MULTI-ELEMENT FINGERPRINTING OF RIVER SEDIMENTS TO IDENTIFY

DIFFUSE POLLUTION SOURCES

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Dimuthu Nilmini Wijeyaratne

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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

DOCTOR OF PHILOSOPHY

ABSTRACT

Wijeyaratne, Dimuthu Nilmini, Ph.D., Program of Environmental and Conservation Sciences, College of Graduate and Interdisciplinary Studies, North Dakota State University, March 2011. Multi-element Fingerprinting of River Sediments to Identify Diffuse Pollution Sources. Major Professor: Dr. Marinus Otte.

The multi-element fingerprinting technique uses natural tracers in combination with field data collection, laboratory analyses of sediments, and statistical modeling techniques to identify sediment source areas in a watershed. In this technique natural tracers are identified and measured for both sediment sources and sediment mixtures collected at the watershed to identify the potential source areas of sediments.

This study was carried out in two watersheds in North Dakota, the Souris River and the Turtle River. The aim of this study was to develop multi-element fingerprints of the Souris River and Turtle River sediments and to evaluate the suitability of these fingerprints to assess the geographic origin of potential pollutants of the two rivers.

In the initial step of this study, existing sediment samples of the Souris River from a previous project were analyzed for multiple elements. This study showed statistically significant variations in element concentrations of surface sediments at different sites and therefore it was confirmed that the multi-element fingerprinting can be used to assess the sediment and contaminant loading patterns.

In the multiple element fingerprinting studies the linear mixing of elements and the absence of enrichments and depletions of elements are assumed. Two laboratory experiments were performed to assess the validity of these assumptions. The results of these experiments verified the assumptions and showed that there is a statistically significant spatial and temporal variation in the element concentrations depending on their mobility and re-deposition.

Field studies were conducted in the Souris River and Turtle River to assess the variation of element concentrations in the top riverbed samples along the main rivers and their tributaries. The sediment contribution from the tributaries and the phosphorus concentrations in the main channel were used to calculate the phosphorus contributions from the tributary sediments to the Souris River. The larger tributaries of the Lower Souris River showed higher phosphorus contribution compared to the smaller tributaries of the Upper Souris River. The differences in phosphorus contributions were related to land use, underlying geology, and the size of the watersheds of the tributaries in the Souris River watershed. Similar analysis was used in the Turtle River to calculate Arsenic, Cadmium and Selenium contribution from the tributaries to the Turtle River. The differences in the contribution of these elements were related to the underlying geology and the size of the watersheds.

This study provides a detailed analysis of element concentrations along the Souris and Turtle Rivers in North Dakota and provides information about relative sediments and element loading rates from the tributaries to the main rivers. Also this study helps to identify the sources and sinks of potentially enriched elements in the two rivers. The multi-element fingerprinting technique can be successfully used as a tool to identify the relative contribution of sediments and assessing and tracing pollution sources in rivers. Multi-element fingerprinting provides a relatively low cost, rapid tool for sediment tracking, without the need for addition of exotic chemicals such radio-tracers or dyes to natural ecosystems.

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CHAPTER 1. GENERAL INTRODUCTION

River sediments are a valuable source of information regarding the occurrence, magnitude and trends of human-associated environmental contaminants. Sediments may act both as sinks and sources of pollutants to the overlying water column and biota. Therefore, river sediments are considered as valuable environmental and geomorphologic resources.

Sediments are chemically heterogeneous. They are coated with various oxides, calcareous substances, and hydroxides of aluminum and iron. These substances greatly enhance the ability of sediments to react with or adsorb other chemicals. Sediment can react with, carry, and/or release a large number of chemicals. There are three broad groups; nutrients, metals, and organics, that can react with and be transported by sediments (Skopp and Daniel 1978, Huanxin et al. 1996, Russell et al. 1998, Xu et al. 2000, Walling et al. 2003, Babek et al. 2008, Beg and Ali 2008). Contaminated sediments can lead to ecotoxicological risks for the aquatic environment. Therefore, identification of sediment sources and associated nutrients and contaminants is important in the ecological management of aquatic ecosystems.

Information regarding the source and transport of river sediments can be used to design non-point source pollution control strategies, to establish sediment budgets and to develop distributed sediment yield models. In some of these situations it is very important to identify the precise spatial location of the origin of a pollutant source within a river basin. Many studies have been done to quantitatively determine the sediment transport along the river basins. These studies used approaches to estimate either how much sediment had been lost from a site, or how much had accumulated at another site. Changes

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were measured in one dimension for surface level at a point, in two dimensions to give a profile or cross-section, or in three dimensions for volumetric measurements of rills or gullies (Yang 1977, Loughran 1989).

These methods provided important information about the amount of sediment transported from one place to another, but they did not provide useful information regarding the spatial origin of sediments. To obtain information about the spatial source of the sediment transported by a river, the sediment load at a large number of points within a river network has to be monitored. Therefore, determination of sediment sources requires frequent sampling, expensive instrumentation, and accurate methods of determination (Klages and Hsieh 1975, Loughran 1989).

To overcome these constraints associated with traditional studies on sediment transport and determination of sediment sources and sinks, sediment fingerprinting was developed. Multi-element fingerprinting is a method based on the assumption that the chemical and physical properties of transported sediments reflect those of the source materials.Multi-element fingerprinting identifies the distribution of chemical elements within a matrix and thus defines its unique signature in comparison to similar matrices (Djingova et al. 2004). It provides a sediment profile, which can be used for direct sediment source tracing. This involves determining the 'fingerprint' concentration of many elements simultaneously. The technique provides quality and efficiency of analysis with the use of Inductively Coupled Plasma spectrophotometry (ICP). A large suite of elements can be analyzed quickly and at very low concentrations. Multi-element fingerprinting has been used in plants (Djingova et al. 2004, Otte and Jacob 2005, Kissoon et al. 2010) and for tracing suspended sediment sources in catchments and river systems (Walling 2005).

This method has been widely used in Europe as a tool to define catchment areas and as a way to identify sediment and pollutant sources in a variety of environments (Jordan et al. 1998, 2001, 2005, Russell et al. 2001, Jordan and Rippey 2003, Krause et al. 2003).

There are two primary steps involved in sediment fingerprinting. The first step is the selection of diagnostic physical and chemical properties which clearly differentiate potential sources and sinks. The second step is comparison of the fingerprints of the sediment samples from downstream sampling sites, for example potential sink areas, with the corresponding values for the source areas (Collins et al. 1996, Collins et al. 1997[a], Walling 2005).

Early fingerprinting studies were based on individual characteristics and they were referred as single component fingerprinting. The single component fingerprinting studies used mineralogical (Griffin 1962, Klages and Hsieh 1975, Wall and Wilding 1976, Sawhney and Frink 1978, Hsieh 1984), mineral-magnetic (Oldfield et al. 1979, Dearing et al. 1986, Caitcheon 1993, Crockford and Fleming 1998, Royall 2001), radiometric(Ritchie and McHenry 1978, McCallan et al. 1980, Campbell et al. 1982, Campbell et al. 1986, Martz and de Jong 1987, Wasson et al. 1987 , Burch et al. 1988, Walling and Woodward 1992), organic (Peart 1993, Walling and Amos 1999, Onstad et al. 2000, Papanicolaou et al. 2003, Fox and Papanicolaou 2007, 2008), chemical (Birch et al. 1999, Simonovski et al. 2003, Melaku et al. 2004, De Miguel et al. 2005, Ahumada and Vargas 2005, Polyakov et al. 2009), and physical (Grimshaw and Lewin1980, Walling and Moorhead 1987, Fenn and Gomez 1989, Parsons et al. 1991, Stone and Saunderson 1992, Kurashige and Fusejima 1997, Krein et al. 2003)properties of sediments to identify spatial distribution of

sediments. Later studies have found that use of a single fingerprint property can lead to invalid or questionable sediment source relationships due to following reasons.

a) Sediments are complex systems. They are in equilibrium with overlying water column and biota. This equilibrium can affect the measured fingerprint properties (Walling 2005).

b) The fingerprint property may occur due to the physical and chemical interactions within the sink or source areas. The pH and redox conditions or changes in water chemistry can affect the measured fingerprint properties. Therefore, the measured fingerprint property can give a relative measurement (Collins et al. 1997[c]).

c) Preferential transport and transformation of some of the fingerprint properties may lead to bias measurements (Peart and Walling 1986).

d) Individual tracers may be subject to physical and chemical changes, which limit their use, e.g. particle size sorting, organic matter selectivity, and geochemical transformation during fluvial erosion and transportation (Walling et al.1993).

To overcome these problems important advances in the fingerprinting methods were employed in the later stages (Collins et al. 2001). The main advancement was to use composite signatures instead of single source fingerprinting (Oldfield and Clark 1990, Walling et al.1993, Walling and Woodward 1992, Collins et al. 1996). Quantitative procedures were then developed incorporating statistical verification of the ability of fingerprint parameters to discriminate sources. Multivariate mixing models were also applied to tracer data to determine sources more reliably and consistently (Yu and Oldfield 1989, 1993, Walling et al. 1993, Walling and Woodward 1992, Collins et al. 1996).

Large and complex combinations of parameters including physical, mineral–magnetic, chemical radiometric organic and inorganic properties are used in composite fingerprinting techniques (Peart and Walling 1986, Walling et al. 1993, Collins et al. 1996, Collins et al 1997[a], Walling et al. 1999, Chandrajith et al. 2000, Collins et al. 2001, Motha et al. 2002,Krause et al. 2003, Dirszowsky 2004, Minella et al. 2004, Botes and Staden 2005, Jarvie et al. 2005, Rhoton et al. 2007, Walling et al. 2008, Stutter et al. 2009). The composite fingerprinting process can yield important spatial information on the nature of the source material (Yu and Oldfield, 1989, Russell et al. 2001) and it helps to identify the selectivity of chemical properties in the erosion process and to estimate erosion under different land uses. Composite fingerprinting can also be used to measure temporal changes in sedimentation. (Owens et al. 2001). Composite fingerprinting methods incorporated with river mixing models are applicable to larger river basins and they provide more accurate and precise information about potential source areas of sediments (Collins et al 1997[b]).

A single universal tracer combination for composite fingerprinting has not yet been identified by researchers. The most widely used composite sediment fingerprinting properties have been inorganic elements (Davis and Fox 2009). This may be due to the large number of inorganic tracers that can be tested simultaneously on instruments that measure inorganic elemental signature (e.g. inductively coupled plasma mass spectrometer allows testing of 15 to 55 elements). Therefore, the inorganic fingerprints produce a higher number of tracers and it increases the potential for identifying source areas in a unique way. These inorganic fingerprints can also be referred as multi-element fingerprints (Davis and Fox 2009).

As the advancements of technology becomes more widespread in the environmental engineering industry, a more quantitative, repetitive strategy to classify sediment sources needs to be applied. One possible quantitative method is using geographical information system (GIS) erosion susceptibility modeling to map sediment sources with differing probable erosion rates. GIS modeling can provide detailed information on surface erosion susceptibility. This method can utilize digital tier models and empirical erosion models in the GIS framework to create maps of erosion. Identifying unique tracers in a watershed is important to find the link between tracers and their controlling watershed variables. Therefore, it will be very important if the tracer signatures and watershed variables can be incorporated to a universal database to be accessed by interested parties. This will help to increase the repeatability of fingerprinting studies.

1.1.   Study area and the description of the problem to be investigated

This project focused on two river basins. The first part of the project focused on Souris River which originates in Saskatchewan, then passes through North Dakota to return to Canada in Manitoba. There is international concern regarding phosphate in the water and the cross-border consequences of pollution transport. The river drains a large watershed which supports a wide range of land uses. In the first part of the project, the potential for tracing sediments acting as phosphate and other pollutant sources to the Souris River was assessed using the 'multi-element fingerprinting' technique.

The second part of the project focused on sediment loading and transport in the Turtle River in North Dakota. The watershed of the Turtle River is approximately 80 km long and about 30 km wide. It is a tributary of the Red River and joins it near Arvilla in Grand Forks. The Turtle River is of concern to the ND Department of Health because of

high concentrations of potentially toxic levels of metals and metalloids such as Cd, Se and As. Therefore, in the second part of the project, the 'multi-element fingerprinting' technique was used to identify the potential source and sink areas of metals and metalloids in the Turtle River and its tributaries.

1.2.   Aims, hypotheses and objectives of the project

The overall aims of the project were to develop multi-element fingerprints of the Souris River and Turtle River sediments and to evaluate the suitability of these fingerprints to assess the geographic origin of potential pollutants of the two rivers.

In this study it was expected that,

1. There is detectable and significant variation in element concentrations in the sediments along the Souris River and the Turtle River.

2. The fingerprints at the tributaries, upstream areas and downstream areas of the tributary-river confluences are different from each other.

3. The element concentration of sediments depends on the mixing ratio of the sediments, assuming linear mixing.

4. The fingerprints become unrecognizable, the sources of sediment origin become difficult to identify, as they move further away from sink/source areas

5. Contribution of pollutants from a source area to the sink area depends on the concentration of sediment-borne pollutants in the source area.

Field studies and laboratory experiments were designed to assess each of these hypotheses. The specific objectives of this study were,

1. To assess the biogeochemical behavior of elements in sediments of the selected areas of the Souris River and Turtle River.

2. To assess the spatial variation in element concentrations in sediments and relate them to the land use patterns.

3. To assess the contribution of elements from source areas at different mixing ratios of sediments.

4. To assess the suitability of using multi-element fingerprinting studies to predict the pollution loading and transport patterns in river systems.

1.3. Dissertation structure

All the field and laboratory studies were written as publications, and have either been published or submitted for publication (not necessarily in the order presented in the theses). This has resulted in some repetitions in the introduction, methodology and discussions of some chapters. The methodologies specific to each study is separately written for each chapter. The General Discussion and Final Conclusions chapter followed by the combined references are presented at the end of the theses.

Chapter 2: Element concentrations in sediments of the Souris River for multi-element fingerprinting and sediment tracking. – Submitted to the Journal of Environmental Engineering.

Chapter 3: Multi-element fingerprinting of sediments: a laboratory study to simulate mixing and transport of chemical elements in river systems.

Chapter 4: A multi-element fingerprinting approach to identify phosphorus contribution to the Souris River sediments.

