3) depositional sediment, maximum of 50 m downstream along the main river. The confluence flow rate of water could result in sediment mixing, and sample collection at 50 m distance would be far enough away to be less influenced by the flow rate. Also it was expected, and observed at the sites, that based on the size of the watershed and flow rate of water, sediment coming from the tributary and upstream locations of the Little Missouri River would deposit downstream in approximately the first 50 m distance.

This sampling design, with 50 m distance as opposed to the 100 m distance used for the Red River (Chapter 3), was selected considering the smaller size of the watersheds, water turbulence, and seasonal factors such as flooding.

Table 4.1 shows the coordinates of the depositional sites (B, G) and downstream location of the confluences on the Little Missouri River (A, C, D, E, and F). Downstream locations on the Little Missouri River were also considered as sites when assessing the element variations or other factors such as particle size along the Little Missouri River.

On Murphy's map (Figure 4.1), uranium deposits were defined using gamma counts interpreted from uranium and coal exploration. In total 85 samples were collected from tributaries and sites along the Little Missouri River

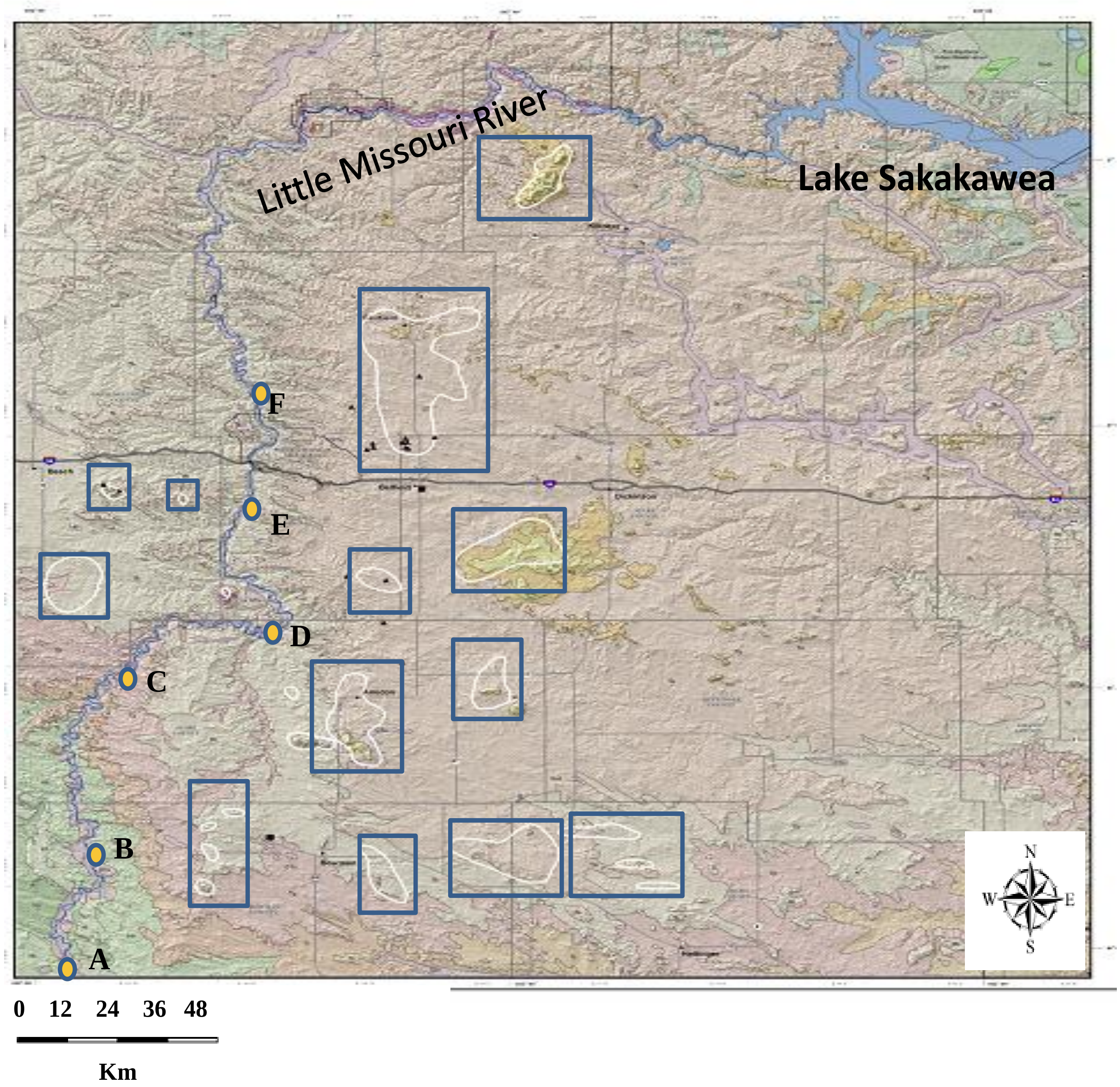


Figure 4.1. Map showing the uranium deposits in western North Dakota (shapes with white out lines that have been put into blue frames for more visibility) and location of sampling sites (A (furthest upstream) B, C, D, E, F, G (furthest downstream)) along the Little Missouri River. Various colors on the base map show the different surface geologic units. Map after Murphy (2007).

Table 4.1. Coordinates of the depositional sites (A (furthest upstream) B, C, D, E, F, G (furthest downstream) along the Little Missouri River in North Dakota.

Sampling Site	Coordinates
A	45°57'52.51"N, 103°57'40.71" W
B	46° 2'50.50"N, 103°57'13.39"W
C	46°08'08.50"N, 103°51'19.00" W
D	46°40'07.16"N,103°28'54.82" W
E	47°04'07.65"N, 103°31'33.18" W
F	47°02'47.86"N, 103°36'04.15"W
G	47°31'4.75"N, 103°37'1.02"W

4.3.3. Particle size, Loss-on-ignition, pH analysis, sample preparation and multi-element analysis.

These procedures are identical to those described in CHAPTER 2.

4.3.4. Data analysis

For this section refer to CHAPTER 3.

4.4. Results

4.4.1. Particle size (f<63 µm), pH and LOI at the Little Missouri River

At the sites along the Little Missouri River, particle size (*f*<63 µm) ranged (n=35) from 18-94% with an average of 41%. LOI ranged (n=35) from 0.3-5.3 % with an average of 3 %, pH ranged (n=35) from 7.58-9.74 with an average of 8.73. LOI and pH did not show significant variation, or any significant correlations with each other and any of the elements at the sites along the Little Missouri River. Particle size showed significant variations at the sites along the

Little Missouri River. Results of Tukey's pair-wise comparisons showed that site D was significantly higher (p-<0.01) in mean percentage particle size relative to other sites (Figure 4.2), site A had the lowest percentage particle size.

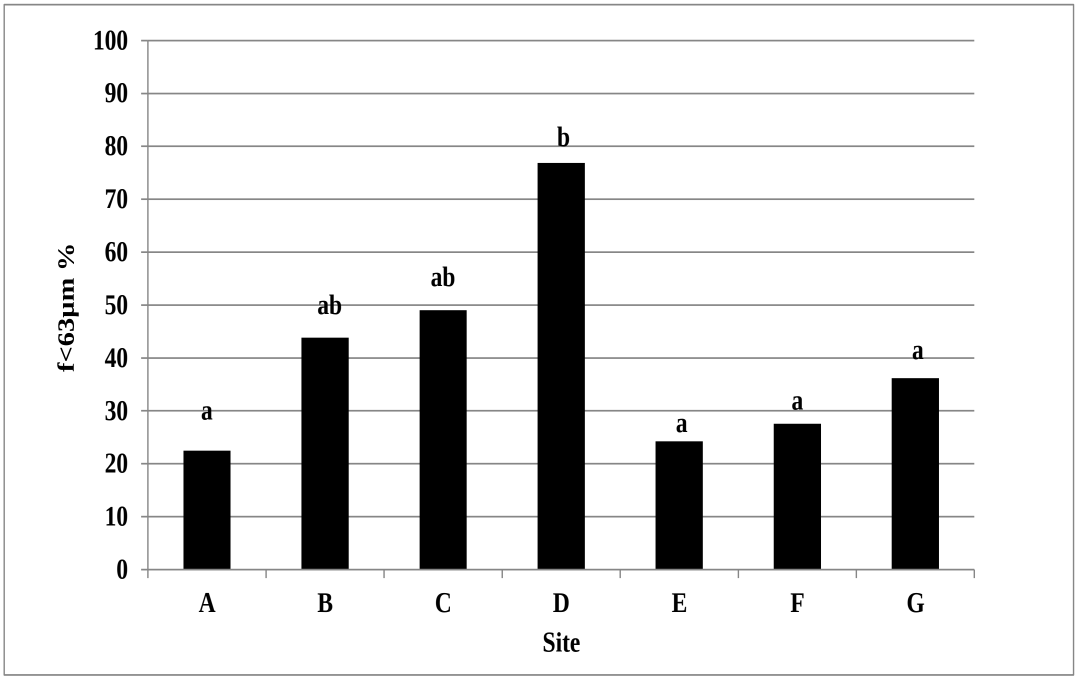


Figure 4.2. Variation in mean percentage particle size (f<63 µm) at the sampling sites (n =5) (A (furthest upstream) B, C, D, E, F, G (furthest downstream)) along the Little Missouri.

4.4.2. Variations in multiple-elements and uranium along the Little Missouri River

The concentrations of elements at the sampling sites are given in Table 4.2. Results of ANOVA showed that concentrations of Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Re, S, Sb, Sc, Se, Sm, Sn, Sr, Te, Th, Ti, U, V, Y, Zn and Zr varied significantly (p<0.05) between the sampling sites.

Table 4.2. Element concentrations ± standard deviation at the sampling sites (A (furthest upstream), B, C, D, E, F, G (furthest downstream)) along the Little Missouri River. Element with significant variations between the sites are in bold. Values are in µmolg^{-1} unless otherwise stated.

Element	**A**			**B**			**C**			**D**			**E**			**F**			**G**		
Al	374	±	17	418	±	109	529	±	124	649	±	124	570	±	40	494	±	36	466	±	224
As	0.06	±	0.004	0.06	±	0.02	0.074	±	0.01	0.09	±	0.014	0.06	±	0.030	0.04	±	0.013	0.04	±	0.027
B	0.44	±	0.04	0.94	±	0.22	1.33	±	0.09	1.59	±	0.09	0.92	±	0.21	0.68	±	0.32	0.65	±	0.09
Ba	0.008	±	0.001	0.009	±	0.001	0.010	±	2.261	0.4	±	2.26	1.90	±	0.002	3.22	±	0.001	3.83	±	0.000
Be	0.10	±	0.01	0.10	±	0.02	0.107	±	0.01	0.12	±	0.01	0.08	±	0.01	0.05	±	0.01	0.05	±	0.02
Bi(nmolg-1)	0.6	±	0.03	0.65	±	0.20	0.81	±	0.09	1	±	0.09	0.69	±	0.10	0.38	±	0.1	0.38	±	0.15
Ca	233	±	24	460	±	187	604	±	65	681	±	65	388	±	109	293	±	73	236	±	198
Cd(nmolg-1)	1.82	±	0.08	1.9	±	0.2	2.23	±	0.1	2.62	±	0.12	1.78	±	0.23	1.28	±	0.37	1.3	±	0.49
Ce	0.19	±	0.022	0.14	±	0.00	0.13	±	0.01	0.15	±	0.010	0.21	±	0.009	0.25	±	0.006	0.25	±	0.010
Co	0.13	±	0.01	0.14	±	0.02	0.157	±	0.02	0.18	±	0.02	0.16	±	0.01	0.15	±	0.01	0.15	±	0.02
Cr	0.29	±	0.04	0.34	±	0.38	0.422	±	0.13	0.62	±	0.13	0.60	±	0.04	0.45	±	0.05	0.43	±	0.08
Cs(nmolg-1)	0.17	±	0.04	0.33	±	0.25	0.50	±	0.56	2.2	±	0.56	6.28	±	0.20	7.6	±	0.153	7.40	±	0.13
Cu	0.19	±	0.01	0.22	±	0.13	0.265	±	0.03	0.38	±	0.03	0.33	±	0.03	0.22	±	0.02	0.19	±	0.04
Dy(nmolg-1)	14.77	±	1.15	14.28	±	0.55	14.52	±	0.80	15	±	0.802	14.77	±	0.702	0.01	±	0.001	13.54	±	0.702
Er(nmolg-1)	6.58	±	0.423	6.82	±	0.00	7.17	±	0.50	7.65	±	0.50	6.94	±	0.53	6.46	±	0.27	6.46	±	0.33
Eu(nmolg-1)	5.40	±	0.294	4.74	±	0.29	4.61	±	0.59	4.87	±	0.59	4.87	±	0.29	4.74	±	0.29	4.74	±	0.00
Fe	205	±	10	225	±	44	278	±	78	332	±	78	299	±	31	263	±	25	260	±	87
Ga	0.03	±	0.01	0.05	±	0.01	0.058	±	0.03	0.07	±	0.03	0.05	±	0.01	0.05	±	0.01	0.04	±	0.02
Gd	0.02	±	0.002	0.02	±	0.00	0.021	±	0.00	0.02	±	0.002	0.02	±	0.001	0.02	±	0.001	0.02	±	0.001
Ho(nmolg-1)	2.55	±	0.27	2.55	±	0.000	2.79	±	0.000	2.91	±	0.000	2.55	±	0.000	2.43	±	0.000	2.43	±	0.271
K	31	±	2.1	38	±	28	37	±	8	46	±	7.8	50	±	4.3	44	±	19.3	40	±	5.8
La	2.88	±	0.68	1.91	±	0.23	1.829	±	0.00	1.58	±	0.004	0.51	±	0.565	0.12	±	0.615	0.12	±	1.584
Li	1.60	±	0.10	1.96	±	0.25	2.403	±	0.12	2.79	±	0.12	2.16	±	0.23	1.74	±	0.13	1.62	±	0.16
Mg	152	±	13	206	±	16	230	±	40	255	±	40	249	±	45	242	±	34	215	±	33
Mn	3.95	±	0.2	5.45	±	0.72	7.235	±	2.96	8.38	±	3.0	5.39	±	0.8	5	±	1	5.64	±	2.8

Table 4.2. Element concentrations ± standard deviation at the sampling sites (A (furthest upstream), B, C, D, E, F, G (furthest downstream)) along the Little Missouri River (continued)

Element	A			B			C			D			E			F			G		
Mo(nmolg-1)	3.42	±	1.28	3.56	±	0.79	5.21	±	2.31	9.34	±	2.31	8.59	±	5.40	4.27	±	2.0	3.25	±	3.09
Na	81	±	12	97	±	49	145	±	65	149	±	65	93	±	56	113	±	63.1	148	±	62
Nd	0.38	±	0.033	0.30	±	0.01	0.268	±	0.01	0.22	±	0.008	0.13	±	0.017	0	±	0	0.11	±	0.021
Ni	0.35	±	0.03	0.38	±	0.27	0.433	±	0.05	0.55	±	0.05	0.41	±	0.12	0.42	±	0.024	0.40	±	0.10
P	16	±	2.1	19	±	0	18.60	±	4	17	±	3.6	19	±	1.5	18.99	±	1.22	16	±	3.2
Pb	0.05	±	0.00	0.05	±	0.02	0.053	±	0.01	0.07	±	0.01	0.05	±	0.01	0	±	0.0	0.04	±	0.01
Pr(nmolg-1)	44	±	4.096	34	±	1.00	32	±	2.15	30	±	2.153	29	±	1.809	30	±	1.6	31	±	2.322
Rb	0.12	±	0.01	0.14	±	0.02	0.17	±	0.02	0.21	±	0.02	0.17	±	0.02	0.16	±	0.011	0.16	±	0.02
S	20	±	3.1	48	±	25	81.35	±	1	87	±	0.8	48	±	34.8	27.70	±	41.97	21	±	18.4
Sb(nmolg-1)	5.16	±	1.09	3.52	±	1.53	4.94	±	0.38	16.74	±	0.38	7.38	±	2.75	1	±	1.6	1.17	±	6.17
Sc	0.06	±	0.00	0.07	±	0.01	0.088	±	0.01	0.11	±	0.01	0.09	±	0.01	0.08	±	0.007	0.08	±	0.02
Se(nmolg-1)	1.77	±	0.69	3.55	±	2.53	5.57	±	2.53	8.87	±	2.53	8.87	±	1.92	0.01	±	0.00	8.87	±	1.13
Sm(nmolg-1)	30.33	±	2.2	24.87	±	0.36	23.54	±	1.97	22.88	±	1.973	21.42	±	1.279	0.021	±	0.001	21.42	±	1.244
Sn(nmolg-1	0.17	±	0.00	0.19	±	0.05	0.226	±	0.78	0.83	±	0.78	2.19	±	0.04	0.26	±	0.048	3.22	±	0.05
Sr	0.68	±	0.07	1.06	±	0.37	1.515	±	0.62	1.85	±	0.62	1.23	±	0.21	1.34	±	0.17	1.48	±	0.66
Tb(nmolg-1)	2.9	±	0.3	2.5	±	0.3	2.5	±	0.0	2.6	±	0.0	2.9	±	0.3	2.8	±	0.0	2.5	±	0
Te(nmolg-1)	2.20	±	0.37	1.71	±	0.33	1.87	±	0.33	2.28	±	0.33	2.28	±	0.98	2.3	±	0.61	2.28	±	7.82
Th	0.035	±	0.004	0.03	±	0.001	0.026	±	0.003	0.026	±	0.003	0.023	±	0.001	0.020	±	0.002	0.02	±	0.002
Ti	12.54	±	2.56	8.78	±	0.00	6.686	±	1.87	4.60	±	1.87	6.27	±	0.00	7.522	±	0.9	7.10	±	0.93
Tl(nmolg-1)	0.6	±	0.07	0.67	±	0.10	0.78	±	0.15	0.95	±	0.15	0.82	±	0.12	0.75	±	0.08	0.68	±	0.12
Tm	0.001	±	0.000	0.829	±	0.000	0.001	±	0.000	0.001	±	0.000	0.001	±	0.000	0.0008	±	0.0	0.829	±	0
U(nmolg-1)	5.5	±	0.3	5.6	±	0.5	6.47	±	1.3	7.4	±	1.3	6.5	±	0.5	5.5	±	0.38	5.8	±	1.1
V	0.46	±	0.02	0.55	±	0.09	0.683	±	0.13	0.84	±	0.13	0.73	±	0.07	0.675	±	0.1	0.63	±	0.12
Y	0.12	±	0.007	0.12	±	0.01	0.125	±	0.01	0.14	±	0.013	0.15	±	0.006	0.15	±	0.01	0.15	±	0.011
Yb(nmolg-1)	4.97	±	0.32	4.85	±	0.00	5.09	±	0.52	5.55	±	0.52	4.62	±	0.26	4.28	±	0.41	4.28	±	0.48
Zn	0.76	±	0.05	0.87	±	0.18	1.03	±	0.13	1.24	±	0.13	1.04	±	0.09	0.920	±	0.070	0.97	±	0.13
Zr	0.06	±	0.01	0.07	±	0.02	0.072	±	0.00	0.09	±	0.00	0.07	±	0.01	0.05	±	0.01	0.05	±	0.01

4.4.3. Mean Percentage sediment contribution from tributaries

For all of the tributaries (A, C, D, E, F), percentage sediment contribution calculated for most elements was between 0-100% and only a few elements showed contributions smaller than 0 or greater than 100% (see Fig. 4.3 for example).

Based on this, it was concluded that tributaries along the Little Missouri meet the linear mixing assumption. Therefore the average sediment contributions (0-100%) to the elements at each tributary were calculated and the mean percentage sediment contributions ± 95% confidence intervals of the tributary to the Little Missouri River are presented in Figure 4.4. The highest mean tributary contribution (71 ± 9) was from the tributary A, which is located upstream in the Little Missouri River, and the lowest from tributary C (45± 6). Also the tributary D (59 ± 5) showed the second highest contribution.