Chapter 5: A multi-element fingerprinting approach to assess contributions of As, Se and

Cd from tributaries to the Turtle River sediments.

Chapter 6: General Discussion.

CHAPTER 2. ELEMENT CONCENTRATIONS IN SEDIMENTS OF THE SOURIS RIVER FOR MULTI-ELEMENT FINGERPRINTING AND SEDIMENT TRACKING

2.1. Abstract

River sediments represent a mixture of sediments derived from different sources within the contributing catchment. This study was carried out to assess if the concentrations and distribution of elements along the Upper Souris River, North Dakota, U.S.A., would be suitable for multi-element fingerprinting for tracking of sediments and pollutants. Sediment core samples were collected along cross-sections at five locations along the river and analysed for multiple elements by inductively coupled plasma spectrometry (ICP). Statistically significant variations in element concentrations of surface sediments at different sites and along cross-sections were observed. The particle size distribution of the river sediments, but not organic matter content, played a key role in determining the distribution of trace element concentrations in the sediments. This study showed that multi-element fingerprinting is a potentially useful tool in assessing sediment loading and transport along the Souris River.

2.2. Introduction

Sediments are a valuable source of information regarding the occurrence, magnitude and trends of human-associated environmental contaminants. Sediments can act both as sinks and sources of pollutants to the overlying water column and biota. The sediments transported by a river commonly represent a mixture of inorganic and organic materials derived from different sources within the contributing catchment. Sediment particles are typically coated with various oxides and hydroxides of aluminum and iron as

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well as calcareous substances. These coatings, as well as organic matter, greatly enhance

the ability of sediments to react with or adsorb substances, including nutrients, metals, and

organic compounds (Skopp and Daniel 1978). Environmental contaminants can originate

from a large number of sources and may enter the fluvial environment via several

pathways. Metals may enter the river system as dissolved species, as free ions, or by

forming organic or inorganic complexes. Sediments provide long-term storage for metals in

the environment (Spencer and Mac Leod 2002).

Watershed sediment transport is one of the primary sources of nonpoint source

pollution of surface waters. Contaminated sediments present an ecotoxicological risk to the

aquatic environment, such as a decrease in water quality and ecological diversity and

functioning, reductions in the operational capacities of water supply facilities such as water

treatment plants and reservoirs, and a decrease in aesthetic properties of rivers and streams

(Davis and Fox 2009). Therefore, identification of sediment sources and associated

nutrients and contaminants is important in the ecological management of aquatic

ecosystems.

Multi-element fingerprinting identifies the distribution of chemical elements within

a matrix and defines its unique signature in comparison to similar matrices (Djingova et al.

2004). It provides a sediment profile, which can then be used for direct sediment source

tracing. This involves determining the concentrations of many elements simultaneously by

inductively coupled plasma spectrometry (ICP). Multi-element fingerprinting has been

used in plants (Djingova et al. 2004, Otte and Jacob 2005) and in tracing suspended

sediment sources in catchments and river systems (Walling 2005). It has been used to

define catchment areas and as a way to identify sediment and pollutant sources in a variety

of environments (Jordan et al. 1998, 2001, 2005, Russell et al. 2001, Jordan and Rippey 2003, Krause et al. 2003).

This study was carried out to evaluate the concentrations and distribution of elements in sediments of the Souris River, a small river in North Dakota, USA, in order to assess the suitability for application of multi-element fingerprinting for tracking sediments and determination of pollutant loadings into the river. It was expected that there would be enough detectable and significant variation in the element concentrations in the sediments along the Souris River to make this technique suitable for further studies on sediment tracking and identification of sediment sources and sinks.

2.3. Materials and methods

2.3.1. Study area

The study was conducted in the Upper Souris River watershed. The Souris River, also known as the Mouse River, originates near Weyburn in southeastern Saskatchewan, Canada, and enters the United States in the northwest of North Dakota, in Renville County. It flows southeast to Velva, North Dakota, and then returns to Canada into Manitoba (Figure 2.1). The Upper Souris includes land in Canada and the United States. The total drainage area of Souris River is 24,778 km^2 and the total length of the river is about 1480 km with 574 km being in North Dakota (Jorde 1978).

2.3.2. Collection of samples

Sediment samples were collected in the summer of 2007 from four locations along the Upper Souris River. One sampling location (Site A - 49°10'48.00"N, 102° 1'39.00"W) was located in Canada and the other three locations, Site B-(48°57'58.68"N, 101°56'51.00"W), Site C- (48°55'21.72"N, 101°55'35.04"W), Site D (48°52'37.95"N,
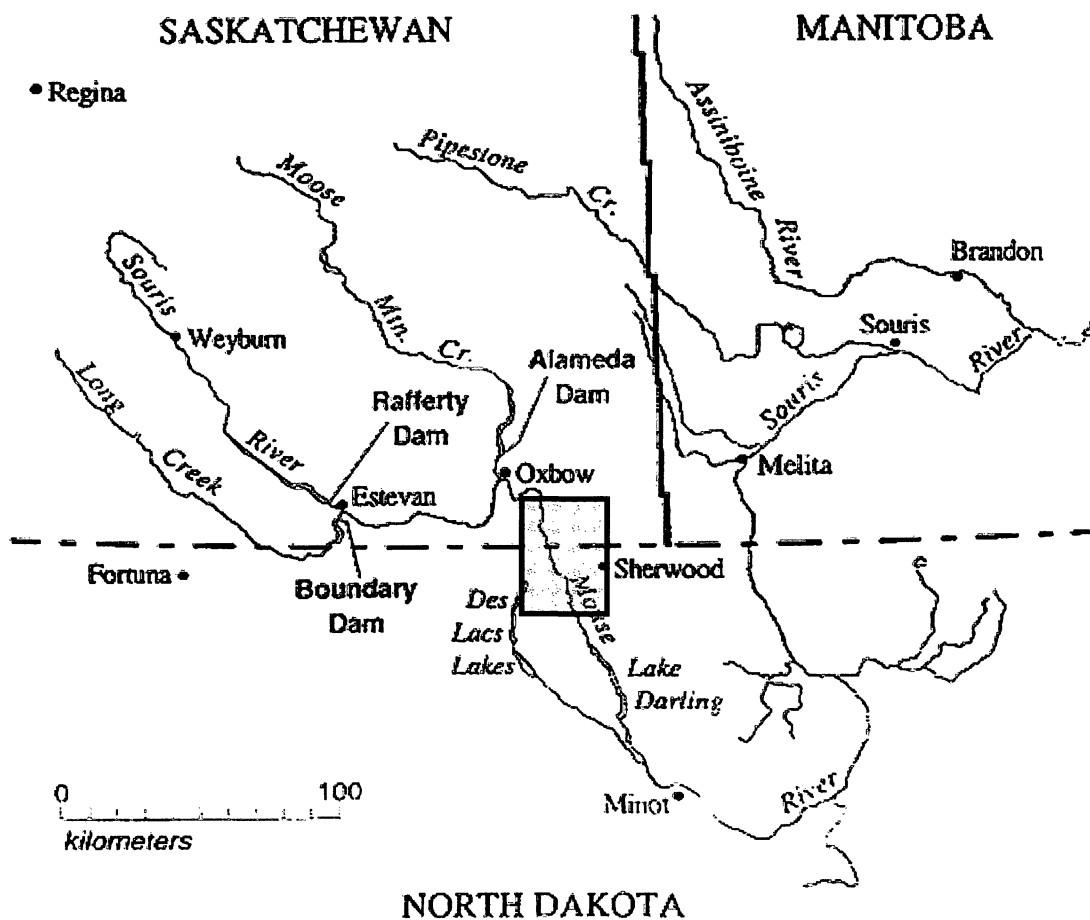
Figure 2.1: Map showing the Upper Souris River area. The general location of sampling area is indicated by the rectangle.

101°52'5.99"W) were in North Dakota, U.S.A. Sediment cores (5 cm diameter) were collected in three replicates from five sites along cross-sections of the river at each of the four locations. The cores were separated into 5 cm slices and the samples were transported to the laboratory and stored at 4 °C in a refrigerator until they were prepared for analysis. Here only the findings regarding the top 5 cm of the cores are reported.

2.3.3. Chemical analysis

The samples were oven dried at 60 °C, then homogenized using a mortar and pestle. About 0.5 g of each homogenized sample was digested in a CEM Mars-Xpress microwave

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digester using 10 ml of concentrated nitric acid (16 total vessels (XPRESS 55 ml 8 PFA Venting Vessels), 1600W, 100% Power, ramped to 185 °C over 10 minutes and held at this temperature for 5 minutes). These were then analyzed using a Spectro Genesis Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) with Cross-flow nebulizer, Side-On-Plasma (SOP) for 31elements (The detection limits in μgL^{-1} are given in brackets): the alkali earth metals [Be(0.07), Ba(0.2), Ca(300), Mg(1) and Sr(0.3)], alkali metals [Na(0.4), K(76) and Li(0.8)], transition metals [Ag(0.2), Cd(17), Co(7), Cu(1), Cr(2), Fe(25), Hg(25), Mo(15), Ni(10), Ti(6), V(6) and Zn(4)], the lanthanide Ce, other so-called poor metals [Al(0.5), Pb(30), Sb(7), Sn(3), and Tl(0.2)] and the non-metals and metalloids [B(11), As(42), P(46), Se(2), and Si(10)]. Throughout the remainder of this paper molar units will be used. This analysis used a four-point calibration using individual or a combination of standards in a five percent HNO_3 matrix. A continuing control verification was done after every 10 samples to check that variability was within 10%.

2.3.4. Loss-on-ignition

Loss-on-ignition (LOI) is a measure of organic matter content. About 15 g of the samples were dried at 105 °C in ceramic crucibles for 2 hours. The dry weight (Wd) of these samples was recorded. They were then ashed at 550 °C for 2 hours in a Sybron Thermoclyne muffle furnace and the weights of the remaining ash recorded (Wa). The percentage LOI was calculated as $((W_d-W_a) / W_d)$ x 100.

2.3.5. Fraction of particles smaller than 63 μm (f<63)

The ash left after determination of LOI was used for measurement of the fraction of particles smaller than 63 μm (f<63). The ash was used because using the initial samples to measure f<63 will lead to over-estimation of results as it includes organic matter that is

smaller than 63 μm. The initial dry weight of the ash was recorded (W_i). These samples were wet sieved through a 63 μm sieve using distilled water. The material remaining on the sieve was collected onto a Whatman No. 1 filter paper, oven-dried at 60 °C and dry weight recorded (W_r). The percentage f< 63 was calculated as ((W_i - W_r) / W_i) x 100.

2.3.6. Statistical analysis

Minitab 15 statistical software (Minitab® 15.1.30.0) was used for all statistical analyses. All data were log-transformed. Correlation analysis was performed on element concentrations, LOI and f<63. Correlations were considered to be important if $r \geq 0.836$, giving $r^2 \geq 0.7$, thus explaining 70% of total variation. Nested ANOVA in the General Linear Model (GLM) module was used to analyze the two-dimensional variation, with LOI and f<63 as covariates to identify their effects on element concentrations along and across the river.

2.4.   Results

The concentrations of Ag, Cd, As, Hg, Mo, Tl, Pb, Sb, Se and Sn were below detection limits and will therefore not be discussed further.

2.4.1. Correlations between element concentrations, LOI and f < 63

Correlations between element concentrations are given in Table 2.1. Be, Co, Cu and Si were not significantly correlated to any other element and so are not listed. Given the number of observations of n=60, low correlation coefficients are often statistically significant, but not important in terms of explaining variation. Therefore, correlations were considered to be important if $r \geq 0.836$, giving $r^2 \geq 0.7$, thus explaining 70% of total variation. Several of the elements showed particularly strong correlations, with $r^2 > 0.800$: Al, Fe, Mn, K, Ba, Cr, Li, and P.

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LOI ranged from 3.2 %-99.6% with an average value of 54.9%. The percentage

f<63 ranged from 10.3 %- 90.3% with an average of 58.4%. None of the elements showed

a statistically significant correlation with LOI, nor did LOI correlate significantly with

f<63. On the other hand, several elements showed strong positive correlations with f<63,

namely Ba, Mg, Ca, Sr, Be, Li, K, Na, P, B, Al, Ce, Cr, V, Zn, Fe, Ni, Ti and Mn (Figure

2.2).
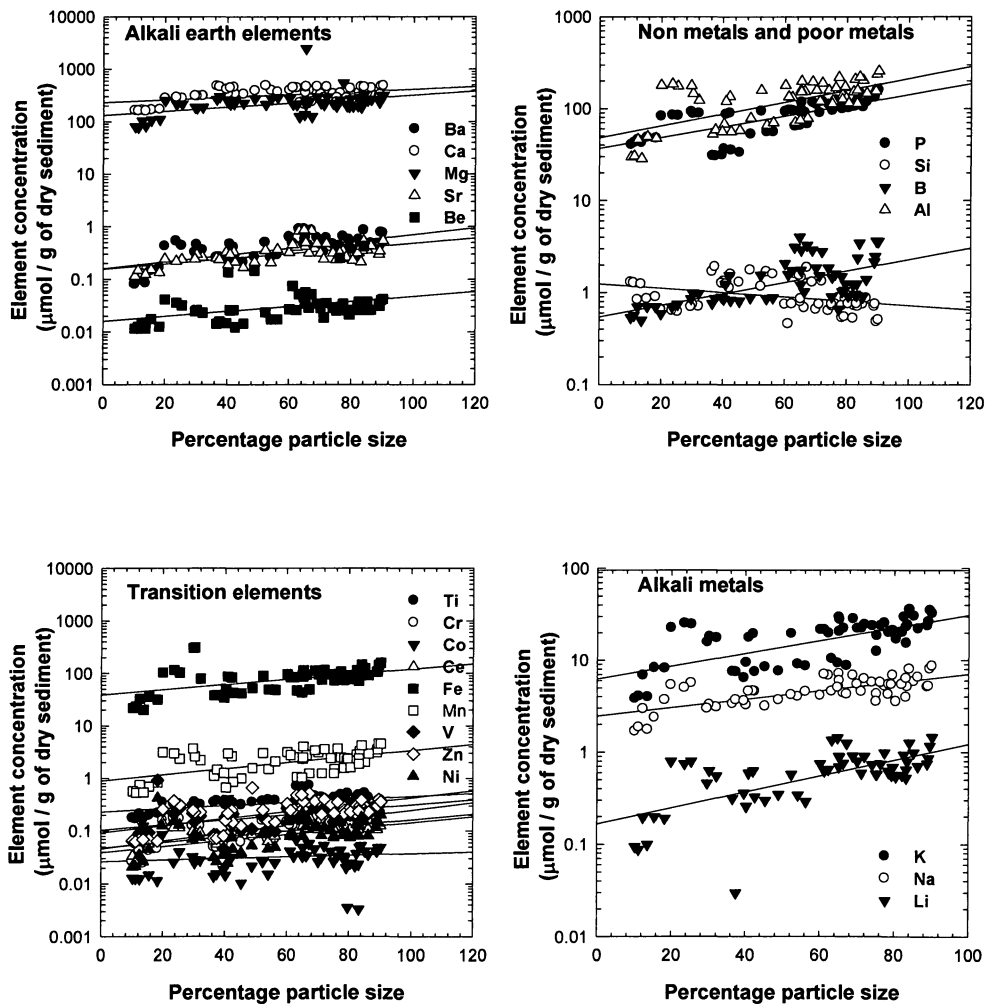
Figure 2.2: Correlations between particle size (the fraction <63 μm) and element
concentrations (n=60).

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Table 2.1: Correlations (r^2) between element concentrations after log-transformation, (n=60).

	Al	B	Ba	Be	Ca	Ce	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Si	Sr	Ti	V
Al																					
B	0.500																				
Ba	0.796	0.738																			
Be	0.473	0.460	0.531																		
Ca	0.581	0.406	0.559	0.320																	
Ce	0.725	0.570	0.836	0.482	0.325																
Co	0.209	0.408	0.399	0.212	0.032	0.223															
Cr	0.848	0.666	0.937	0.538	0.441	0.879	0.390														
Cu	0.217	0.26	0.182	0.385	-0.139	0.267	0.251	0.213													
Fe	0.918	0.410	0.689	0.411	0.516	0.631	0.162	0.775	0.126												
K	0.971	0.517	0.762	0.447	0.553	0.723	0.172	0.830	0.225	0.868											
Li	0.789	0.668	0.867	0.508	0.377	0.812	0.386	0.916	0.225	0.693	0.779										
Mg	0.587	0.328	0.510	0.285	0.725	0.402	0.066	0.452	-0.036	0.495	0.557	0.391									
Mn	0.915	0.526	0.737	0.424	0.698	0.585	0.214	0.721	0.166	0.878	0.877	0.674	0.617								
Na	0.793	0.645	0.805	0.490	0.662	0.668	0.181	0.766	0.241	0.627	0.815	0.739	0.573	0.766							
Ni	0.670	0.545	0.705	0.435	0.148	0.745	0.237	0.744	0.392	0.561	0.695	0.745	0.309	0.558	0.640						
P	0.884	0.584	0.690	0.420	0.352	0.672	0.189	0.773	0.278	0.801	0.894	0.764	0.379	0.819	0.710	0.660					
Si	0.603	0.068	0.227	0.136	0.011	0.330	0.034	0.370	0.243	0.572	0.642	0.397	0.002	0.476	0.381	0.428	-0.649				
Sr	0.553	0.828	0.871	0.487	0.523	0.693	0.429	0.774	0.279	0.453	0.527	0.745	0.397	0.56	0.723	0.551	0.524	0.003			
Ti	0.387	0.484	0.712	0.309	0.365	0.701	0.167	0.687	-0.029	0.303	0.347	0.591	0.425	0.276	0.507	0.417	0.280	0.196	0.708		
V	0.616	0.560	0.693	0.414	0.136	0.695	0.342	0.740	0.385	0.518	0.644	0.708	0.227	0.479	0.636	0.888	0.620	0.347	0.543	0.459	
Zn	0.770	0.651	0.865	0.649	0.418	0.779	0.397	0.889	0.217	0.678	0.717	0.857	0.427	0.691	0.683	0.680	0.718	0.254	0.721	0.599	0.654

2.4.2. Variation in element concentrations in surface sediments along and across the river

The concentrations of elements along the cross-sections at the four sampling sites along the river are given in Table 2.2. On average, ranges of element concentrations varied about 10-fold among the sites and the cross-section samples, with the lowest variation of about 3-fold shown in concentrations of Ca and Si. The highest range in concentrations of about 65-fold was observed for Cr. A nested ANOVA was used to statistically analyze the two-dimensional variation in the element concentrations between sites along the river and across the river nested within sites (Table 2.3). Be, Ni and Zn concentrations showed statistically significant variations along the cross-sections of the river($P \leq 0.01$), but not between different sites along the river ($P \geq 0.01$). The B and Mg concentrations did not show statistically significant variations along the cross-sections ($P \geq 0.01$), but did show significant variation between sites along the river ($P \leq 0.01$). The concentrations of Ba, Mn,Na, K, P, Cr, Li, Si, Sr, Al, Ca, and Fe showed statistically significant variations both along the cross sections and at different sites along the river ($P \leq 0.01$). Co, Cu and Ti did not show any statistically significant variation either along cross sections or along the river ($P \geq 0.01$) (Table 2.2).

Table 2.2: The concentrations of elements in soil from four sampling sites (A, B, C, D) along the cross-section (1-5) of the Upper Souris River (μmol g^{-1} dry weight, mean±standard deviation, n=3).

Element	Site	Cross-section				
		1	2	3	4	5
Al	A	61± 6	56±3	71±7	164±13	210±7
Al	B	156±2	162±6	149±28	179±4	155±16
Al	C	145±14	138±19	140±11	238±18	195±5

		48±2	29±1	74±4	123±3	113±2
Al	D	48±2	29±1	74±4	123±3	113±2
B	A	0.83±0.02	0.84±0.07	0.87±0.01	1.43± 0.56	0.84±0.15
B	B	2.32±0.16	1.76±0.15	0.94±0.07	0.68±0.08	1.09±0.10
B	C	1.29±0.09	1.44±0.07	1.68±0.10	3.53±0.09	2.86±0.06
B	D	0.70±0.01	0.53±0.03	3.46±0.49	1.49±0.03	0.91±0.01
Ba	A	0.23±0.02	0.26±0.01	0.27±0.02	0.56±0.10	0.56±0.09
Ba	B	0.44±0.029	0.45±0.015	0.38±0.07	0.46±0.06	0.40±0.06
Ba	C	0.49±0.03	0.46±0.05	0.48±0.05	0.79±0.05	0.62±0.01
Ba	D	0.15±0.02	0.09±0.010	0.89±0.03	0.34±0.02	0.36±0.01
Be	A	0.054±0.007	0.015±0.001	0.060± 0.004	0.031±0.006	0.037±0.001
Be	B	0.032±0.001	0.105±0.032	0.025±0.001	0.036±0.005	0.026±0.005
Be	C	0.025±0.003	0.025±0.001	0.053±0.003	0.169±0.022	0.035±0.001
Be	D	0.015±0.003	0.012±0.001	0.050±0.004	0.024±0.004	0.026±0.001
Ca	A	337±3	447± 31	382±14	382±22	355±5
Ca	B	312±8	338±6	307±2	281±7	275±19
Ca	C	439±17	461±22	446±5	465±13	463±5
Ca	D	168±3	161±2	225±12	284±3	253±17
Ce	A	0.054±0.021	0.064±0.008	0.076±0.011	0.166± 0.064	0.136±0.014
Ce	B	0.112±0.010	0.104±0.001	0.093±0.002	0.124±0.016	0.107±0.005
Ce	C	0.149±0.036	0.084±0.004	0.082±0.004	0.136±0.019	0.121±0.004
Ce	D	0.062±0.005	0.028±0.005	0.184±0.004	0.151±0.009	0.107±0.003
Co	A	0.049±0.004	0.016 0.002	0.020±0.005	0.109±0.030	0.040±0.001
Co	B	0.044±0.004	0.033±0.007	0.028±0.004	0.050±0.031	0.023±0.005
Co	C	0.014±0.018	0.157±0.002	0.035±0.005	0.049±0.003	0.049±0..003
Co	D	0.013±0.002	0.050±0.004	0.252±0.009	0.030±0.003	0.136±0.005
Cr	A	0.075±0.014	0.051±0.005	0.072±0.005	0.185±0.057	0.196±0.004
Cr	B	0.153±0.009	0.143±0.017	.154±0.053	0.167±0.008	0.139±0.003
Cr	C	0.154±0.005	0.143±0.018	0.133±0.011	0.235±0.030	0.186±0.004

Table 2.2: (continued)

Cr	D	0.004±0.002	0.024±0.003	0.261±0.041	0.149±0.003	0.136±0.005
Cu	A	0.037±0.028	0.045±0.003	0.033±0.024	0.078±0.010	0.079±0.001
Cu	B	0.077±0.007	0.068±0.007	0.036±0.006	0.093±0.007	0.149±0.008
Cu	C	0.054±0.009	0.045±0.003	0.052±0.003	0.122±0.021	0.077±0.002
Cu	D	0.080±0.001	0.085±0.001	0.090±0.005	0.037±0.004	0.034±0.001
Fe	A	45±5	37±2	50±2	94±1	115±8
Fe	B	108±1	95±1	230±32	107±7	86±3
Fe	C	89±2	86±4	84±1	150±7	113±1
Fe	D	33±2	22±2	46±3	74±1	73±3
K	A	8±1	7±1	8±1	24±4	28±3
K	B	25±1	23±1	17±1	24±1	20±0.2
K	C	22±1	19±.02	20±1	34±2	27±2
K	D	8±1	4±1	9±1	20±2	15±3
Li	A	0.29±0.04	0.23± 0.18	0.33±0.03	0.80± 0.09	0.97±0.04
Li	B	0.80±0.05	0.075±0.03	0.54±0.09	0.78±0.03	0.58±0.02
Li	C	0.68±0.03	0.59±0.03	0.65±0.03	1.29±0.15	0.89±0.01
Li	D	0.19±0.01	0.09±0.01	1.34±0.10	0.60±0.03	0.55±0.03
Mg	A	239±13	274±22	278±8	261±17	353±17
Mg	B	244±10	235±17	187±2	227±22	197±4
Mg	C	274±11	216±3	212±3	316±4	1026±64
Mg	D	107±4	80±2	128±7	211±3	193±6
Mn	A	0.8±0.2	1.3±0.2	1.7±0.3	2.7±0.4	2.4±0.4
Mn	B	3.3±0.2	3.1±0.6	2.3±0.8	2.8±0.4	2.2±0.2
Mn	C	2.5±0.3	2.9±0.2	2.6±0.2	4.4±0.2	3.7±0.3
Mn	D	0.8±0.1	0.5±0.1	1.1±0.1	1.4±0.2	1.6±0.3
Na	A	3.6±0.8	3.5± 0.2	4.1± 0.4	4.5±0.5	5.6±0.3
Na	B	5.2±0.1	5.6±0.1	3.1±0.1	5.3±0.3	5.4±0.1
Na	C	6.6±0.3	4.5±0.2	7.0±0.1	8.2±0.4	6.3±0.4

Na	D	3.0±0.7	1.8±0.1	4.6±0.4	4.3±0.2	3.7±0.2
Ni	A	0.041±0.005	0.031±0.004	0.049±0.003	0.163± 0.048	0.142 ± 0.001
Ni	B	0.132±0.024	0.120±0.023	0.076±0.008	0.136±0.014	0.085±00003
Ni	C	0.086±0.005	0.062±0.003	0.079±0.001	0.174±0.030	0.128±0.022
Ni	D	0.168±0.021	0.023±0.003	0.157±0.009	0.084±0.005	0.076±0.003
P	A	35±2	31±1	54±2	91±1	106±2
P	B	133±8	115±7	89±2	83±1	103±2
P	C	117±2	90±4	96±2	155±6	118±2
P	D	47±1	42±1	66±2	95±4	103±6
Si	A	1.40±0.16	1.62±0.32	1.67±0.08	0.74±0.05	0.78±0.08
Si	B	0.72±0.02	0.68±0.06	0.72±0.02	0.64±0.02	0.53±0.01
Si	C	0.87±0.01	1.17±0.06	0.69±0.01	0.61±0.01	1.36±0.10
Si	D	0.86±0.03	1.27±0.03	1.67±0.17	0.73±0.02	0.75±0.01
Sr	A	0.19±0.02	0.27± 0.05	0.26 ± 0.09	0.36±0.06	0.34±0.02
Sr	B	0.33±0.03	0.32±0.01	0.27±0.03	0.23±0.01	0.27±0.04
Sr	C	0.43±0.01	0.33±0.03	0.46±0.06	0.53±0.01	0.49±0.02
Sr	D	0.18±0.013	0.13±0.02	0.85±0.01	0.25±0.02	0.23±0.01
Ti	A	0.32±0.02	0.36±0.01	0.37±0.02	0.32±0.06	0.48±0.04
Ti	B	0.26±0.02	0.34±0.02	0.32±0.03	0.33±0.02	0.32±0.01
Ti	C	0.47±0.04	0.33±0.03	0.27±0.02	0.38±0.01	0.46±0.04
Ti	D	0.21±0.01	0.17±0.01	0.72±0.02	0.42±0.01	0.36±0.01
V	A	0.16±0.06	0.07±0.02	0.11±0.01	0.25±0.02	0.33±0.01
V	B	0.26±0.04	0.26±0.02	0.18±0.03	0.24±0.03	0.23±0.03
V	C	0.22±0.01	0.19±0.01	0.18±0.01	0.34±0.02	0.27±0.02
V	D	0.37±0.01	0.07±0.01	0.42±0.01	0.21±0.01	0.17±0.03
Zn	A	0.14±0.02	0.07±0.01	0.32±0.29	0.37±0.07	0.31±0.01
Zn	B	0.30±0.01	0.35±0.03	0.23±0.01	0.31±0.06	0.23±0.02
Zn	C	0.24±0.01	0.24±0.02	0.25±0.01	0.38±0.02	0.37±0.02

Zn	D	0.07±0.01	0.07±.0.01	0.49±0.02	0.21±0.01	0.23±0.01

2.4.3. Variation in LOI and particle size (f<63 µm) and relationships with element concentrations

LOI did not show statistically significant variation across or along the river ($P{\geq}0.01$). Particle size, on the other hand, varied at different sites and along cross-sections ($P{\leq}0.01$) (Figure 2.3).
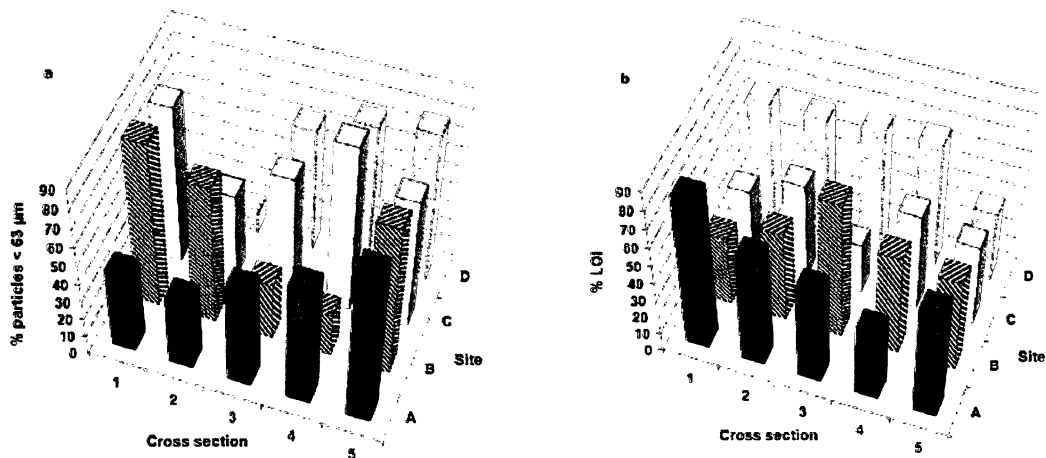
Figure 2.3: The variation of A) particle size and B) loss on ignition in soils across (cross-section 1-5) and along (site A-D) the Souris River.