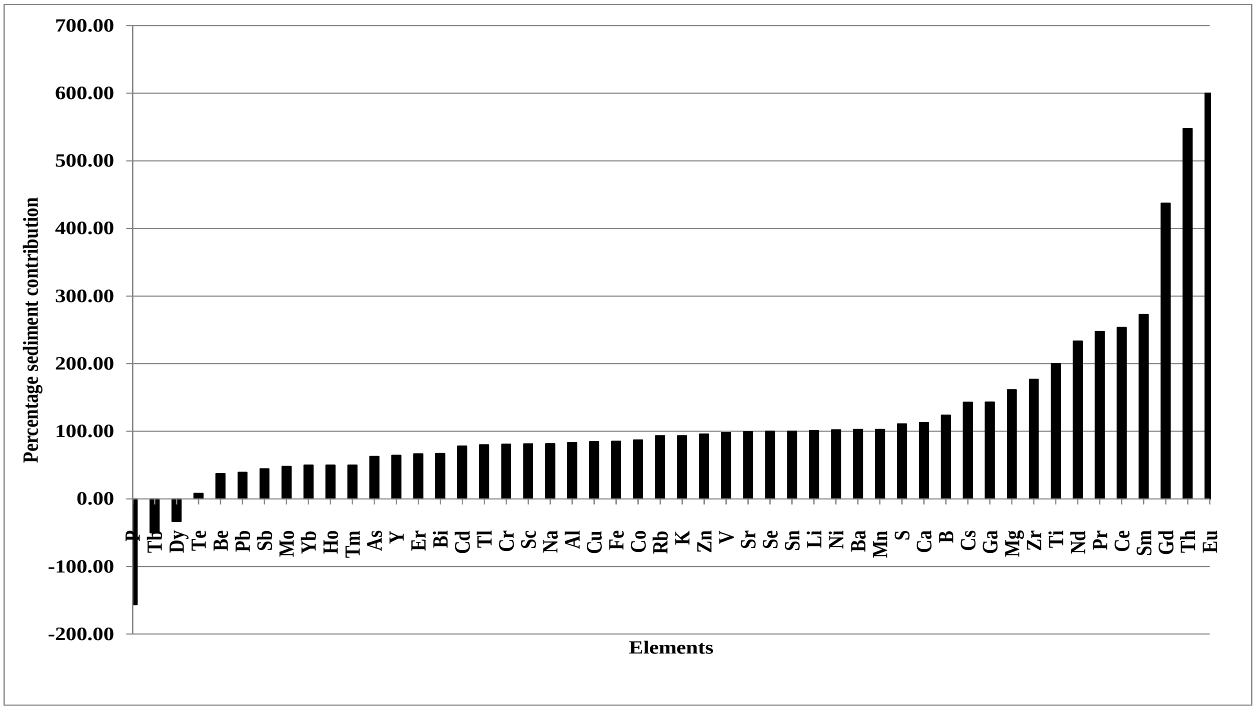


Figure 4.2. Example showing the percentage contribution of elements from the tributary sediments of site A to the Little Missouri River. Percentage contributions are ordered from low to high.

4.4.4. Percentage contribution of tributaries to the uranium concentrations at the Little Missouri River

Uranium concentrations at the upstream, downstream and inside tributaries (A, C, D, E, and F) are shown in Figure 4.5. Mean uranium concentrations (nmol g^{-1}) along the little Missouri ranged from 4.8-7.8 with an average of 6.8. The upstream (7.8) and downstream (7.1) sites (nmol g^{-1}) of the confluence of tributary D with the Little Missouri both show the highest concentrations in comparison to the same sites at other tributaries. Results of Tukey's comparisons at each tributary and it's upstream and downstream locations of the confluence with the Little Missouri showed that at the tributary A the uranium concentrations significantly varied between the three sites, and at the upstream of the confluence uranium concentration was significantly higher than downstream and tributary ($p<0.01$) (Figure 4.5). The same pattern is observed for tributary D. At the tributaries C, E and F no significant variations in uranium concentrations were observed between the sites.

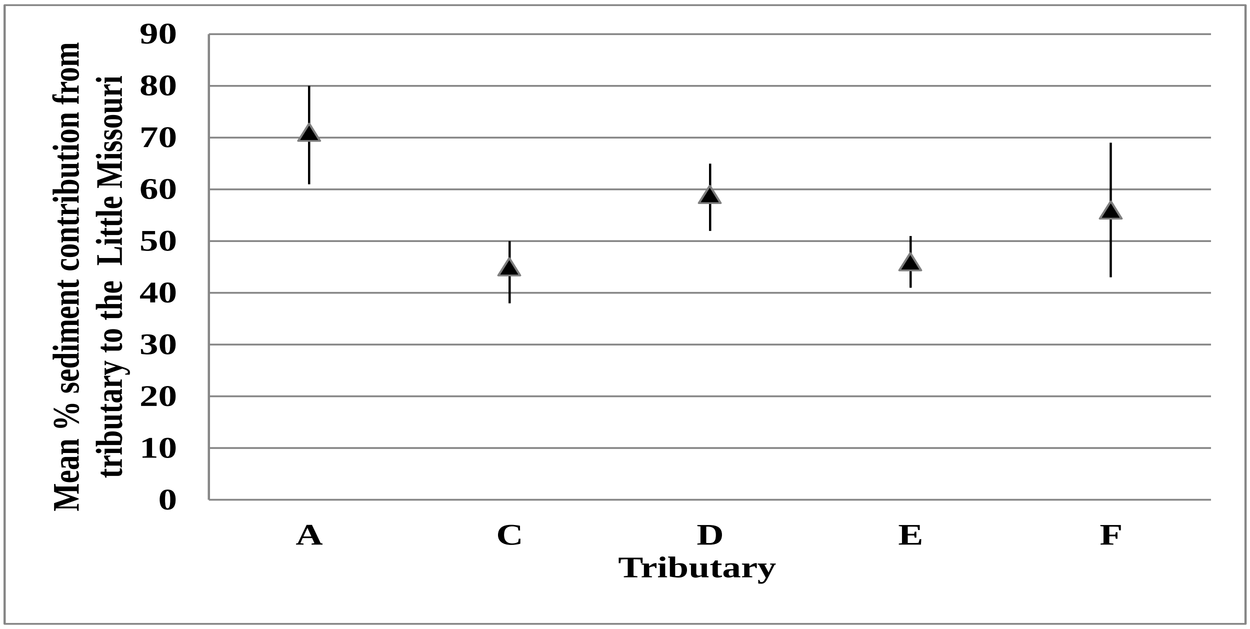


Figure 4.3. Percentage contribution of sediments± % 95 confidence interval from the tributaries (A (furthest upstream), C, D, E, F (furthest downstream)) to the Little Missouri River.

Percentage contribution of uranium from the tributaries to the main river was calculated using the mean sediment contribution from the upstream and tributary and the concentration of uranium in the upstream and tributary sediments (Table 4.3). Tributary A the most southern tributary upstream in the Little Missouri River in North Dakota, showed the highest percentage contribution (63%), followed by tributary D (58 %) and F (56 %). Tributary C (47 %) and E (42 %) had the lowest contribution to the uranium concentrations at the Little Missouri River.

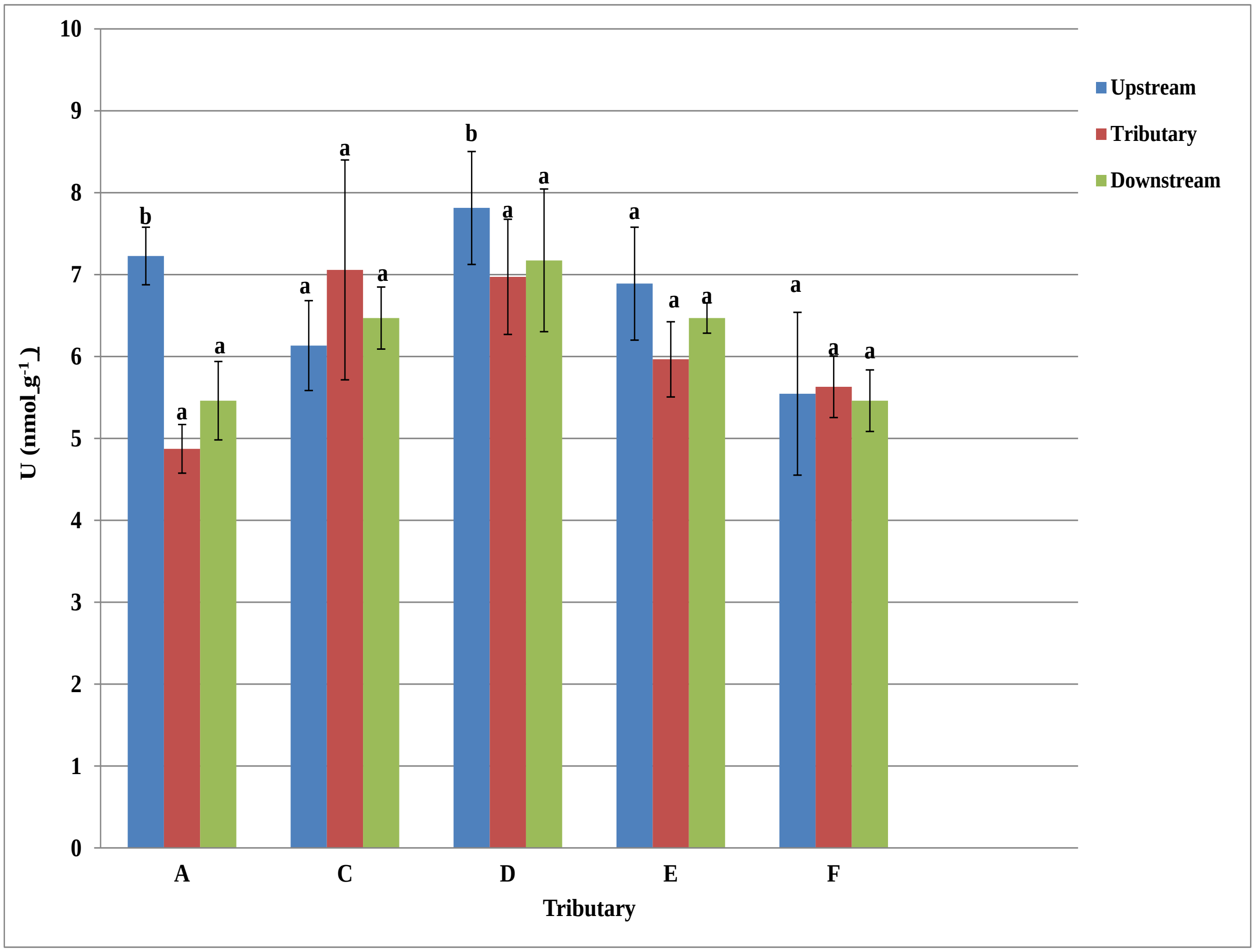


Figure 4.4. Uranium concentrations (nmol g^{-1}) upstream and downstream of the confluence of tributaries (A (furthest upstream), C, D, E, F (furthest downstream)) with the Little Missouri River (*n*=5). Different letters above the bars shows the significant variations at each tributary and the upstream and downstream locations (this does not include the comparisons between the tributaries) ($p<0.01$).

Table 4.3. Mean sediment contribution from upstream and tributary, mean concentration of uranium in the tributary and upstream sediments of the Little Missouri River, and calculated percentage contribution of uranium from tributaries. Tributaries are shown as A(furthest upstream) B, C, D, E, F(furthest downstream).

Site	**Mean sediment contribution from the upstream of the river (%)**	**Mean sediment contribution from tributary (%)**	**Mean measured concentrations in upstream sediments** (nmol g^{-1})	**Mean measured concentrations in tributary sediments** (nmol g^{-1})	**Contribution of tributary to U (%)**
A	29	71	7.2	4.8	63
C	55	45	6.1	7.1	47
D	41	59	7.8	7.0	54
E	54	46	6.9	6.0	42
F	44	56	5.5	5.6	56

4.5. Discussion

Elements could be exchanged and transported along the rivers through sediment-water reactions (Jaynes and Carpenter 1986; Weis and Weis 2004; Nurminen and Horppila 2009). Element mobility is influenced by the soil/sediment solution composition and the reactive surface area (Cataldo and Wildung 1978). In this study, element concentrations (Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Re, S, Sb, Sc, Se, Sm, Sn, Sr, Te, Th, Ti, U, V, Y, Zn, Zr) in the sediment deposits at the Little Missouri showed significant variations ($p<0.05$) along the river. Particle size influences sedimentation processes and the capacity to bind elements (Håkanson and Jansson 2002), the presence of metals in sediments is partly impacted by the particle size and composition of the sediments (Horowitz and Elrick 1987; Singh et al 2005).

Particle size (*f*<63 µm) showed statistically significant variation between the sites (Figure 4.1) and one explanation for the variations in elements along the river could be due to the binding with the particle size and being influenced by the variations in percentage particle size *f*<63 µm. Local geology and land use within watersheds is an important factor impacting the sediment and water chemistry (Moyle 1945; Newton et al. 1987; Nilsson and Håkanson 1992; Fraterrigo and Downing 2008), at the Little Missouri variation in elements and particle size along the river could be due to both the geology and land use in the area. In fact different activities such as mining, grazing and natural processes such as flooding in the Little Missouri basin could dramatically change the sediment and water chemistry. In our study samples were passed through a 63 µm sieve and because this method does not assess the particle size distributions on the samples, we were unable to determine the relationship between particle size of soils/sediment and multi-element correlations.

At the Little Missouri River, uranium concentrations showed statistically significant variation along the river. Positive correlations were observed between uranium and Dy, Fe, V, Zn, at the sampling sites along the Little Missouri River. Uranium ions in water have been shown to be absorbed onto metal oxides and clays under proper chemical conditions (Prikryl et al. 2001 Krestou et al. 2003; Han et al. 2007). Uranium may co-precipitate with iron sulfides thus reducing their mobility (Jenne 1976; Choi et al 2006). Fe is known to play a significant role in the element distributions in wetlands (Otte et al. 1991; Doyle and Otte 1997; Kissoon et al. 2010). In fact one of the important oxides that impact the mobility of elements is iron oxide because it provides sorption sites for cations (McBride 1994). In our study the positive correlations between uranium and iron shows that iron might play an important role in behavior of uranium along the Little Missouri River.

Trace element and nutrient distributions in the sediment can be influenced by pH and organic matter (Guilizzoni 1991). Generally, LOI (percentage organic matter content) in the sediment samples did not show very high content and a narrow range from 0.32-5.3 % was observed. pH was slightly alkaline (7.0-9.8) with an average of 8.7. In other studies, it has been shown that decreasing pH of wetland soil could result in increased mobility of elements such as Al, Cu, Fe, Mn, Mo and Zn in soil (Kirk and Bajita 1995; Jones et al. 1996; Jungk et al. 2002). Studies have shown that organic matter content provides binding surfaces for trace element ions. Coquery and Welbourn (1995) reported that concentration of elements in the sediments of Lake Bentshoe showed significant positive correlations with organic matter content. Both of pH and LOI did not show significant variations between the sampling sites, indicating 1) relatively homogeneous sediments and 2) the variations in the element concentrations is not related to the LOI and pH in the sediment.

4.5.1. Percentage uranium contribution from tributaries to the Little Missouri River

The stable form of uranium (UIV) in rivers, due to different factors such as variations in reduction-oxidation conditions or weathering, might become soluble (UO_2^{2+}) (uranyl ion) and transported by the rivers (Schöner et al. 2006). Lignite is a good extractor of the uranium in the solution (Moore 1954).

As it is shown in Figure 4.5, results of the Tukey’s comparisons showed that uranium concentrations at the tributaries A and D showed significant variations between the three locations (downstream, upstream and tributary). Therefore the tributary contributions from tributaries A and D to the uranium will be discussed because although tributary F shows high percentage contribution to the uranium but the uranium concentrations does not significantly change in the downstream location of the confluence of this tributary and the Little Missouri River.

Generally, three hypothesis of the origin have been suggested to explain the uranium bearing lignite deposits of the North and South Dakota and Montana regions. Result of studies and reports proposed these two hypothesis of origin: 1) The uranium initially was deposited with other minerals in sediments overlying or marginal to the lignite and got fixed by the carbon in the lignite 2) the uranium was deposited from surface waters through action of living organisms or organic matter at the time that lignite was forming (Denson and Gill 1955). The third hypothesis is as a result of the study of Denson et al. 1954, saying that the uranium was extracted by the lignite from the ground water passing by the lignite and carrying uranium from overlying source rocks.

Tributary contributions to the uranium at the Little Missouri showed variations with the highest percentage sediment contribution (63 %) to the Little Missouri River from tributary A. Based on the site observations and from the maps of the North Dakota, tributary A was the first tributary sampled upstream of the Little Missouri and largest tributary sampled in width from one river bank to another, and this tributary flows through Montana and joins the Little Missouri River a few kilometers above the border of North Dakota and South Dakota. The highest percentage contribution from tributary A could be due to the fact that this tributary flows through the areas in which volcanic –rich rocks are known to exist. In the mid-1950s, the volcanic-rich rocks of White River (a tributary of Missouri River that flows 930 km through the states of Nebraska and South Dakota in united states) were identified as likely source rocks for the uranium found in sandstone and lignite in southwestern North Dakota and northwestern South Dakota and Montana (Denson et al. 1954; Denson and Gill 1955). Factors such as size of watershed, magnitudes of rainfall, geology and land use and water flow rate have been shown in many studies to effect the contribution of sediments from the watersheds (Trimble 1997, Lopes and Canfield 2004). Wijeyaratne (2011) found a significant correlation between the size of watersheds at the Souris River, ND and the percentage contribution of watersheds to the phosphorus, in their study smaller watersheds contributed smaller amount in comparison to the larger watersheds. Another explanation for the contribution of tributary A could be the fact that this tributary due to the size of watershed transports a higher sediment load in comparison with other tributaries and therefor the relative percentage contribution to the cadmium is higher than other tributaries.

The upstream concentrations of uranium (nmolg^{-1}) (7.8) and downstream (7.1) sites of the confluence of tributary D with the Little Missouri both show to be higher in comparison to the same sites at other tributaries. The best explanation for the high tributary contribution at D (54%) is that these tributaries as shown in Figure 4.1 are close to the uranium lignite depositions. Murphy (2007) in his report stated that out of 21 uranium deposits in North Dakota, seven of these cover more than 400 km^2 and one of these deposits at the north of Belfield, extends over an area of more than 335 km^2, this could explain the high concentrations of uranium at the sampling sites nearby these areas. Also, the Department of Energy, North Dakota (1989) reported that high levels of radioactivity are present in and around the old processing sites at Griffin and Belfield.

Table 4.4 shows the lignite in ton present in states of North Dakota, South Dakota and Montana and the percentage uranium present in the lignite, as presented by Hansen in 1981. South Dakota has the highest amount of lignite followed by North Dakota. The percentage uranium present in the lignite shows the highest value in North Dakota.

Table 4.4. Lignite present in states of South Dakota, North Dakota and Montana with the percentage uranium content.

State	Lignite (kg)	U (%)
South Dakota	45,000,000,000	0.007
North Dakota	25,000,000,000	0.011
Montana	15,000,000,000	0.004

4.6. Conclusion

This research shows that there was statistically significant variation of element concentrations in the Little Missouri sediments. As expected linear mixing was observed for all the tributaries sampled, and generally sites close to uranium lignite depositions showed higher mean uranium concentrations. The multi-element fingerprinting approach was used successfully to identify possible sediment/element sources to the Little Missouri River and also assess the spatial variation of U.

CHAPTER 5. GENERAL DISCUSSION AND FINAL CONCLUSIONS

In this thesis Chapter 2 (2011) focused on the element compositions and patterns in the riparian sediment of the Red, Sheyenne, James, Missouri, and Little Missouri rivers in North Dakota, and Chapters 3 and 4 (2012) on sediment source tracing and percent sediment contribution of selected tributaries to the elements at the Red and Little Missouri rivers.

5.1. Differences between the rivers, based on multi-element variation within the rivers

In general, results of multi-element fingerprinting and ANOVA analysis demonstrated that many elements showed significant variation ($p < 0.05$) in the samples collected from riparian sites within the Red, Sheyenne, James, Missouri and Little Missouri rivers (Chapter 2, 2011) and sediment depositional sites within the Red and Little Missouri rivers (Chapter 3 and 4, 2012) (Table 5.1).

Looking at the results of both years (Table 5.1), at the Red and Little Missouri rivers, more elements showed significant variation in the sediment depositional sites (Chapters 3 and 4) in comparison to the riparian sediment sites (Chapter 2). One possible explanation for this difference in the results of two years is the differences between the type of samples (riparian wetland sediment, depositional sediment). Riparian plants stabilize the element concentrations and less variation could be observed in riparian wetland sediment in comparison to the sediment deposits by the river that are imposed to constant change due to water fluctuations. Riparian plants acquire most of their nutrients from the sediment and from the water column (Barko and Smart 1980; Barko et al. 1991; Clarke and Wharton 2001). Riparian vegetation impacts and changes the biogeochemistry of various soils (Wright and Otte 1999; Stoltz and Greger 2002; Jacob and Otte 2004). Wetland plants stabilize sediments (Barko and James 1998) by inhibiting the erosion and suspension of sediment. The differences in the location of sampling sites along the river, and different conditions present in two years of sampling such as flooding could also impact this variation in the element concentrations. However further study is needed to address these impacts on the element variation, and it is ideal to study the same site and samples from the same location during different conditions and between different years or seasons.

Table 5.1. Results of two years of study on riparian sites and river sediments, showing the multi-element variation ($p<0.05$) in riparian sediments along Red, Sheyenne, James, Missouri, Little Missouri Rivers (2011) and in depositional sediments along Red and Little Missouri Rivers in (2012) ($n=20$ at each river).