The effect of f<63 on element concentrations was further analyzed using ANOVA with f<63 as a co-variable. For many elements, co-variation with f<63 was significant. Therefore, the element concentrations were normalized for the particle size to remove the effect of this influence, and two-way ANOVA was performed again to evaluate if the variation in total element concentrations in the river sediments could be explained solely by variation in the relative contributions of small particles to the sediments. For many

elements, the results for normalized concentrations were different from the results obtained for non-normalized values (Table 2.3).

If we consider variation to be significant at $P<0.01$ the following patterns are observed. Before normalization, concentrations of Al, Fe, Mn Se and P showed statistically significant variations between and across sites. Upon normalization, differences between sites were still significant, but across sites no significant variation was observed. Non-normalized concentrations of Ca, Cr, and Sr also showed statistically significant variation between and across sites, but upon normalization for f<63 variation across sites only remained significant. Any significant variation between or across sites for non-normalized concentrations of B, Ba, Be, Ce, K, Li, Mg, Ni, Na and V was no longer significant upon normalization. Only Si showed statistically significant variations both along and across the river regardless of whether the values were normalized or not, while concentrations of Co, Cu, Ti and Zn did not vary in either direction, regardless of normalization (Table 2.3).

2.5. Discussion

This study has shown that there is considerable variation in element concentrations in the sediments of the Souris River. Sediment movement in streams and rivers is usually in two forms, (a) finer particles which are held in suspension by eddy currents and are also referred to as suspended sediments, which settle as stream velocity decreases, and (b) larger solid particles that roll along the streambed and are referred to as bed load. Suspended sediments mostly consist of fine clay and silt particles, usually with a size smaller than 63 µm (Loughran 1989). The high surface area of the fine grain particles compared to their volume, provides more binding surface area for the element ions. These fine particles are an important transport medium of elements in rivers because they provide

Table 2.3: Significance ($P<0.01$) of variation between sites ('site') and across sites (cross-section = CS) upon nested ANOVA before and after normalization for f<63 (n=3). (Significant P values are in bold).

Element	Before Site, CS	After Site, CS
Al	**0.000, 0.000**	**0.001**, 0.041
B	**0.000**, 0.027	0.238, 0.201
Ba	**0.004, 0.002**	0.201, 0.021
Be	0.384, .0.314	0.838, 0.149
Ca	**0.000, 0.001**	0.478, **0.001**
Ce	**0.008, 0.000**	0.037, 0.052
Co	0.897, 0.323	0.409, 0.090
Cr	**0.001, 0.000**	0.017, **0.008**
Cu	0.209, 0.236	0.104, 0.204
Fe	**0.000, 0.000**	**0.003**, 0.332
K	**0.000, 0.000**	0.123, 0.206
Li	**0.003, 0.003**	0.055, 0.056
Mg	**0.000**, 0.099	0.380, 0.550
Mn	**0.000, 0.000**	**0.000**, 0.047
Na	**0.000, 0.003**	0.509, 0.073
Ni	0.081, **0.004**	0.047, 0.089
P	**0.000, 0.000**	**0.000**, 0.306
Si	**0.000, 0.000**	**0.002, 0.000**
Sr	**0.006, 0.002**	0.166, **0.001**
Ti	0.321, 0.122	0.016, 0.066
V	**0.002, 0.001**	0.040, 0.369
Zn	0.026, **0.001**	0.097, **0.009**

greater biding capacity compared to larger particles and remain suspended for longer periods of time. (Fórstner and Wittman 1979, Ongley et al.1982, Huang and Zhang

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1990).There was a strong correlation between metal concentrations and the soil particle size fraction less than 63 μm. Most of the element concentrations were significantly correlated with the fraction of small particles. This point at a causal relationship between particle size and element concentrations. Absorbance of metal ions onto clay and silt particles is a widely researched topic. The adsorption interactions between trace metals on suspended clay minerals in an estuarine system and under controlled laboratory conditions were studied by Gagnon et al. (1992). They showed that clay and silt particles have a higher affinity for binding with trace element ions than organic compounds. Murray et al. (1999) recorded significant correlations between element concentrations and sediment particle size in a study in the Rouge River, Michigan. They showed that Cr, Fe, Ni, Pb, and Zn concentrations in the reducible phase, under reducing soil conditions, were strongly correlated with particle size with the fraction of particles smaller than 63 μm. Sakai et al. (1986) too reported that the concentrations of Mn, Zn, Cu, Pb, Cr, and Cd in the Toyohira river sediments increased with decreasing particle size.

Normalization of element concentrations for particle size makes it possible to compare element concentrations of sediments with different particle size distributions. (Helmke et al. 1977, Förstner and Wittman 1979, Jenne et al. 1980, de Groot et al. 1982). The study presented here showed that the particle size distribution of the Souris River sediments can play a key role in determining the distribution of element concentration in sediments. When normalized for f<63, the concentrations of most elements no longer varied either between or across sites, or both. An example of this is given for K (Figure 2.4), showing that the variation between and across sites along the river of non-normalized concentrations was greater compared to variation in normalized values.
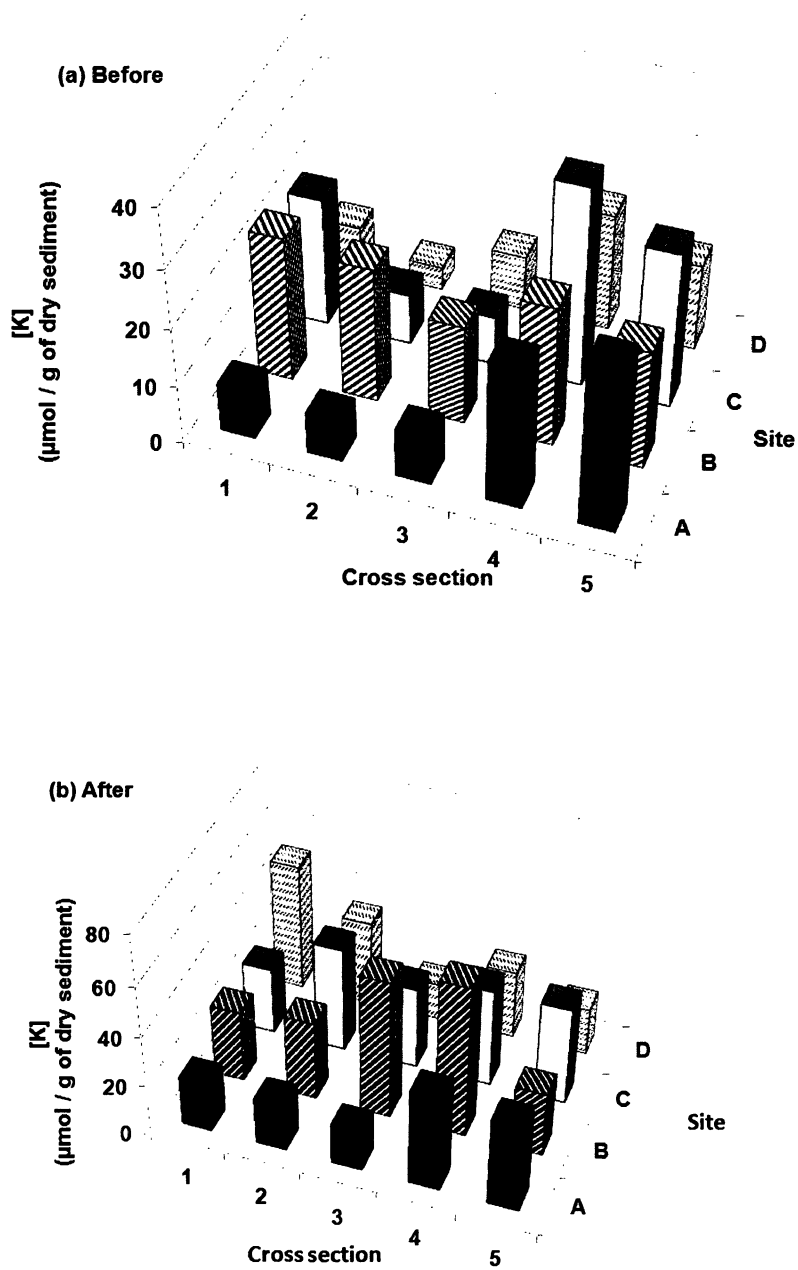
Figure 2.4: The concentration of K before (a) and after (b) normalizing for particle size for different sampling locations on a cross section (1-5) at four different sites (A-D)

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Normalization did not change the significance of spatial variation for Cu, Co, Si and Ti concentrations. For Si that is not surprising because in sediments its content is determined by the amounts of silicates, not so much by adsorption to clays or organic matter. Si concentrations also showed very little variation across the study area (about 3-fold), as did Cu and Ti (about 4-fold). Low levels of variation may obscure causal relationships as indicated by correlation analyses. Co, on the other hand, showed above average variation across the study area of about 20-fold. This suggests that other mechanisms, such as local enrichment or depletion, may be more important in determining levels of concentrations than binding to small sediment particles or organic matter.

Several studies have recorded that the organic matter content in the sediments can play an important role in determining trace element concentrations because it can provide binding surfaces for the trace element ions. Coquery and Welbourn (1995) recorded that the Hg, Pb, Cd and Fe concentrations of the Bentshoe Lake sediments showed significant positive correlations with the sediment organic matter content. Another study carried out to assess the element concentrations in 210 lakes in Norway recorded that the concentrations of mercury, bismuth, arsenic, and lead showed strong associations to organic matter while zinc and cadmium showed weak associations (Rognerud and Fjeld 2001). LOI is a simple, inexpensive method widely used to estimate organic matter in the water column and sediment of marine and freshwater ecosystems (Boyer et al. 2003). This study showed high variation in LOI, with values ranging between 3.2% and 99.6%, but it did not significantly vary across or between sites along the river, nor did it correlate with either f< 63 or element concentrations. This indicates that variation in organic matter content in this river is not related to variation in particle size distribution of the sediments.

It also indicates that this particular type of organic matter does not affect element mobility in the Souris River. This may be due to the sources of organic matter - most of the watershed draining to this part of the river consists of grasslands – as well as to the biogeochemistry of this particular river, and deserves further investigation.

2.6. Conclusion

In conclusion, the current study showed that there is significant variation in element concentrations in sediments along the Souris River. The variation of element concentrations can be partly attributed to the particle size distribution of the river sediments because the element concentrations were significantly correlated to the fraction of particles smaller than 63 μm. The organic matter content does not play a vital role in determining the trace element concentrations of the sediments of the Souris River. The results suggest that the variation in element concentrations is indeed sufficient to use the multi-element fingerprinting technique to identify trace element transport along the sediments of the Souris River.

CHAPTER 3. MULTI-ELEMENT FINGERPRINTING OF SEDIMENTS: A LABORATORY STUDY TO SIMULATE MIXING AND TRANSPORT OF CHEMICAL ELEMENTS IN RIVER SYSTEMS

3.1. Abstract

Water and sediments play an important role in storage and transport of chemical elements entering into aquatic environments. The aim of this study was to test the validity of the assumption underlying multi-element fingerprinting studies that all elements are mixing conservatively. In this study two laboratory experiments were designed to assess the effects of water and different mixing ratios on the concentration variation of elements in river sediments. In the first experiment, sediments from two sites of the Souris River, ND, were mixed at different mixing ratios under wet and dry conditions. In the second experiment an artificial river was constructed with water running through plastic trays containing sediment arranged at different tiers to simulate downstream water movement. The sediments of these experiments were analyzed for particle size, organic matter content and element concentrations. The organic matter content and particle size of sediments did not play a role in determining element concentrations in the sediments. The presence of water enhanced the mobility of some elements and some of the mobilized elements were re-deposited in another location "downstream." All the elements showed a conservative mixing behavior in both dry and wet conditions.

3.2. Introduction

Chemical elements are natural constituents of rocks, soils, sediments and water. Many elements are important to the natural functioning of ecosystems. They enter water bodies due to both natural and anthropogenic reasons. Elements that accumulate in

ecosystems in concentrations higher than the normal concentrations can cause disturbances to the normal functions of the ecosystems. Eventually this will lead to major disruptions of the ecosystems(Gibbs 1973, Pojasek and Zajicek 1978).

Water is the primary carrier of elements entering into the aquatic environments. Sediments can serve both as a carrier and sink to these elements (Gibbs 1973, Pojasek and Zajicek 1978). The elements in the aquatic system can be present either as dissolved ions or attached to the sediments (Fórstner 1990). The dissolved ions can be trapped, by sediments, when their concentrations in the water column are relatively high and released to the water column when the concentrations are relatively low. Therefore, elements are in equilibrium between the water column and the sediments (Fórstner 1990). This equilibrium is controlled by many factors such as, pH, redox potential, availability of complexing agents, availability of chelating agents, dissolved oxygen concentrations, physical and geochemical characteristics of sediments and biological components in the environment (Gibbs 1973, Pojasek and Zajicek 1978, Tessier and Campbell 1987, Fórstner 1990, Gadd 2004, Hochella et al. 2005).