River	**Year**	**Elements with significant variation**
Riparian wetland sediments		
Red	**2011 Chapter 2**	Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu,Fe, Ga, In, K, Li, Mn, Ni, P, Pb, Rb, S, Sc, Se, Sn, Ti, V, Zn and Zr
Sheyenne		As, Ca, Cd, Co, Er, Eu, Gd, Ho, La, Li, Mg, Mn, Na, Nb, Nd, Ni, P, Pr, S, Sb, Sm, Th, Ti, U, V, Y
James		Ba, Be, Ca, Cd, Cu, Ga, Li, Mg, Mn, Mo, Ni, P, Pb, Re, S, Sn, Th, Ti, U, Zn
Missouri		Al, As, Ba, Be, Bi, Ca, Co, Cr, Cu, Fe, Ga, K, Li, Lu, Mg, Na, Nb, Ni, Pb, Rb, Sc, Se, V, Zn
Little Missouri		Ca, Mg, S
Depositional sediments		
Red	**2012 Chapter 3**	Al, As, B, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Rb, S, Sb, Sc, Sm, Sn, Sr, Tb, Te, Th, Ti, Tm, U, V, Y, Yb, Zn, Zr
Little Missouri	**2012 Chapter 4**	Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Re, S, Sb, Sc, Se, Sm, Sn, Sr, Te, Th, Ti, U, V, Y, Zn, Zr

5.2. Similarities between the rivers with regards to the biogeochemistry of riparian sediment

Figure 5.1 summarizes the factors that impacted the riparian sediment biogeochemistry in this study (Chapter 2) variation and shows that land use/soils and geology in North Dakota played an important role in element and particle size variation at the rivers. Based on the results of study on the riparian sediments in Chapter 2, rivers in North Dakota are divided in two groups of 1) eastern rivers (Red, Sheyenne and James) and 2) western rivers (Missouri and Little Missouri).

1) Similarities between the eastern rivers in North Dakota

Among the element concentrations that showed significant variation ($p<0.05$) between the rivers in North Dakota, the Red, Sheyenne and James rivers show generally the highest concentrations for particular elements, such as nutrients (Ca, Mn, K) or metals (Cd, Cr) (Table 5.2) and, the percent fraction of particles smaller than 63 µm shows the highest values at the Red, Sheyenne and James Rivers (Figure 5.1).

Table 5.2. Elements with highest mean concentrations (µmol g^{-1}) (n=20 at each river) in the riparian sediments along the Red, Sheyenne and James rivers.

Element	Red	Sheyenne	James	Missouri	Little Missouri
B	4.61	5.11	4.5	3.6	3.47
Bi	0.0008	0.00078	0.00078	0.00065	0.0006
Ca	1159	953	1026	804	573
Cd	0.0034	0.0029	0.0025	0.0022	0.0018
Cr	0.58	0.5	0.5	0.47	0.46
Ga	0.069	0.059	0.057	0.051	0.049
K	73	76	70	50	50
Mn	15	34	21	6	9
Sn	0.0071	0.0051	0.0051	0.0042	0.0038

The fact that these rivers show similar characteristics in element concentrations and particle size could be explained by soil types, land use and underlying geology of these rivers.

The Red, James and Sheyenne rivers mostly flow in the Red River Valley and soils in the Red River Valley are developed and derived predominantly from late-glacial erosion deposition of suspended sediments into Lake Agassiz (Schwert 2003), resulting in higher proportion of small particles. Generally, some elements such as nutrients (K and Ca) are associated with clay particles (Vital and Stattegger 2000). Also the land use is dominantly agricultural areas (US EPA 2004). Wetlands impacted by agricultural activities tend to have higher nutrient concentrations, compared to wetlands not influenced by agriculture (Lougheed et al. 2001; Atkinson et al. 2011; Rowan et al. 2012) as observed in our study for the Red, Sheyenne and James rivers. In the Northern Plains because of the existence of shale-derived soils such as Pierre shale (Holmgren et al. 1993; Hopkins et al. 1999; Jacob et al. 2013), some elements such as Cd are naturally present in soils.

2) Similarities between the western rivers in North Dakota

Rare earth metals such as Lu and Cs showed their highest concentrations in North Dakota at the Little Missouri and Missouri Rivers (Table 5.3). Particle size percentage fraction smaller than 63 μm, showed the lowest values at the Little Missouri and Missouri rivers (Figure 5.1).

Table 5.3. Elements with highest mean concentrations (μmol g^{-1}) (*n*=20 at each river) in the riparian sites along the Little Missouri and Missouri rivers.

Element	Red	Sheyenne	James	Missouri	Little Missouri
Ba	1.35	1.35	1.29	2.72	2.67
Ce	0.31	0.31	0.27	0.32	0.32
Cs	0.0085	0.0082	0.0072	0.0095	0.0096
Eu	0.025	0.026	0.023	0.027	0.027
Mo	0.0012	0.0005	0.0012	0.0018	0.0034
Sm	0.0003	0.00026	0.00023	0.00027	0.00027
Th	0.024	0.021	0.018	0.026	0.028

The Missouri and Little Missouri have sandy coarser soils in comparison to the eastern rivers and run through areas dominated by mining activities such as uranium mining (Murphy and Kehew 1984; Karsmizki 1990; Murphy 2007). Water chemistry is influenced by surrounding land use (Nilsson and Håkanson 1992; Fraterrigo and Downing 2008). Biogeochemistry of wetlands and riverine systems, plant communities and variation is dramatically changed by land use and geology as proposed in different studies (Moyle 1945; Stewart and Kantrud 1972; Barko and Smart 1986; Koch 2001; Lougheed et al. 2001; Hansel-Welch et al. 2003; Bayley et al. 2007; Del Pozo et al. 2011).

5.3. Tributary contributions and source-sink relationships

In Chapters 3 and 4, the multi-element fingerprinting technique was applied to study the tributary contributions to the concentrations of elements of concern at the Red River (Cd and Se), and at the Little Missouri River (U). It was hypothesized that selected tributaries at the Red River (Sheyenne and Turtle) and the Little Missouri River (five tributaries) will contribute to the concentrations of these elements, because they pass through sediment that have high concentrations of these elements. The tributary contributions were calculated using a linear mixing model (refer to Chapters 3 and 4). Metals entering the riverine ecosystems could occur in various forms, such as attached to sediments, bound to organic matter, or as dissolved cations (Evans 2001; Dhakal et al. 2005). Several chemical mechanisms are included in transport and speciation of metals in the rivers and streams, such as; 1) precipitation, 2) incorporation with biological and crystalline structures (Gibbs 1973; Pojasek and Zajicek 1978; Tessier and Campbell 1987). These factors could be different from place to place depending on the chemical, physical and biological properties of the environment (Li et al. 2001).

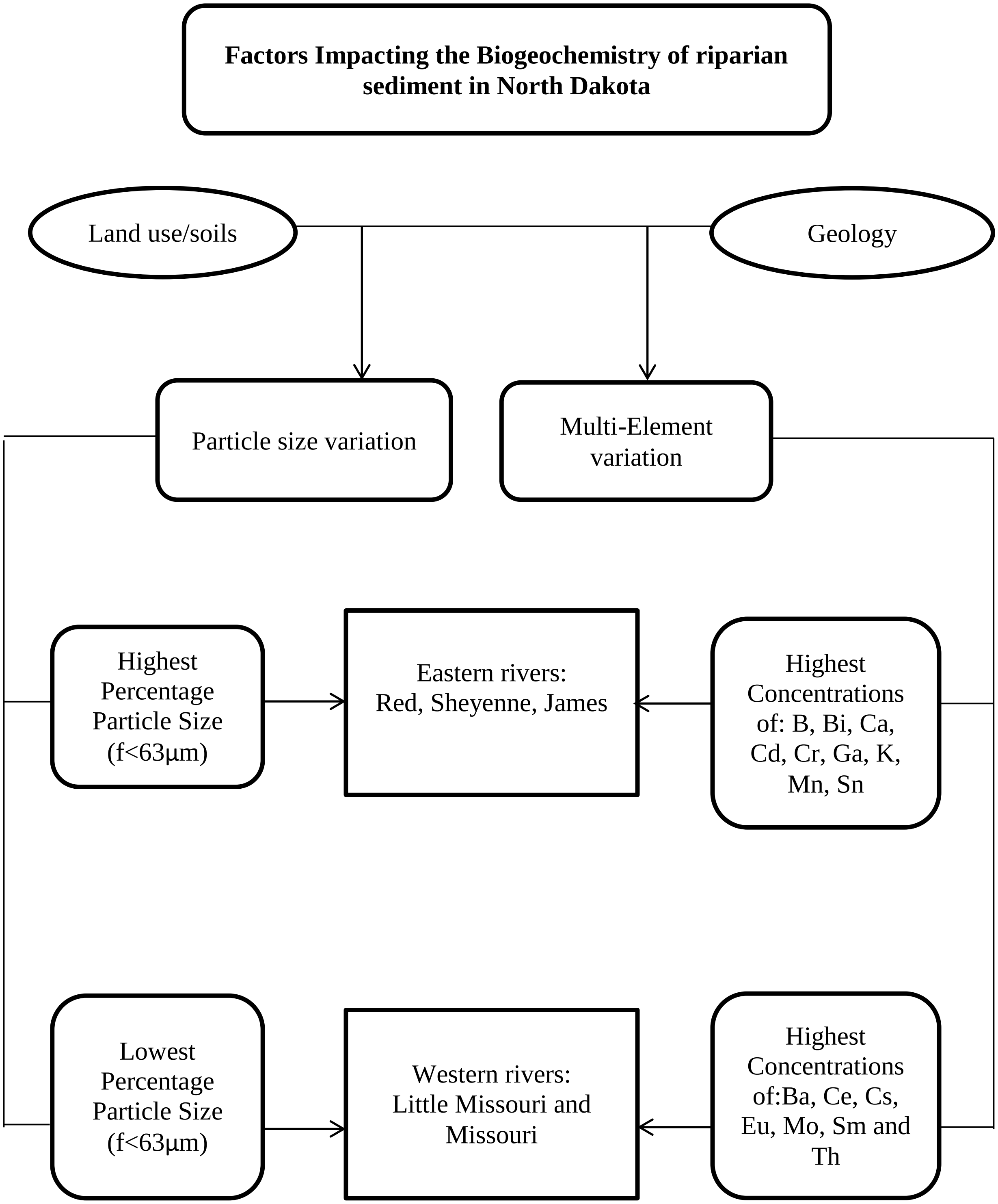


Figure 5.1. Conceptual diagram of the factors (land use/soils, geology) that influence the biogeochemistry (element and particle size variation) of the riparian sediments in North Dakota (Red, Sheyenne, James, Missouri and Little Missouri Rivers**).**

Table 5.4 shows the Se and Cd concentrations in the Sheyenne and Turtle rivers measured in this study and at the Turtle and Souris rivers as measured by Wijeyaratne 2011.