Multi-element fingerprinting of sediments is an increasingly popular approach for sediment tracing (Davis and Fox 2009). This technique uses a wide range of sediment properties such as geochemistry, mineral magnetic properties, radionuclides, inorganic element concentrations and biological properties to develop unique fingerprints to identify sediment source and sink areas (Jenkins et al. 2002, Collins et al. 1997[a], Walling et al. 2008, Davis and Fox 2009). The multi-element fingerprinting methodology consists of five steps as follows: 1) classifying sediment sources;2) identifying unique tracers for each sediment source; 3) representing sediment sources and sinks; 4) accounting for sediment

and tracer fate and 5) utilizing mixing models to model sediment source and fate (Davis and Fox 2009). Multi- element fingerprinting technique is based on two main assumptions: 1) potential sediment sources can be discriminated on the basis of fingerprints; and 2) comparison of fingerprints of suspended sediment with those of source material samples helps to determine the relative importance of individual sources (Collins et al. 1997[a], Walling et al. 2008). These multi-element fingerprinting techniques has been widely used to distinguish the sources of sediments and potential environmental contaminants in the river basins, to quantify sediment loading into watersheds and to perform total maximum daily load assessments (Jenkins et al. 2002, Collins and Walling 2004, Martínez-Carreras et al. 2009, Collins et al. 2010). All these were field studies conducted in natural environmental conditions. In these studies conservative behavior of elements and the absence of enrichment or dilution effects were assumed (Jenkins et al. 2002, Martínez-Carreras et al. 2009), but none of these studies have evaluated the validity of these assumptions.

The main objective of the study presented here was to test the validity of the assumptions used in the multi-element fingerprinting field studies, i.e. that the majority of the elements mix in a linear, conservative fashion. Two laboratory experiments were designed, using sediments from the Souris River, to 1) assess the effect of water and different mixing ratios on the concentration variation of elements in river sediments and 2) to assess the effect of flowing water on element concentrations and distribution in sediments. In the first experiment sediments from two different locations in the Souris River were mixed both dry and wet. It was hypothesized that all the elements would mix linearly both under wet and dry conditions. It was also hypothesized that soluble elements

are removed from the sediments due to continuous interaction with water. The second experiment was a river simulation experiment conducted to assess the relationship of element concentrations in the upstream and downstream sediments of the main river. In this experiment it was hypothesized that 1) the concentrations of soluble elements in the sediments would decrease with time as they move along the system, and that 2) for some elements the upstream sediments would act as sources of elements for the downstream sediments.

3.3.   Materials and methods

This study consisted of two experiments. The sediment samples used in the laboratory experiments were collected from the Souris River of North Dakota.

3.3.1. Collection of samples

Top river bed sediment (maximum depth of sampling = 2 cm) samples were collected in the summers of 2008 and 2009 along the Souris River. The samples were collected by inverting a plastic zip-lock bag as a glove to grab the sample, then folding it back over the sample. The sealed bags were stored in ice and transported to the laboratory. In the laboratory, samples were dried until they reached a constant weight at 60 °C and then homogenized in a mortar and pestle. These homogenized samples were used in the laboratory experiments.

3.3.2. Mixing of soil at different mixing ratios

Sediment from two different sites of Souris River (Site G north of Lake Darling and the Des Lacs River) was mixed under dry or wet conditions. Soil mixtures were prepared in evaporation-proof plastic bottles. The mixing ratios used were 10:1, 4:1, 1:1; 1:4 and 1:10 by dry weight of sediment samples for a total weight of 20g. In the wet mixtures, distilled

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water was added to the mixtures at 10 mLof water per 1g of soil ratio. The dry mixtures were prepared by mixing the soil in evaporation proof plastic bottles The wet and dry mixtures containing plastic bottles were shaken for 72 hours in a Burrell wrist action shaker (Model 75) in the speed of 50 motions per minute. After 72 hours of mixing, water was removed from the wet samples by filtering through No. 1 Whatman filter paper. Then the wet and dry samples were processed and analyzed for multiple elements (see section below).

3.3.3. Simulation of water and sediment movement in river systems

An artificial 'river' was constructed in the greenhouse with tap water running through connected plastic trays (30cmx 20cm x 10cm) at three different tiers. The trays were connected in a way that all the overflowing water from the tray at the top tier(Level I) entered to the tray at the immediate bottom tier (Level II). The water from the tier III were flowed to the ground and was not recycled. The water from a large plastic storage container continuously fed to the trays using vinyl tubes (Figure 3.1).
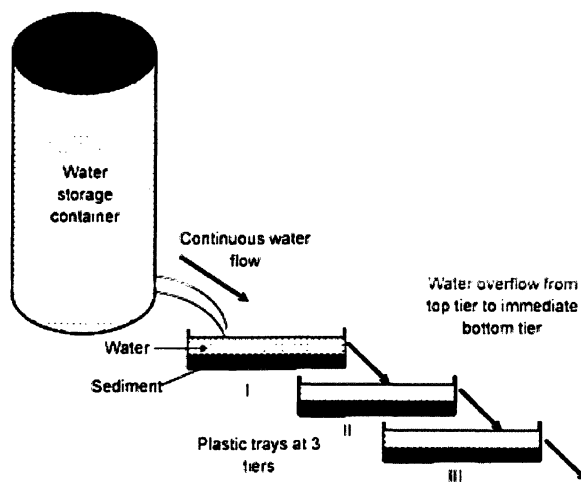
Figure 3.1: Experiment set-up of the river simulation experiment. The trays at different tiers were connected to each other in a way that all the overflowing water from the tray at the top tier (Tier I) entered to the tray at the immediate bottom tier (Tier II).

Each tray contained 5kg of sediments from the Souris River. The water flow rate was maintained at 1.4 L per minute using a valve. The initial sampling was done after 1 week of experiment set up. Three replicate sediment samples were taken from the each tray at each tier(I, II, III).Continuous replicate sampling was done in trays at different tiers(I, II, III) at 4 week intervals (0, 1M, 2M, 3M) for 12 weeks. These samples were processed and analyzed for multiple elements (see below).

3.3.4. Chemical analysis

The samples were oven dried at 60 $^\circ$C, then homogenized using a mortar and pestle. About 0.5 g of each homogenized sample was digested in a CEM Mars-Xpress microwave digester using 10 ml of concentrated nitric acid (16 total vessels (XPRESS 55 ml 8 PFA Venting Vessels), 1600W, 100% Power, ramped to 185 °C over 10 minutes and held at this temperature for 5 minutes). Blank samples and about 0.5 g of standard soil reference materials were also digested following the same digestion procedure. These samples, blanks and standard reference materials were then analyzed using a Spectro Genesis Inductively Coupled Plasma Optical Emission Spectrometer (ICP OES)with Cross-flow nebulizer, Side-On-Plasma (SOP)for 34 elements (instrument detection limits in $\mu gL^{-1}$are given in brackets):Ag(0.2), Al(0.5), As(42), Ba(0.2), B(11), Be(0.07), Ca(300), Cd(17), Ce(0.1), Co(7), Cr(2), Cu(1), Fe(25), Hg(25), K(76), Li(0.0.8), Mg(1), Mn(1), Mo(15), Na(0.4), Ni(10), P(46), Pb(30), S(0.2), Sb(7), Se(2), Si(10), Sn(3), Sr(0.3), Ti(6), Tl(0.2), V(6), Zn(4), Zr(0.1). Throughout the remainder of this chaptermolar units will be used. This analysis used a four-point calibration using individual or a combination of standards in a five percent HNO_3 matrix. Continuing control verification was done after every 10 samples to check that variability was within 10%.

3.3.5. Loss-on-ignition

Loss-on-ignition (LOI) is a measure of organic matter content. About 15 g of the samples were dried at 105°C in ceramic crucibles for 2 hours. The dry weight (W_d) of these samples was recorded. They were then ashed at 550 °C for 2 hours in a Sybron Thermoclyne muffle furnace and the weights of the remaining ash recorded (W_a). The percentage LOI was calculated as ((W_d-W_a) / W_d) x 100.

3.3.6. Fraction of particles smaller than 63 μm (f<63)

The ash left after determination of LOI was used for measurement of the fraction of particles smaller than 63 μm (f<63). The initial dry weight of the ash was recorded (W_i). These samples were wet sieved through a 63 μm sieve using distilled water. The material remaining on the sieve was collected onto a Whatman No. 1 filter paper, oven-dried at 60 °C and dry weight recorded (W_r). The percentage f< 63 was calculated as ((W_i - W_r) / W_i) x 100.

3.3.7. Statistical analysis

Minitab 15 statistical software (Minitab® 15.1.30.0) was used for all statistical analyses. All data were log-transformed to obtain homogeneity of variance. Pearson correlation analysis was performed on element concentrations, LOI and f<63. In the sediment mixing experiment, nested ANOVA in the General Linear Model (GLM) module was used to analyze the two-dimensional variation, with mixing ratios and dry/wet conditions as factors to identify their effects on element concentrations. The element concentrations at different dry or wet mixing ratios were predicted from the element concentrations measured in the initial sediment samples. Then the deviations of the

measured element concentrations from the predicted concentrations for each element at each mixing ratio were calculated as follows:

$$D_e = C_m - C_p$$

Where,

D_e - Deviation of measured element concentration from predicted concentration for element i

C_m - Measured concentration of element i

C_p - Predicted concentration of element i

The deviations (D_e) were normalized for the predicted element concentrations using the following formula:

$$ND_e = D_e/C_p$$

Where,

ND_e - Normalized deviation of measured concentration from predicted concentration for element i

D_e —Deviation of measured concentration from predicted concentration for element i

C_p - Predicted concentration of element i

The average value for ND_e and the 95% confidence intervals (CI) were calculated for each dry or wet mixing ratio.

In the river simulation experiment, nested ANOVA in the General Linear Model (GLM) module was used to analyze the two-dimensional variation, with different levels and time of sampling as covariates to identify their effects on element concentrations.

3.4. Results

The concentrations of Ag, B, Ce, Hg, Si and Zr were below detection limits and will therefore not be discussed further.

3.4.1. Correlations with LOI and f < 63

In the soil mixing experiment, LOI ranged from 2.2% to 8.2 % with an average of 4.6%. f<63 ranged from 1.9 to 9.8% with average of 5.2%. In the river simulation experiment, LOI ranged from 2.2 to 9.2% with average of 4.3%.f<63 ranged from 3.5% to 7.4% with an average of 3.8%. Correlations were considered statistically significant if r ≥ 0.707, i.e. the correlations that explain 50% or more variation (McClave and Sincich 2006). In both experiments, none of the elements showed a statistically significant correlation with LOI or f<63, nor did LOI correlate significantly with f<63.

3.4.2. Variation in element concentrations in different mixing ratios in dry/wet conditions

The mean element concentrations in the initial sediment samples (before mixing) and in different mixing ratios at wet or dry conditions are given in Table 3.1. Most of the elements showed a significantly higher concentration in the dry sediments compared to the wet sediments both in initial sediments and mixtures (Table 3.2).

Nested ANOVA was used to statistically analyze the two dimensional variation of element concentrations with mixing ratios and wet/dry condition. All the elements except Zn and Ce showed a statistically significant concentration variation with dry/wet conditions. Al, Be, Co, Cr, Cu, Fe, K, Li, Mg, Pb, Sn, Sr, Tl and V showed statistically significant variations both at different mixing ratios and at wet/dry conditions. Zn and Ce

Table 3.1: Element concentrations (μmol / g of dry sediment; unless otherwise stated) of sediments A and B at different mixing ratios in wet or dry conditions. Data are presented as mean ± SD. (n=3).

Element	Dry/Wet Condition	Mixing ratio						
		A	A10B1	A4B1	A1B1	A1B4	A1B10	B
Al	Dry	198.3±3.1	227.3±5.6	248.3±3.7	264.3±5.6	266.8±7.4	276.7±2.1	317.27±1.9
	Wet	149.4±47.2	151.9±11.1	135.9±14.1	166.79±3.7	201.3±10.7	190.2±9.3	224.8±54.2
As	Dry	0.03±0.00	0.04±0.00	0.04±0.00	0.05±0.00	0.04±0.00	0.05±0.00	0.05±0.00
	Wet	0.03±0.01	0.03±0.00	0.03±0.00	0.03±0.00	0.03±0.00	0.03±0.00	0.03±0.01
Ba	Dry	0.59±0.02	0.73±0.02	0.75±0.02	0.79±0.03	0.79±0.01	0.77±0.03	0.94±0.01
	Wet	0.56±0.13	0.54±0.01	0.52±0.01	0.54±0.02	0.6±0.01	0.56±0.02	0.62±0.13
Be	Dry	0.03±0.00	0.03±0.00	0.03±0.00	0.04±0.00	0.04±0.00	0.05±0.01	0.05±0.00
	Wet	0.03±0.01	0.03±0.01	0.02±0.00	0.03±0.01	0.03±0.00	0.04±0.01	0.03±0.01
Ca	Dry	471±14	622±13	636±11	629±25	613±11	606±9	754±6
	Wet	574±31	565±21	546±24	560±27	574±26	557±19	551±37
Cd (nmol/g)	Dry	1.6±0.01	1.7±0.02	1.8±0.01	1.9±0.01	2.3±0.02	2.4±0.01	2.6±0.01
	Wet	1.0±0.01	1.01±0.01	1.02±0.1	1.1±0.02	1.2±0.02	1.3±0.01	1.4±0.01
Co	Dry	0.08±0.00	0.09±0.00	0.09±0.00	0.1±0.00	0.11±0.00	0.11±0.00	0.12±0.00
	Wet	0.06±0.01	0.07±0.00	0.06±0.00	0.07±0.00	0.08±0.00	0.08±0.00	0.09±0.02
Cr	Dry	0.21±0.00	0.24±0.00	0.26±0.01	0.27±0.01	0.27±0.01	0.28±0.00	0.33±0.00
	Wet	0.18±0.04	0.18±0.01	0.17±0.02	0.19±0.00	0.22±0.01	0.21±0.01	0.24±0.05
Cu	Dry	0.14±0.00	0.16±0.00	0.17±0.01	0.19±0.01	0.2±0.0	0.21±0.00	0.23±0.00
	Wet	0.1±0.04	0.1±0.01	0.1±0.01	0.13±0.02	0.14±0.01	0.13±0.01	0.16±0.05
Fe	Dry	168±3	206±4	214±3	224±5	225±4	230±1.	268±1
	Wet	140±42	141±11	126±8	145±5	170±8	162±5	189±44
K	Dry	28.2±0.8	32.5±1.4	35.1±1.4	37.6±1.4	39.3±1.4	41±1	45±1
	Wet	20±7	20±3	19±1	23±0	27±1	26±1	32±8
Li	Dry	0.9±0.0	1.1±0.0	1.2±0.0	1.3±0.0	1.3±0.0	1.3±0.0	1.5±0.0

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Table 3.1: (continued)

	Wet	0.8±0.2	0.8±0.1	0.7±0.04	0.9±0.01	1.0±0.04	0.9±0.04	1.1±0.2
Mg	Dry	348.6±11.3	453.8±12.5	471.6±10.3	464.8±20.5	449.7±6.2	448.3±8.2	557.8±5.4
	Wet	388±38.2	383.9±23.7	360.6±24.8	386.6±18.8	400.3±22.6	389.4±16.6	393.5±40.5
Mn	Dry	3.8±0.07	4.8±0.08	4.9±0.06	5.1±0.1	5.2±0.1	5.2±0.07	6.1±0.03
	Wet	3.2±1.07	3.1±0.2	2.8±0.2	3.1±0.07	3.5±0.2	3.3±0.1	4±1
Mo (nmol/g)	Dry	2.1±0.01	2.2±0.01	2.3±0.01	2.3±0.01	2.6±0.01	2.5±0.01	2.6±0.01
	Wet	1.3±0.01	1.2±0.01	1.1±0..02	1.3±0.01	1.6±0.02	1.5±0.01	1.8±0.02
Na	Dry	11.2±0.1	14.5±0.5	15.5±0.2	14.9±0.2	14.3±0.4	14.2±0.3	17.9±0.1
	Wet	6.8±5.0	3.9±0.4	3.7±0.2	4.1±0.2	5.1±0.2	4.2±0.2	7.6±5.0
Ni	Dry	0.2±0.0	0.2±0.0	0.2±0.01	0.3±0.01	0.3±0.0	0.3±0.0	0.3±0.0
	Wet	0.2±0.04	0.2±0.09	0.1±0.01	0.2±0.01	0.2±0.01	0.2±0.03	0.2±0.04
P	Dry	18.9±0.4	24.5±0.3	26±0.6	25.2±0.7	24.5±0.5	23.7±0.6	30.3±0.3
	Wet	22±2.2	22.7±0.8	21.2±0.7	21.3±0.3	22.9±0.9	22.2±0.6	22.7±1.4
Pb	Dry	0.02±0.001	0.03±0.001	0.03±0.002	0.03±0.001	0.04±0.001	0.03±0.001	0.04±0.002
	Wet	0.02±0.01	0.02±0.00	0.02±0.00	0.02±0.00	0.03±0.00	0.03±0.00	0.03±0.01
S	Dry	45±1	46±2	49±2	51±2	54±1	56±1	57±1
	Wet	22±2	14±2	12.4±0.1	12.4±1	17±2	16±0	27±2
Sb (nmol/ g)	Dry	1.12±0.01	0.96±0.02	0.98±0.01	0.93±0.02	1.2±0.01	1.21±0.01	1.32±0.02
	Wet	0.71±0.01	0.66±0.0.1	0.63±0.02	0.68±0.01	0.74±0.03	0.71±0.02	0.85±0.02
Se (nmol/ g)	Dry	4.2±0.1	3.8±0. 1	4.2±0. 1	4.3±0. 1	4.2±0. 1	4.3±0.2	5.6±0.2
	Wet	3.2±0. 1	2.9±0. 1	2.9±0. 1	2.4±0.2	3.3±0. 1	2.9±0. 1	3.4±0. 1
Sn (nmol/ g)	Dry	2.2±0.1	2.4±0.1	2.5±0.1	2.6±0.2	2.8±0.2	2.8±0.1	3.2±0.2
	Wet	1.2±0.1	1.5±0.1	1.6±0.1	1.7±0.1	1.9±0.2	2.1±0.2	2.8±0.1
Sr	Dry	0.3±0.01	0.4±0.01	0.4±0.01	0.5±0.02	0.5±0.01	0.5±0.01	0.6±0.01
	Wet	0.3±0.06	0.3±0.01	0.3±0.02	0.3±0.01	0.4±0.01	0.4±0.01	0.4±0.07
Ti	Dry	0.4±0.03	0.5±0.05	0.5±0.03	0.5±0.05	0.5±0.03	0.4±0.05	0.6±0.01

	Wet	0.6±0.03	0.6±0.03	0.6±0.03	0.6±0.07	0.6±0.06	0.6±0.05	0.6±0.06
Tl (nmol/ g)	Dry	5.2±0.1	5.8±0.2	6.2±0.2	6.4±0.2	6.8±0.1	6.3±0.1	7.5±0.1
	Wet	4.2±0.1	4.3±0.1	3.7±0.1	4.6±0.1	5.3±0.1	4.9±0.1	5.5±0.1
V	Dry	0.3±0.01	0.3±0.01	0.4±0.01	0.4±0.01	0.4±0.01	0.4±0	0.5±0.01
	Wet	0.2±0.07	0.2±0.02	0.3±0.02	0.2±0.01	0.3±0.02	0.3±0.02	0.4±0.06
Zn	Dry	0.5±0.01	0.6±0.01	0.6±0.02	0.7±0.02	0.6±0.01	0.7±0.01	0.8±0.01
	Wet	0.4±0.1	0.9±0.3	0.4±0.07	0.6±0.2	0.5±0.0	0.5±0.0	0.8±0.1

did not show a significant concentration variation either with dry/wet condition or mixing ratios (Table 3.2).

Table 3.2: Significance (P) of variation between mixing ratios (Ratio) and dry/wet conditions (D/W) upon nested ANOVA (n=3).

Element	Significant concentration variation		Element	Significant concentration variation	
	Ratio	D/W		Ratio	D/W
Al	0.000	0.000	Mo	0.021	0.000
As	0.328	0.000	Na	0.203	0.000
Ba	0.242	0.000	Ni	0.062	0.000
Be	0.001	0.000	P	0.935	0.000
Ca	0.888	0.000	Pb	0.001	0.000
Cd	0.072	0.000	S	0.175	0.000
Ce	0.322	0.124	Sb	0.119	0.000
Co	0.000	0.000	Se	0.871	0.000
Cr	0.005	0.000	Sn	0.000	0.000
Cu	0.001	0.000	Sr	0.000	0.000
Fe	0.008	0.000	Ti	0.263	0.000
K	0.000	0.000	Tl	0.001	0.000
Li	0.000	0.000	V	0.003	0.000
Mg	0.988	0.000	Zn	0.074	0.074
Mn	0.077	0.000			

3.4.3. Deviation of measured concentrations from the predicted concentrations at different mixing ratios

The concentrations of elements at different mixing ratios were predicted using the element concentrations measured in the initial sediment samples. An example of a graph comparing the predicted and measured element concentrations of Fe and P is given in Figure 3.2.

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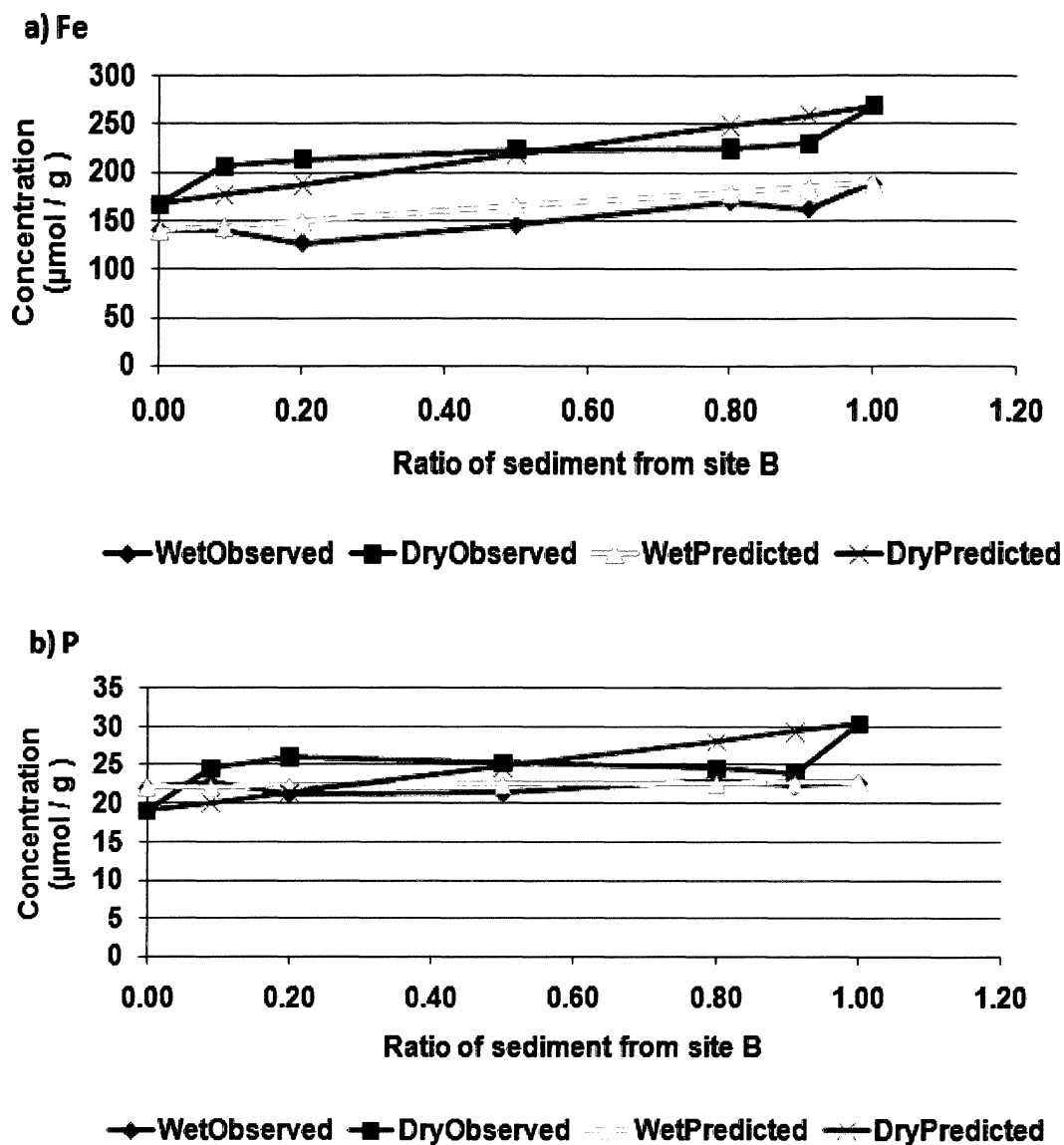
Figure 3.2: An example for comparison of predicted and measured element concentrations in different mixing ratios at wet and dry mixing conditions (a: Fe; b: P).

The normalized deviations averaged for all elements (ND_e) and their 95% confidence intervals (95 % CI) at different mixing ratios are given in Table 3.3. The normalized deviation of the measured concentrations from the predicted concentrations for each element (D_e) were compared with the ND_e and 95 % CI. Figure 3.3 shows the

comparison of D_e with ND_e ± 95 % CI. In the dry sediment mixtures the D_e for all

elements were within the 95% confidence interval limits of ND_e (Figure 3.3 a). In wet

sediment mixtures, the A10:B1 mixture showed a higher deviation than the ND_e for Zn,

while Tl showed higher deviations than the ND_e in the A1:B4 and A1:B10 mixtures

(Figure 3.3b).

Table 3.3: Normalized average deviation for all element concentrations from the predicted
values at different mixing ratios ± 95 % confidence interval.

Mixing ratio(A:B)	Dry mixing condition	Wet mixing condition
10:1	0.1±0.5	0.01±0.9
4:1	0.1±0.8	-0.1±0.7
1:1	0.02±0.7	-0.09±0.8
1:4	-0.07±0.8	-0.03±0.6
1:10	-0.1±0.9	-0.07±0.9

3.4.5. Spatial and temporal variation in element concentrations in a river simulation experiment

The mean element concentrations at different tiers and at different sampling times

are given in Table 3.4. Some elements showed spatial and temporal variations in the

concentrations (Table 3.4).