Cadmium shows the lowest concentrations and Se shows the highest concentrations at the Sheyenne River. Se concentrations at the Turtle River, measured in this study were higher than Se concentrations in the Turtle River measured by Wijeyaratne. Generally the ranges for Cd and Se were similar to the ones measured by Wijeyaratne 2011.

Table 5.4. Cd and Se concentrations in the sediment (μmol g^{-1}) of the Turtle and Sheyenne Rivers (measured in this study) and at the Turtle and Souris (measured by Wijeyaratne et al 2011).

River	Cd	Se	References
Turtle	0.004- 0.005	0.005-0.009	
Sheyenne	0.003-0.004	0.004- 0.03	
Turtle	0.0009-0.007	0.003-0.003	(Wijeyaratne 2011)
Souris	0.0005-0.005	0.001-0.01	(Wijeyaratne 2011)

Considering the fact that sediments tend to deposit immediately downstream from a tributary river confluence due to flow convergence (Fairbridge 1968; Rosgen and Silvery 1996) and based on the results and general contribution patterns including Cd and Se at the Red River and U at the Little Missouri River, two major source-sink relationships (presented in Figure 5.2) are found for the river sediments in North Dakota,

1: Both Sheyenne and Turtle tributaries at the Red River did not follow the linear mixing assumption and for most of the elements percentage sediment contribution from the tributary was lower than 0 or higher than 100%. It could be concluded that in this case, these tributaries might/might not be the source of concentrations of elements in the deposited sediment at the main river (downstream of the confluence).

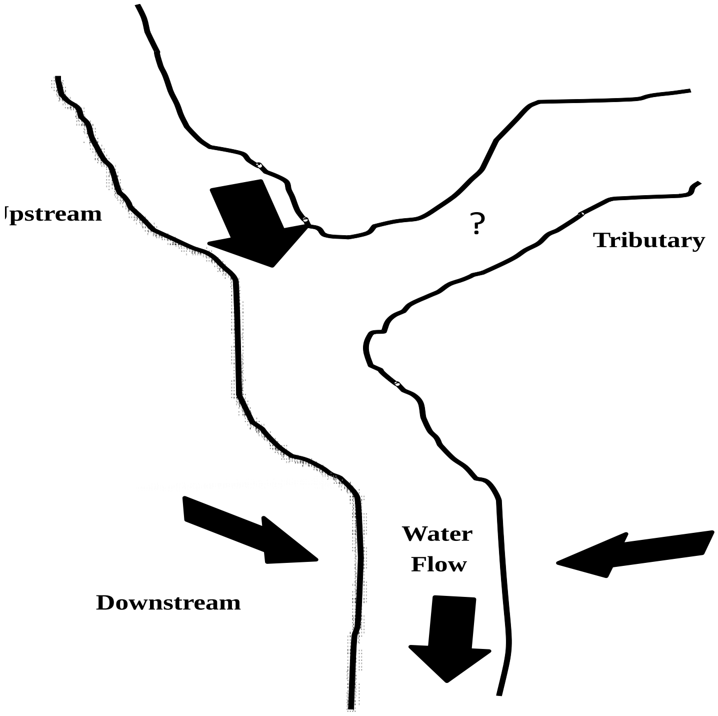
This means that percentage element contribution for most of the elements is less than 0 or higher than %100, which could be the result of factors (considering the dominant land use in the area) such as an unidentified diffusion/non- point sources such as upwelling groundwater and /or runoff waters dilute the water at the confluence of the tributary with the main river and this might change the flow rate of water at the confluence and sediment might stay in the suspended form and does not deposit in the upstream sites as expected , or/and b) chemistry of waters is different at the confluence of the river and tributary and this would result in the release of elements from the sediment to the water at the confluence (Figure 5.2 (a)).

The Turtle River is fed by Dakota aquifer which has high salinity and total dissolved solids (Kelly and Paulson 1970). Sheyenne River gets the highly saline waters of the Devils Lake (Hollis 2007).

2: At the Little Missouri River all of the tributaries sampled followed the linear mixing model and for most of the elements percentage sediment contribution from the tributary was between 0-100%.

It could be concluded that in this case, tributary is one of the sources of concentrations of elements in the deposited sediment at the main river (downstream of the confluence), meaning that percentage element contribution for most of the elements is between 0-100 Figure 5.2 (b)

a)
Tributary might/might not be a sediment source to the downstream sediments, and other unidentified sources (such as runoff waters from agricultural lands) enter the river in downstream and dilute the water.



(b)
Tributary is a sediment source to the downstream sediments, and the tributary contributions to the elements follow the linear mixing model.

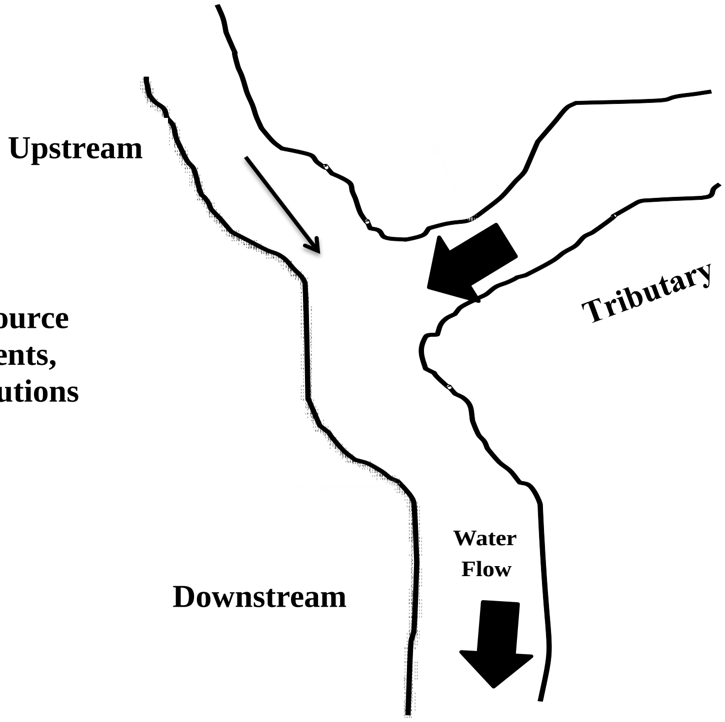


Figure 5.2. Major source-sink relationships: (a) tributaries might/ might (shown as question mark) not act as sources for the river sediments (left and right arrows outside of the edge of the river in downstream are the symbol for other unidentified sources) and (b) tributaries act as one of the sources for the river sediments.

5.4. Recommendations and implications

In this study when sampling the riparian sediment to address the element variation within and between the rivers (Chapter 2), five replicates were collected in a transect perpendicular to the river and with approximate distance of 2 m from each other. The multi-element concentrations and particle size variation for each of these replicates could be impacted by the river pulsing and the fact that the samples collected closer to the river bank might have been under the water for a longer period of time. It is recommended that for future studies, at each of the replicates along transect more than one sample could be collected, and this would assist with the study of the element variation along each transect at each of the sites within the river. This is more suitable for studies on dynamic rivers such as Red River in North Dakota where riparian wetlands closer to the river are flooded or saturated for several months. Riparian plant responses to the flooding are different, some species such as willows are often found closer to the stream in comparison to other species such as cottonwoods (Busch et al. 1992; Everson and Boucher 1998; Shafroth et al. 1998). The study of element variation along a transact also could address the ideal situations such as moisture, grain size and element concentrations for these particular species.

At the Red, Sheyenne and James rivers over-bank flooding and at the Little Missouri and Missouri River the difficulties in accessing to the sites due to the mountainous landscape could be a problem during the sampling. In this study prior to the sampling extra sites were chosen at near distances to each other and if sampling at one site failed, this minimized the consequences.

5.5. Future studies

The following section and experiments would address questions that emerged during this project and also assist in better understanding the riparian wetlands of North Dakota.

5.5.1. Multi-element concentrations in riparian wetlands (water, soil, plant)

In this study focus was on the element concentrations in the riparian sediment and soils, showing that there is a great variation in multi-element concentrations at the rivers and between the rivers. The relationships between water, soil and plants are important, and it could be hypothesized that element uptake by plants would also vary between wetland sites. In a study by Zhang et al., (2010) they found that metals show different concentrations in soil, plant and water samples with the highest concentrations in soil, and metal accumulation mostly occurred in roots of the plants. Root zone studies and element variation at different depths and distances from the root could give us important information regarding the impacts of flooding on element uptake by riparian wetlands. Uptake of elements by plants is significantly higher in flooded soils compared to non-flooded (Kissoon et al. 2011). Kissoon et al. (2010) suggested that element accumulation near the roots and following with element uptake demonstrates that wetland plants may indeed be exposed to more metals that are available for uptake.

Future studies on riparian wetlands in North Dakota could focus on the following objectives: (1) investigate the distribution and enrichment of multi-elements in water, soils and plants of riparian wetlands; (2) analyze distributions and correlations of elements among these compartments; (3) address the links between multi-element concentrations and the wetland conditions.

5.5.2. Multi-element concentrations in riparian wetlands (the effect of hydrologic pulsing)

The integrity of rivers and riparian wetlands is impacted by recent water movements such as flooding (Junk et al. 1989). Riparian wetlands receive hydrologic pulses in winter and spring when over- bank flow occurs; this would provide new sediment containing nutrients and contaminants to riparian wetlands (Loucks 1990; Odum et al. 1995; Heimann and Roell 2000).

Natural pulsing that occurs through flooding results in dispersal and germination of seeds into riparian wetlands (Middleton 2000). In North Dakota, mainly because of climate and geology riparian wetlands experience frequent flooding. Robertson et al. (2001) reported that spring pulsing significantly increases the riparian plant biomass. Study of element concentrations in riparian sediments before, during and after flooding, could also give us valuable information regarding the impacts of flooding on element concentrations and speciation.

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APPENDIX

Element concentrations µmolg^{-} ± standard deviation at the tributaries (A (furthest upstream), C, D, E, F (furthest downstream)) and their upstream and downstream locations along the Little Missouri River.

Element	Site	Upstream			Tributary			Downstream		
Al	**A**	490	±	62	351	±	17	374	±	27
	C	470	±	47	583	±	124	529	±	71
	D	695	±	122	628	±	146	649	±	105
	E	603	±	132	480	±	40		±	15
	F	490	±	88	471	±	36	494	±	43
As	**A**	0.07	±	0.004	0.05	±	0.004	0.06	±	0.003
	C	0.07	±	0.008	0.08	±	0.014	0.07	±	0.014
	D	0.10	±	0.028	0.08	±	0.024	0.09	±	0.011
	E	0.07	±	0.007	0.04	±	0.030	0.06	±	0.009
	F	0.04	±	0.004	0.04	±	0.013	0.04	±	0.008
B	**A**	1.50	±	0.26	0.65	±	0.04	0.44	±	0.09
	C	1.18	±	0.24	1.57	±	0.09	1.33	±	0.22
	D	1.79	±	0.29	1.37	±	1.29	1.59	±	0.29
	E	1.20	±	0.32	0.81	±	0.21	0.92	±	0.23
	F	0.74	±	0.22	0.65	±	0.32	0.68	±	0.12
Ba	**A**	0.011	±	0.001	0.008	±	0.001	0.008	±	0.000
	C	0.010	±	0.459	0.011	±	2.261	0.010	±	0.831
	D	0.012	±	0.527	0.79	±	0.202	0.400	±	0.091
	E	1.37	±	0.002	2.31	±	0.002	1.90	±	0.002
	F	0.05	±	0.001	0.05	±	0.001	0.05	±	0.001
Be	**A**	0.11	±	0.01	0.09	±	0.01	0.10	±	0.02
	C	0.11	±	0.00	0.12	±	0.01	0.11	±	0.01
	D	0.14	±	0.01	0.11	±	0.02	0.12	±	0.01
	E	1.37	±	0.03	2.31	±	0.01	1.90	±	0.03
	F	0.05	±	0.01	0.05	±	0.01	0.05	±	0.01
Bi	**A**	0.0008	±	0.0001	0.0005	±	0.0000	0.0006	±	0.0000
	C	0.0007	±	0.0001	0.0009	±	0.0001	0.0008	±	0.0001
	D	0.0011	±	0.0002	0.0009	±	0.0002	0.0010	±	0.0001
	E	0.0008	±	0.0001	0.0005	±	0.0001	0.0007	±	0.0001
	F	0.0004	±	0.0001	0.0004	±	0.0001	0.0004	±	0.0001
Ca	**A**	792	±	187	296	±	24	233	±	49
	C	524	±	95	741	±	65	604	±	218
	D	831	±	107	587	±	99	681	±	49
	E	531	±	109	286	±	109	388	±	63
	F	276	±	74	248	±	73	293	±	56
Cd	**A**	0.002	±	0.0004	0.002	±	0.0001	0.002	±	0.0003
	C	0.002	±	0.0002	0.003	±	0.0001	0.002	±	0.0006
	D	0.003	±	0.0002	0.002	±	0.0004	0.003	±	0.0003
	E	0.002	±	0.0004	0.001	±	0.0002	0.002	±	0.0011
	F	0.001	±	0.0003	0.001	±	0.0004	0.001	±	0.0002
Ce	**A**	0.12	±	0.013	0.15	±	0.022	0.19	±	0.014
	C	0.14	±	0.011	0.13	±	0.010	0.13	±	0.024
	D	0.12	±	0.011	0.17	±	0.032	0.15	±	0.025
	E	0.19	±	0.011	0.24	±	0.009	0.21	±	0.003
	F	0.24	±	0.003	0.25	±	0.006	0.25	±	0.005
Co	**A**	0.16	±	0.02	0.12	±	0.01	0.13	±	0.01
	C	0.15	±	0.01	0.17	±	0.02	0.16	±	0.04
	D	0.19	±	0.02	0.18	±	0.03	0.18	±	0.01
	E	0.17	±	0.02	0.15	±	0.01	0.16	±	0.01
	F	0.15	±	0.02	0.15	±	0.01	0.15	±	0.01

Element concentrations µmolg^{-} ± standard deviation at the tributaries (A (furthest upstream), C, D, E, F (furthest downstream)) and their upstream and downstream locations along the Little Missouri River (continued).

Element	Site	Upstream			Tributary			Downstream		
Cr	**A**	0.34	±	0.07	0.28	±	0.04	0.29	±	0.03
	C	0.37	±	0.02	0.45	±	0.13	0.42	±	0.11
	D	0.66	±	0.07	0.63	±	0.10	0.62	±	0.11
	E	0.61	±	0.12	0.42	±	0.04	0.60	±	0.06
	F	0.44	±	0.10	0.44	±	0.05	0.45	±	0.03
Cs	**A**	0.0005	±	0.000	0.0003	±	0.000	0.0002	±	0.000
	C	0.0005	±	0.000	0.0005	±	0.001	0.0005	±	0.002
	D	0.0006	±	0.001	0.0035	±	0.001	0.0022	±	0.001
	E	0.0048	±	0.000	0.0078	±	0.000	0.0063	±	0.000
	F	0.0075	±	0.000	0.0076	±	0.000	0.0076	±	0.000
Cu	**A**	0.24	±	0.04	0.18	±	0.01	0.19	±	0.03
	C	0.24	±	0.03	0.30	±	0.03	0.27	±	0.07
	D	0.39	±	0.04	0.37	±	0.08	0.38	±	0.04
	E	0.35	±	0.07	0.26	±	0.03	0.33	±	0.04
	F	0.24	±	0.05	0.19	±	0.02	0.22	±	0.03
Dy	**A**	0.01	±	0.001	0.01	±	0.001	0.01	±	0.001
	C	0.01	±	0.001	0.01	±	0.001	0.01	±	0.002
	D	0.02	±	0.001	0.02	±	0.002	0.02	±	0.001
	E	0.02	±	0.001	0.01	±	0.001	0.01	±	0.001
	F	0.01	±	0.001	0.01	±	0.001	0.01	±	0.001
Er	**A**	0.007	±	0.001	0.006	±	0.000	0.007	±	0.001
	C	0.007	±	0.001	0.007	±	0.001	0.007	±	0.001
	D	0.008	±	0.001	0.008	±	0.001	0.008	±	0.001
	E	0.007	±	0.001	0.007	±	0.001	0.007	±	0.001
	F	0.006	±	0.000	0.006	±	0.000	0.006	±	0.000
Eu	**A**	0.005	±	0.000	0.005	±	0.000	0.005	±	0.000
	C	0.005	±	0.000	0.005	±	0.001	0.005	±	0.001
	D	0.005	±	0.001	0.005	±	0.001	0.005	±	0.000
	E	0.005	±	0.000	0.005	±	0.000	0.005	±	0.000
	F	0.005	±	0.000	0.005	±	0.000	0.005	±	0.000
Fe	**A**	271	±	24	193	±	10	205	±	7
	C	251	±	19	302	±	78	278	±	91
	D	350	±	46	321	±	55	332	±	31
	E	313	±	58	262	±	31	299	±	12
	F	260	±	20	264	±	25	263	±	14
Ga	**A**	0.05	±	0.01	0.04	±	0.01	0.03	±	0.01
	C	0.05	±	0.00	0.06	±	0.03	0.06	±	0.02
	D	0.08	±	0.01	0.07	±	0.02	0.07	±	0.02
	E	0.06	±	0.02	0.04	±	0.01	0.05	±	0.01
	F	0.05	±	0.01	0.04	±	0.01	0.05	±	0.01
Gd	**A**	0.02	±	0.001	0.02	±	0.002	0.02	±	0.001
	C	0.02	±	0.001	0.02	±	0.002	0.02	±	0.002
	D	0.02	±	0.003	0.02	±	0.002	0.02	±	0.001
	E	0.02	±	0.001	0.02	±	0.001	0.02	±	0.001
	F	0.02	±	0.000	0.02	±	0.001	0.02	±	0.000
Ho	**A**	0.003	±	0.000	0.002	±	0.000	0.003	±	0.000
	C	0.003	±	0.000	0.003	±	0.000	0.003	±	0.000
	D	0.003	±	0.000	0.003	±	0.000	0.003	±	0.000
	E	0.003	±	0.000	0.002	±	0.000	0.003	±	0.000
	F	0.002	±	0.000	0.003	±	0.000	0.001	±	0.000
K	**A**	53	±	4.6	30	±	2.1	31	±	2.3
	C	43	±	3.9	43	±	7.8	37	±	11.9
	D	52	±	3.1	44	±	13.2	46	±	7.8
	E	53	±	7.8	45	±	4.3	50	±	19.0
	F	45	±	4.4	42	±	19.3	44	±	2.3

Element concentrations µmolg^{-} ± standard deviation at the tributaries (A (furthest upstream), C, D, E, F (furthest downstream)) and their upstream and downstream locations along the Little Missouri River (continued).

Element	Site	Upstream			Tributary			Downstream		
La	A	1.94	±	0.339	1.94	±	0.678	2.88	±	0.193
	C	1.92	±	0.004	1.85	±	0.004	1.83	±	0.010
	D	1.87	±	0.004	1.24	±	0.016	1.58	±	0.012
	E	0.91	±	0.657	0.12	±	0.565	0.51	±	0.521
	F	0.12	±	0.379	0.12	±	0.615	0.12	±	0.583
Li	A	2.42	±	0.27	1.60	±	0.10	1.59	±	0.12
	C	2.22	±	0.13	2.69	±	0.12	2.40	±	0.22
	D	3.06	±	0.11	2.62	±	0.51	2.79	±	0.28
	E	2.43	±	0.43	1.87	±	0.23	2.16	±	0.06
	F	1.83	±	0.16	1.68	±	0.13	1.74	±	0.07
Lu	A	0.0006	±	0.0000	0.0006	±	0.0000	0.0006	±	0.0000
	C	0.0006	±	0.0000	0.0006	±	0.0000	0.0006	±	0.0000
	D	0.0006	±	0.0000	0.0006	±	0.0000	0.0006	±	0.0000
	E	0.0006	±	0.0000	0.0006	±	0.0000	0.0006	±	0.0000
	F	0.0006	±	0.0000	0.0006	±	0.0000	0.0006	±	0.0000
Mg	A	249	±	11	189	±	13	152	±	9
	C	216	±	14	242	±	40	230	±	27
	D	258	±	30	254	±	41	255	±	58
	E	254	±	23	240	±	45	249	±	38
	F	235	±	77	226	±	34	242	±	36
Mn	A	9.14	±	2.7	4.09	±	0.2	3.95	±	0.5
	C	6.43	±	1.0	8.36	±	3.0	7.23	±	4.5
	D	9.60	±	2.3	7.23	±	1.3	8.38	±	0.6
	E	6.64	±	1.9	4.07	±	0.8	5.39	±	1.0
	F	4.28	±	2.8	5.39	±	1.1	4.73	±	0.7
Mo	A	0.005	±	0.001	0.002	±	0.001	0.003	±	0.001
	C	0.005	±	0.002	0.006	±	0.002	0.005	±	0.003
	D	0.010	±	0.003	0.009	±	0.003	0.009	±	0.001
	E	0.009	±	0.001	0.005	±	0.005	0.009	±	0.002
	F	0.005	±	0.003	0.004	±	0.002	0.004	±	0.000
Na	A	146	±	32	67	±	12	81	±	8
	C	132	±	9	162	±	65	145	±	35
	D	178	±	33	119	±	18	149	±	42
	E	110	±	884	79	±	56	93	±	15
	F	96	±	77	134	±	63	113	±	35
Nd	A	0.25	±	0.027	0.30	±	0.033	0.38	±	0.027
	C	0.29	±	0.007	0.26	±	0.008	0.27	±	0.013
	D	0.25	±	0.009	0.19	±	0.013	0.22	±	0.010
	E	0.17	±	0.022	0.11	±	0.017	0.13	±	0.006
	F	0.10	±	0.005	0.11	±	0.014	0.11	±	0.011
Ni	A	0.42	±	0.07	0.35	±	0.03	0.35	±	0.03
	C	0.40	±	0.03	0.58	±	0.05	0.43	±	0.10
	D	0.56	±	0.05	0.54	±	0.07	0.55	±	0.06
	E	0.53	±	0.07	0.44	±	0.12	0.41	±	0.06
	F	0.43	±	0.09	0.41	±	0.02	0.42	±	0.04
P	A	18	±	1.3	19	±	2.1	16	±	1.6
	C	19	±	0.9	18	±	3.6	19	±	2.8
	D	17	±	4.3	18	±	0.5	17	±	0.9
	E	18	±	1.0	19	±	1.5	19	±	3.1
	F	19	±	1.6	18	±	1.2	19	±	1.8
Pb	A	0.055	±	0.003	0.041	±	0.002	0.049	±	0.004
	C	0.049	±	0.004	0.066	±	0.008	0.053	±	0.010
	D	0.076	±	0.008	0.070	±	0.010	0.074	±	0.005
	E	0.066	±	0.012	0.043	±	0.007	0.052	±	0.011
	F	0.040	±	0.007	0.039	±	0.024	0.041	±	0.004