Nested ANOVA was used to statistically analyze the two dimensional variation of

elemental concentrations with different levels and with time. The results of Nested

ANOVA are given in Table 3.5. Most elements (Ba, Be, Cd, Ce, Mo, Pb, Sb, Se, Sn, Tl)

did not show significantly different concentrations with time or at different tiers, but Al,
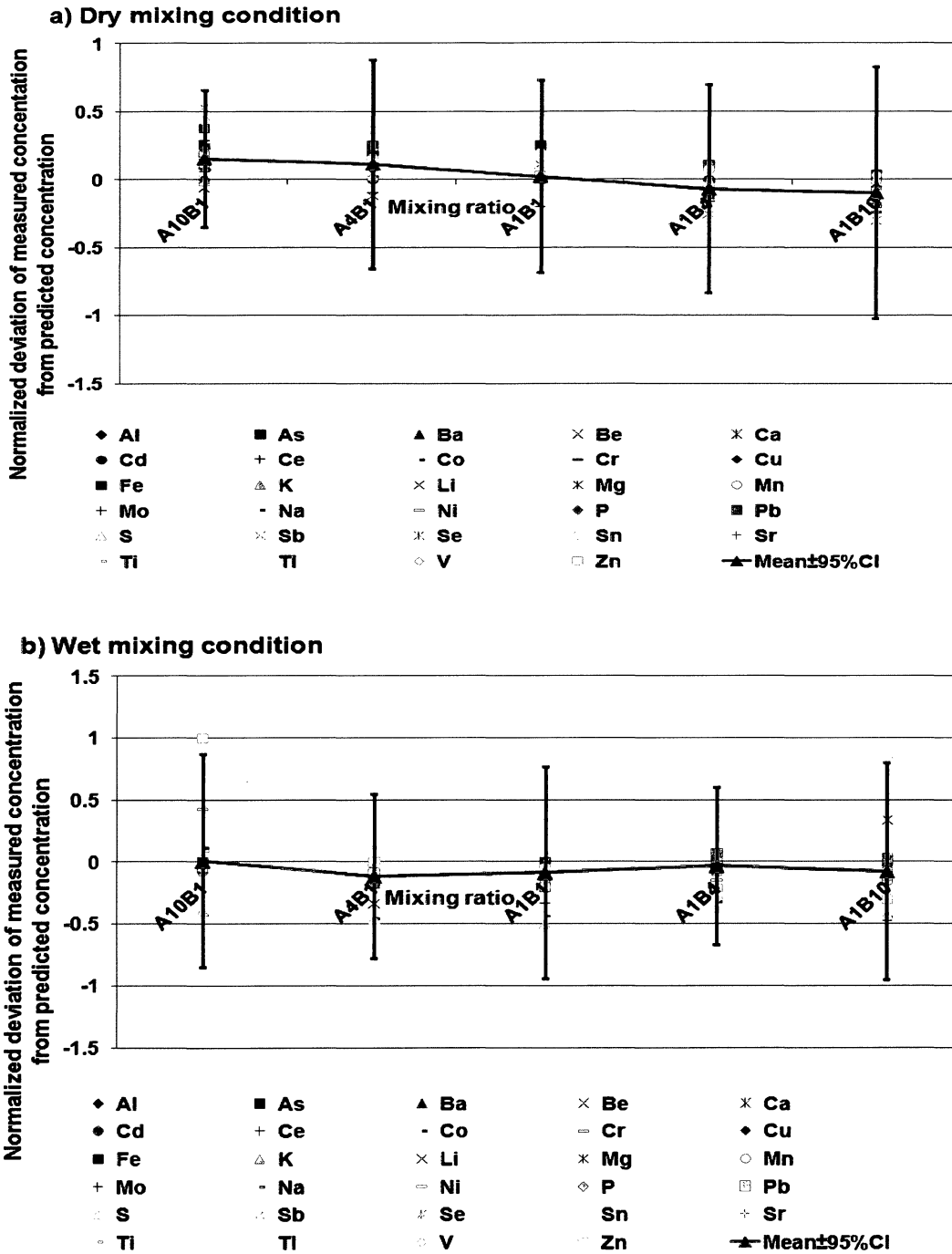
Figure 3.3: The normalized deviations of measured element concentrations from the predicted element concentrations at different mixing ratios of soil A and Soil B. (a: Dry mixing conditions; b: Wet mixing conditions).

Table 3.4: Element concentrations (μmol / g of dry sediment; unless otherwise stated) of sediments at different tiers and at different sampling times in the river simulation experiment. Data are presented as mean ± SD (n=3).

Element	Tier	Sampling time			
		week 1	week 5	week 9	week 13
Al	I	194±4.3	186.6±4.3	184.1±15.4	158.1±10.7
	II	199±6	195±6	194±22	170±21
	III	168±8	163±6	152±11	136±6
As	I	0.05±0.001	0.05±0.001	0.04±0.001	0.04±0.001
	II	0.05±0.001	0.05±0.001	0.04±0.001	0.04±0.001
	III	0.05±0.001	0.04±0.001	0.04±0.001	0.04±0.001
Ba	I	0.9±0.1	0.9±0.1	0.8±0.1	0.9±0.1
	II	0.9±0.001	0.8±0.001	0.9±0.1	0.9±0.1
	III	0.8±0.1	0.8±0.001	0.8±0.001	0.8±0.1
Be	I	0.03±0.001	0.04±0.01	0.03±0.01	0.03±0.01
	II	0.03±0.001	0.04±0.01	0.03±0.002	0.02±02
	III	0.03±0.001	0.03±0.01	0.03±0.02	0.03±0.02
Ca	I	395±16	383±8	372±32	369±15
	II	384±11	383±21	383±38	380±8
	III	353±12	368±20	373±22	378±25
Cd (nmol/g)	I	1.2±0.01	1.2±0.01	1.2±0.01	1.2±0.01
	II	1.4±0.01	1.2±0.02	1.2±0.01	1.2±0.02
	III	1.1±0.01	1.1±0.01	1.5±0.01	1.1±0.01
Co	I	0.08±0.01	0.09±0.01	0.09±0.02	0.08±0.01
	II	0.09±0.01	0.09±0.01	0.09±0.02	0.09±0.01
	III	0.08±0.01	0.08±0.01	0.07±0.01	0.07±0.0.01
Cr	I	0.22±0.01	0.22±0.01	0.21±0.02	0.18±0.01
	II	0.23±0.02	0.21±0.01	0.23±0.02	0.19±0.02
	III	0.19±0.01	0.19±0.02	0.15±0.02	0.19±0.01
Cu	I	0.13±0.01	0.13±0.02	0.13±0.01	0.12±0.02
	II	0.14±0.01	0.12±0.03	0.14±0.04	0.12±0.02
	III	0.11±0.02	0.11±0.03	0.10±0.01	0.10±0.04
Fe	I	189±6	195±7	186±18	172±10
	II	199±3	187±22	194±7	187±10
	III	176±8	171±7	157±6	163±4
K	I	29±1	27±1	26±2	22±1
	II	30±1	27±3	27±1	25±1
	III	25±1	24±1	20±0	19±1
Li	I	1±0.2	1.1±0.1	1±0.1	0.9±0.2
	II	1±0.1	1±0.1	1±0.2	1±0.1
	III	0.9±0.1	0.9±0.0.2	0.8±0.1	0.9±0.0.2
Mg	I	287±20	271±15	271±34	265±16

	II	296±23	289±38	289±10	289±6
	III	230±10	240±13	245±17	251±18
Mn	I	4.4±0.2	4.1±0.2	3.8±0.5	3.8±0.3
	II	4.7±0.2	3.9±0.4	4.2±0.3	4.1±0.3
	III	4.3±0.2	3.9±0.3	3.6±0.2	3.8±0.3
	I	2.2±0.1	1.7±0.1	1.4±0.1	1.1±0.2
Mo (nmol/g)	II	2.1±0.2	1.5±0.2	1.4±0.1	1.2±0.1
	III	2.0±0.1	1.6±0.1	1.3±0.2	1.1±0.1
Na	I	12.8±0.3	9.7±0.3	6.2±0.3	6.1±0.4
	II	13.3±0.5	9.1±1.2	6.2±0.3	6.1±0.4
	III	14.4±0.4	9.1±0.4	6.5±0.4	5.7±0.4
Ni	I	0.2±0.0	0.2±0.0	0.2±0.0	0.2±0.0
	II	0.2±0.0	0.2±0.0	0.2±0.0	0.2±0.0
	III	0.2±0.0	0.2±0.0	0.2±0.0	0.2±0.0
P	I	23±2	23±1	22±1	21±0.8
	II	24±1	22±1	22±1	22±2
	III	20±2	20±1	20±1	23±1
Pb	I	0.029±0.01	0.32±0.01	0.031±0.02	0.031±0.01
	II	0.037±0.01	0.029±0.01	0.034±0.01	0.031±0.02
	III	0.029±0.02	0.028±0.02	0.033±0.01	0.029±0.02
S	I	32±2	17±4	12±3	10±2
	II	23±2	10±2	10±2	8±2
	III	26±5	22±3	22±3	9±1
	I	1.0±0.1	0.9±0.1	0.9±0.1	0.6±0.1
Sb (nmol/g)	II	1.3±0.1	0.9±0.1	1.0±0.1	0.7±0.1
	III	1.0±0.2	1.0±0.1	1.1±0.2	0.7±0.2
	I	2.5±0.1	2.5±0.1	3.0±0.1	2.5±0.2
Se (nmol/g)	II	2.5±0.2	2.1±0.1	2.5±0.1	3.4±0.1
	III	3.4±0.1	3.0±0.1	3.4±0.1	3.4±0.1
Sn	I	0.004±0.001	0.003±0.000	0.002±0.000	0.003±0.000
	II	0.009±0.011	0.003±0.000	0.003±0.000	0.003±0.000
	III	0.002±0.000	0.003±0.000	0.003±0.000	0.003±0.001
Sr	I	0.4±0.0	0.4±0.0	0.3±0.0	0.3±0.0
	II	0.4±0.0	0.3±0.0	0.3±0.0	0.3±0.0
	III	0.4±0.0	0.3±0.0	0.3±0.0	0.3±0.0
Ti	I	0.7±0.0	0.7±0.0	0.6±0.0	0.5±0.0
	II	0.7±0.0	0.6±0.0	0.7±0.0	0.6±0.0
	III	0.6±0.0	0.6±0.0	0.5±0.0	0.5±0.0
Tl (nmol/g)	I	5.2±0.1	5.1±0.2	5.1±0.2	4.4±0.1

	II	5.5±0.1	5.4±0.1	5.2±0.2	4.8±0.1
	III	4.7±0.1	4.4±0.2	3.9±0.1	3.8±0.1
V	I	0.3±0.0	0.3±0.0	0.3±0.0	0.3±0.0
	II	0.4±0.0	0.3±0.0	0.3±0.0	0.3±0.0
	III	0.3±0.0	0.3±0.0	0.2±0.0	0.3±0.0
Zn	I	0.5±0.0	0.6±0.0	0.6±0.0	0.5±0.0
	II	0.6±0.0	0.5±0.1	0.6±0.0	0.5±0.0
	III	0.5±0.0	0.5±0.0	0.5±0.0	0.5±0.0

As, Ca, Cr, K, Li, Mg, Na, P, and V did show significant variation both with time and at different tiers. Mn, S, Sr and Ti showed significant concentration variations only with time, while Co, Cu, Fe, Ni and Zn varied significantly only at different tiers.

Table 3.5: Significance ($P<0.05$) of variation between top and bottom tiers('tier') and sampling times (time) upon Nested ANOVA (n=3).

Element	Significant concentration variation	
	Tier	time
Al	0.000	0.001
As	0.001	0.000
Ba	0.022	0.234
Be	0.366	0.612
Ca	0.001	0.276
Cd	0.045	0.123
Ce	0.012	0.235
Co	0.000	0.132
Cr	0.000	0.000
Cu	0.000	0.016
Fe	0.000	0.025
K	0.000	0.000
Li	0.000	0.002
Mg	0.000	0.000

Mn	0.016	0.000
Mo	0.045	0.062
Na	0.001	0.000
Ni	0.000	0.282
P	0.002	0.001
Pb	0.223	0.531
S	0.057	0.000
Sb	0.256	0.147
Se	0.156	0.089
Sn	0.489	0.284
Sr	0.154	0.000
Ti	0.072	0.000
Tl	0.125	0.045
V	0.000	0.000
Zn	0.000	0.822

Figures 3.4 and 3.5 show the spatial and temporal variations in the concentrations of some elements that showed significant patterns. The concentrations of Na, Al and K in sediments at all the tiers significantly decreased over the experiment time (Figure 3.4). The element concentrations of Ca, Mg and P decreased with time in the top two tiers (Tiers I and II) and increased with time in the bottom tier (Figure 3.5).

3.5.   Discussion

In natural river systems, the organic matter content, and the fine clay and silt particles play an important role in determining the element concentration in the sediments (Bogen 1992, Coquerry and Welbourn 1995, Stone et al. 1995, Jain and Ram 1997, Schorer 1997, Murray et al 1999, Thayyen et al. 1999, Onstad et al. 2000, Walling et al. 2000,

Al

K

Na
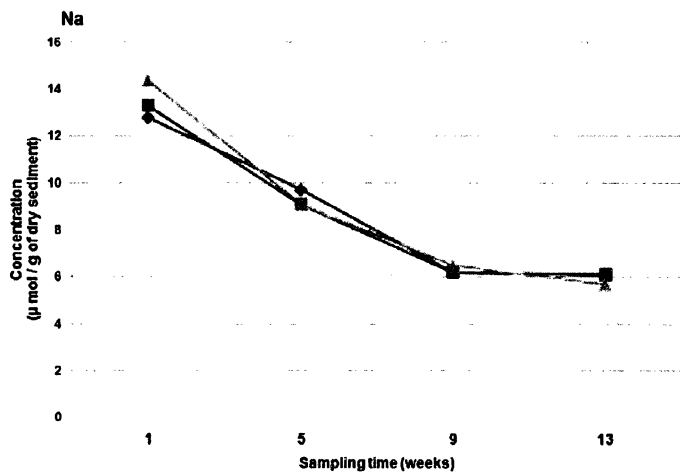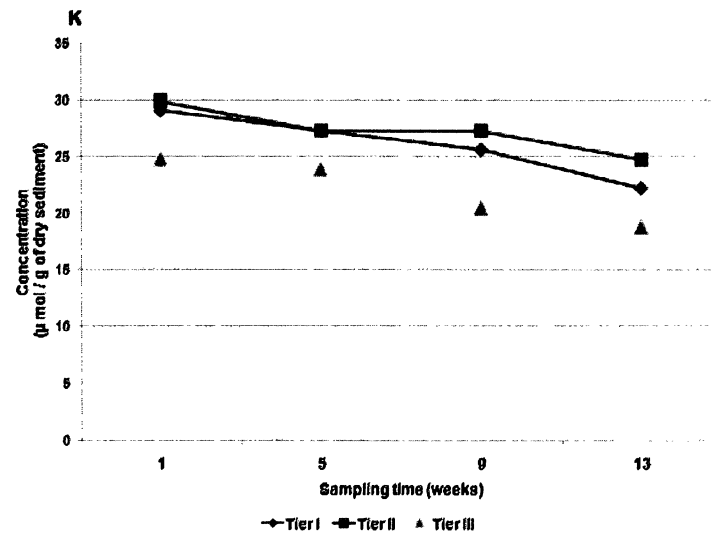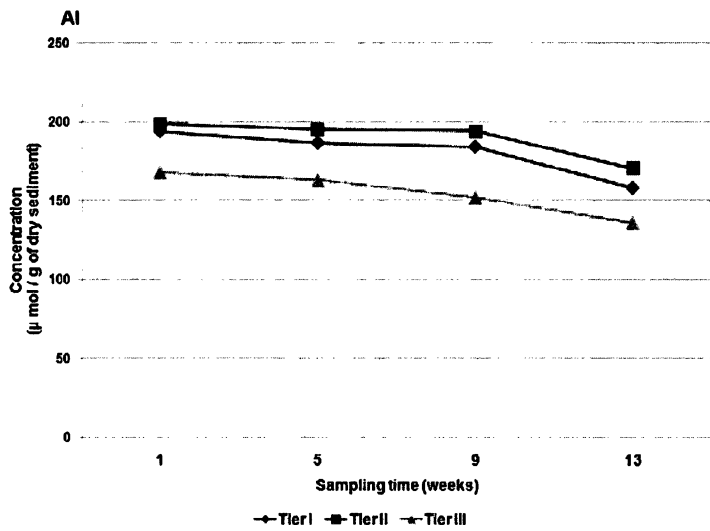
Figure 3.4: Spatial and temporal variation of Al, K and Na in the river simulation experiment.