Element concentrations µmolg^{-} ± standard deviation at the tributaries (A (furthest upstream), C, D, E, F (furthest downstream)) and their upstream and downstream locations along the Little Missouri River (continued).

Element	Site	Upstream			Tributary			Downstream		
Pr	**A**	0.03	±	0.003	0.04	±	0.004	0.04	±	0.003
	C	0.03	±	0.002	0.03	±	0.002	0.03	±	0.003
	D	0.03	±	0.002	0.03	±	0.004	0.03	±	0.003
	E	0.03	±	0.002	0.03	±	0.002	0.03	±	0.001
	F	0.03	±	0.001	0.03	±	0.002	0.03	±	0.001
Rb	**A**	0.19	±	0.02	0.12	±	0.01	0.12	±	0.01
	C	0.16	±	0.01	0.20	±	0.02	0.17	±	0.03
	D	0.23	±	0.01	0.20	±	0.05	0.21	±	0.03
	E	0.19	±	0.03	0.16	±	0.02	0.17	±	0.01
	F	0.16	±	0.01	0.16	±	0.01	0.16	±	0.00
S	**A**	116	±	35.7	29	±	3.1	20	±	2.9
	C	69	±	15.3	91	±	0.8	81	±	11.9
	D	103	±	6.1	70	±	4.8	87	±	14.9
	E	57	±	31.0	42	±	34.8	48	±	42.6
	F	36	±	61.2	25	±	42.0	28	±	20.8
Sb	**A**	0.0069	±	0.004	0.0030	±	0.001	0.0052	±	0.001
	C	0.0045	±	0.000	0.0118	±	0.000	0.0049	±	0.000
	D	0.0174	±	0.001	0.0155	±	0.000	0.0167	±	0.000
	E	0.0146	±	0.005	0.0016	±	0.003	0.0074	±	0.008
	F	0.0014	±	0.004	0.0012	±	0.016	0.0014	±	0.001
Sc	**A**	0.08	±	0.01	0.06	±	0.00	0.06	±	0.01
	C	0.08	±	0.01	0.10	±	0.01	0.09	±	0.01
	D	0.12	±	0.02	0.10	±	0.02	0.11	±	0.02
	E	0.10	±	0.02	0.08	±	0.01	0.09	±	0.00
	F	0.08	±	0.01	0.08	±	0.01	0.08	±	0.00
Se	**A**	0.006	±	0.002	0.002	±	0.001	0.002	±	0.001
	C	0.005	±	0.003	0.007	±	0.003	0.006	±	0.003
	D	0.009	±	0.003	0.009	±	0.003	0.009	±	0.003
	E	0.009	±	0.003	0.009	±	0.002	0.009	±	0.003
	F	0.009	±	0.002	0.009	±	0.003	0.009	±	0.003
Sm	**A**	0.02	±	0.002	0.03	±	0.002	0.03	±	0.002
	C	0.02	±	0.001	0.02	±	0.002	0.02	±	0.002
	D	0.02	±	0.002	0.02	±	0.003	0.02	±	0.002
	E	0.02	±	0.002	0.02	±	0.001	0.02	±	0.001
	F	0.02	±	0.000	0.02	±	0.001	0.02	±	0.001
Sn	**A**	0.0002	±	0.0000	0.0002	±	0.0000	0.0002	±	0.0000
	C	0.0002	±	0.0002	0.0003	±	0.0008	0.0002	±	0.0006
	D	0.0003	±	0.0009	0.0013	±	0.0012	0.0008	±	0.0008
	E	0.0025	±	0.0001	0.0030	±	0.0000	0.0026	±	0.0000
	F	0.0025	±	0.0001	0.0030	±	0.0000	0.0026	±	0.0000
Sr	**A**	2.12	±	0.48	0.68	±	0.07	0.68	±	0.10
	C	1.31	±	0.14	1.87	±	0.62	1.52	±	0.17
	D	2.12	±	0.24	1.62	±	0.13	1.85	±	0.15
	E	1.53	±	0.22	1.10	±	0.21	1.23	±	0.13
	F	1.20	±	0.20	1.40	±	0.17	1.34	±	0.11
Tb	**A**	0.003	±	0.000	0.003	±	0.000	0.003	±	0.000
	C	0.003	±	0.000	0.003	±	0.000	0.003	±	0.001
	D	0.003	±	0.000	0.003	±	0.000	0.003	±	0.000
	E	0.003	±	0.000	0.003	±	0.000	0.003	±	0.000
	F	0.003	±	0.000	0.003	±	0.000	0.003	±	0.000
Te	**A**	0.0022	±	0.000	0.0016	±	0.000	0.0022	±	0.000
	C	0.0018	±	0.000	0.0020	±	0.000	0.0019	±	0.000
	D	0.027	±	0.000	0.026	±	0.000	0.026	±	0.000
	E	0.0023	±	0.000	0.0023	±	0.001	0.0023	±	0.001
	F	0.0023	±	0.000	0.0023	±	0.001	0.0023	±	0.000
Th	**A**	0.024	±	0.002	0.026	±	0.004	0.035	±	0.002
	C	0.027	±	0.001	0.026	±	0.003	0.026	±	0.003
	D	0.027	±	0.003	0.025	±	0.003	0.026	±	0.002
	E	0.024	±	0.002	0.021	±	0.001	0.023	±	0.001
	F	0.020	±	0.001	0.020	±	0.002	0.020	±	0.001

Element concentrations µmolg^{-} ± standard deviation at the tributaries (A (furthest upstream), C, D, E, F (furthest downstream)) and their upstream and downstream locations along the Little Missouri River (continued).

Element	Site	Upstream	Tributary	Downstream
Ti	**A**	6.69 ± 0.93	9.61 ± 2.56	12.54 ± 1.14
	C	7.94 ± 1.14	5.43 ± 1.87	6.69 ± 1.87
	D	4.18 ± 1.87	5.01 ± 0.00	4.60 ± 0.93
	E	5.43 ± 1.14	7.10 ± 0.00	6.27 ± 0.93
	F	7.10 ± 1.04	7.94 ± 0.93	7.52 ± 0.00
Tl	**A**	0.0008 ± 0.0001	0.0006 ± 0.0001	0.0006 ± 0.0001
	C	0.0007 ± 0.0000	0.0009 ± 0.0002	0.0008 ± 0.0002
	D	0.0010 ± 0.0001	0.0009 ± 0.0001	0.0009 ± 0.0001
	E	0.0009 ± 0.0001	0.0008 ± 0.0001	0.0008 ± 0.0001
	F	0.0007 ± 0.0001	0.0007 ± 0.0001	0.0008 ± 0.0001
Tm	**A**	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000
	C	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000
	D	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000
	E	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000
	F	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000
V	**A**	0.66 ± 0.07	0.46 ± 0.02	0.46 ± 0.04
	C	0.61 ± 0.04	0.77 ± 0.13	0.68 ± 0.17
	D	0.89 ± 0.09	0.82 ± 0.20	0.84 ± 0.14
	E	0.79 ± 0.14	0.65 ± 0.07	0.73 ± 0.04
	F	0.66 ± 0.07	0.66 ± 0.05	0.68 ± 0.02
Y	**A**	0.13 ± 0.009	0.11 ± 0.007	0.12 ± 0.009
	C	0.12 ± 0.012	0.13 ± 0.013	0.13 ± 0.021
	D	0.14 ± 0.018	0.15 ± 0.026	0.14 ± 0.018
	E	0.15 ± 0.012	0.15 ± 0.006	0.15 ± 0.007
	F	0.15 ± 0.006	0.15 ± 0.007	0.15 ± 0.004
Yb	**A**	0.005 ± 0.000	0.005 ± 0.000	0.005 ± 0.000
	C	0.005 ± 0.001	0.005 ± 0.001	0.005 ± 0.001
	D	0.006 ± 0.001	0.005 ± 0.001	0.006 ± 0.000
	E	0.005 ± 0.000	0.004 ± 0.000	0.005 ± 0.001
	F	0.004 ± 0.000	0.004 ± 0.000	0.004 ± 0.000
Zn	**A**	0.99 ± 0.08	0.75 ± 0.05	0.76 ± 0.05
	C	0.95 ± 0.06	1.13 ± 0.13	1.03 ± 0.32
	D	1.31 ± 0.08	1.20 ± 0.20	1.24 ± 0.11
	E	1.13 ± 0.20	0.90 ± 0.09	1.04 ± 0.08
	F	0.91 ± 0.13	0.95 ± 0.07	0.92 ± 0.05
Zr	**A**	0.07 ± 0.01	0.07 ± 0.01	0.06 ± 0.01
	C	0.07 ± 0.02	0.08 ± 0.00	0.07 ± 0.01
	D	0.09 ± 0.01	0.08 ± 0.01	0.09 ± 0.01
	E	0.08 ± 0.01	0.06 ± 0.01	0.07 ± 0.03
	F	0.05 ± 0.13	0.05 ± 0.01	0.05 ± 0.01