Ca

Mg

P
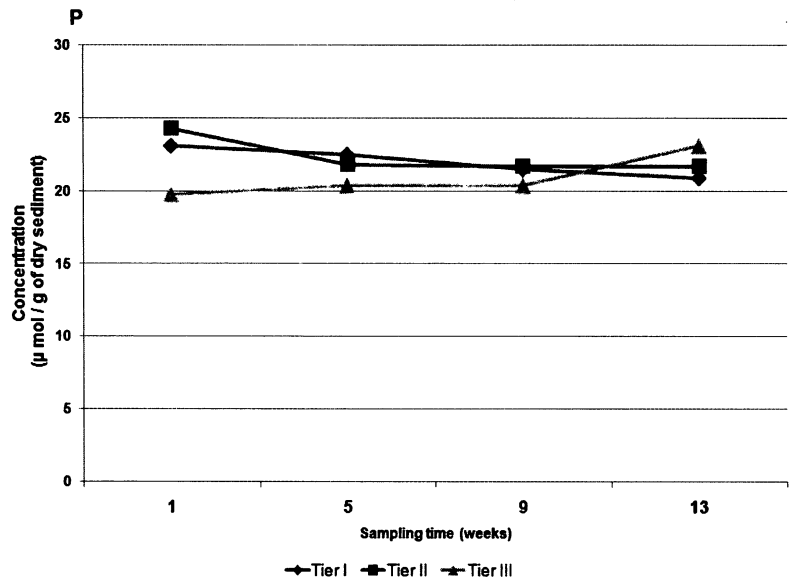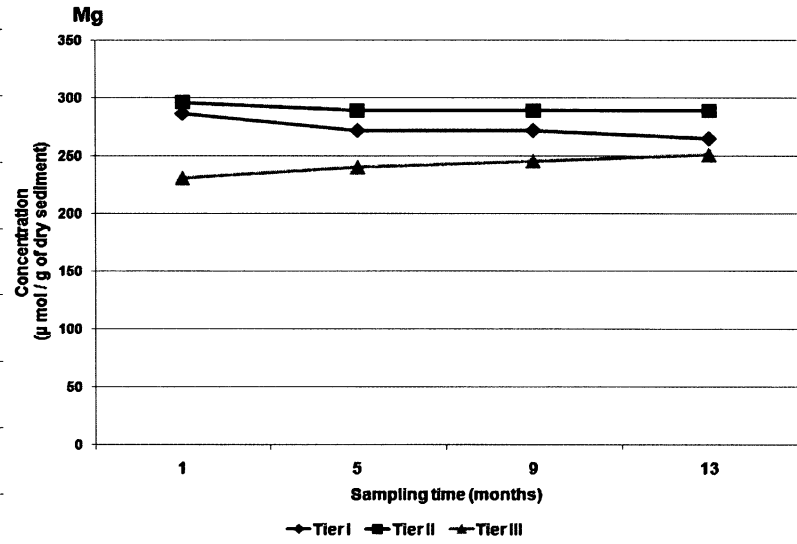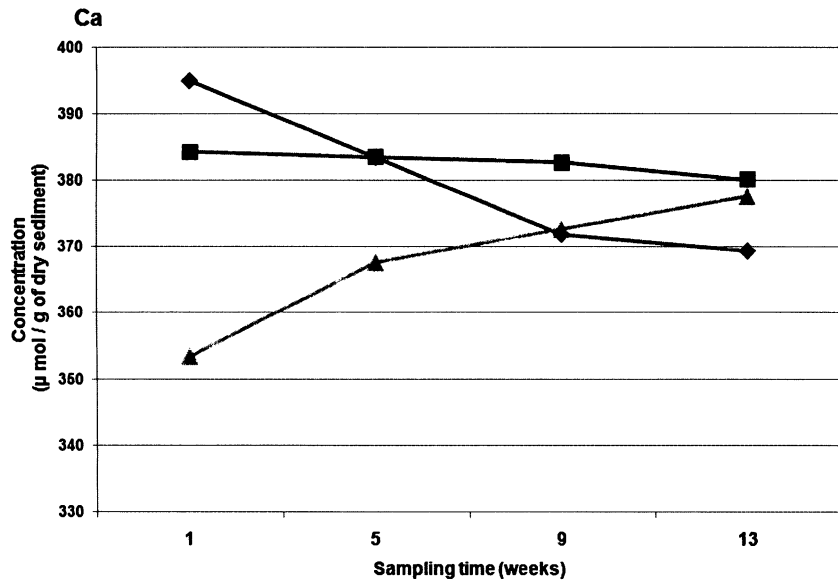
Figure 3.5: Spatial and temporal variation of Ca, Mg and P in the river simulation experiment.

Rognerud and Fjeld 2001,Ranville et al. 2005, Puyate et al. 2007). In this study the samples originated from the same river and sampling locations were in close proximity. It is therefore not surprising that values varied little and that no relationships between LOI and $f<63$ were observed.

In the soil mixing experiment, as expected, some elements showed significant concentration variations at different mixing ratios. The soil mixing study was done to confirm that it would result in element concentrations intermediate between those of the original two sediments in a linear fashion, in other words, to confirm that at least the majority of elements would show conservative behavior. In the dry mixtures, the deviations of measured element concentrations from the predicted concentrations were within the 95 % confidence interval of the normalized average deviation, i.e. all the elements showed linear mixing at all the mixing ratios (Figure 3.4 a). All the elements except Zn and Tl showed linear mixing behavior in wet conditions (Figure 3.4 b). However, given that the deviation was tested at the 95% confidence level, it would be expected that one or two elements out of all the elements tested would show a 'significant' difference due to type II error. In other words, this can be explained by the chance of observing a difference, when in fact there was none.

The concentrations of many elements (eg: Al, Fe, K, Na, S) in the wet sediments were lower compared to that of the dry sediments. This was observed both in the initial sediment samples and mixtures (Table 3.1). The element concentrations in the river sediments are in equilibrium with the concentration in the water column. Sediments have a limited capacity to adsorb trace elements from water. When the element concentrations in sediments exceed this capacity, the elements are released to the overlying water column

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and will be mobilized by water (Botes and Staden 2005).In this experiment, the wet sediments were in contact with distilled water for 72 hours, and then the water was removed from the system when the soil was filtered. The continuous interaction of water and sediments may have caused the diffusion of these elements into the water column, as it was expected. This shows that water can play a key role in determining the element concentrations in the sediments.

The river simulation experiment is an extension of the sediment mixing experiment, in which a continuous water flow was maintained to simulate the flowing water in a natural river system. In this experiment the concentrations of Na, Al and K in sediments at all the levels significantly decreased over time (Figure 3.4). This observation shows that these elements are removed from the sediments by running water. Not much research has been done to study the diffusion of elements from the sediments to the water column. A study done on the sediments of Lake Lagu, China has revealed that Na and K can be diffused into the overlying water column from the sediments (Fengchang et al. 1996). Some studies have revealed that the salts containing Al can be dissolved in water and thereby add these elements to the water column (Vojteková et al. 2003, 2008). These results agree with the hypothesis that the concentration of soluble elements in the sediments will decrease with time. Studies have revealed that river sediments contain ligands or functional groups (eg: carboxyl, phenolic, alcoholic and carbonyl) that can form stable complexes with some metal cations (eg: Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}). It was recorded that Cu^{2+}, Fe^{2+} Pb^{2+} and Zn^{2+} can maintain stable complexes over a wide range of pH (Johns and Jarvis 1981). The results of the river simulation experiment agreed with these results showing no significant concentration variations with time in Cu, Pb and Zn concentrations. This

observation showed that these elements are immobile in these sediments under the conditions that prevailed in the experiment.

Significant spatial and temporal differences in concentrations of Ca, P and Mg were identified (Figure3.6). These element concentrations decreased with time in the top two tiers (Tiers I and II) and it increased with time in the bottom tier. The temporal variations of the magnitude of difference of concentrations of these elements at the different levels of the river simulation experiment are given in Figure 3.6. The concentration of Ca, P and Mg increase in the bottom tiers were lower or equal to the concentrations lost at the top tiers (Figure 3.6). This showed that trace amounts of these elements in top levels were mobilized by running water and they were re-deposited in lower tier sediments.

In this experiment, the top tiers simulated upstream locations and the bottom tiers simulated downstream locations of a river. Therefore, these results also agreed with the hypotheses that, for some elements, the upstream sediments were acting as sediment sources for the downstream sediments. In natural conditions along rivers, sediments are released from actively eroding sites, while they deposit downstream in areas of low flow rates. They may be released again and consequently sinks become sources for deposition further downstream. Therefore the upstream and tributary sediments can act as sediment sources to the downstream sediment sink areas (Fairbridge 1978, Rosgen 1996, Leopold 2006, Charlton 2008).

These spatial and temporal variations of element concentrations can be due to both element mobility and sediment mobility along the experiment system. Use of tap water as the water source may have added elements into the system externally and it can be
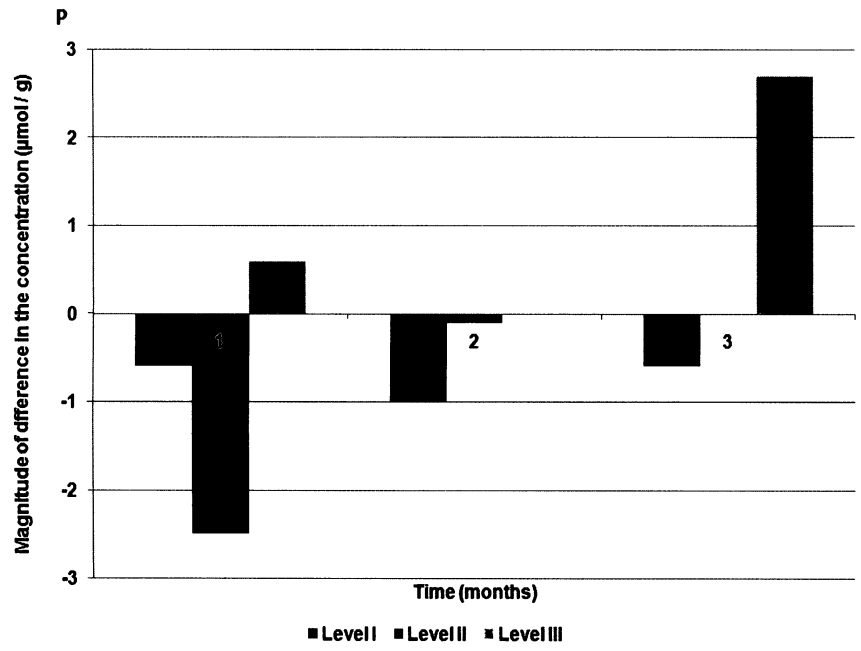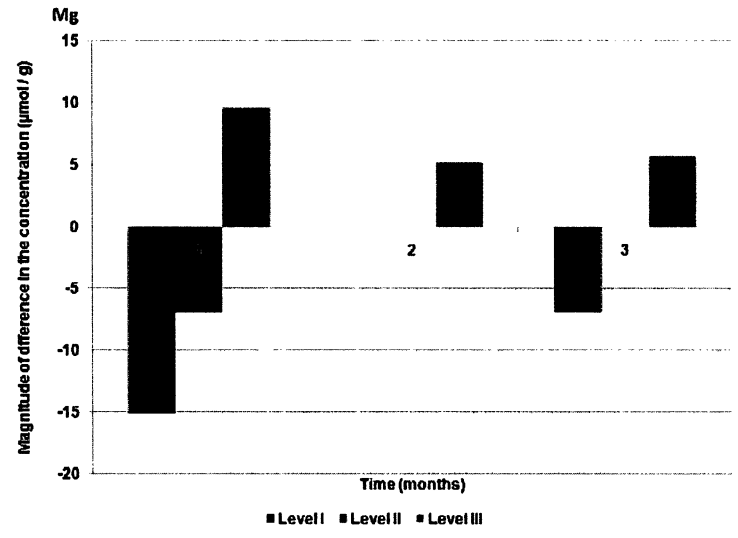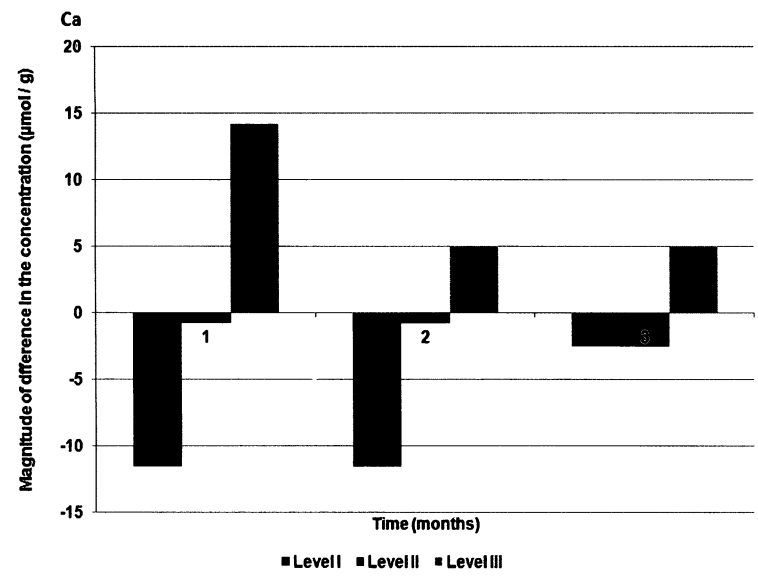
Figure 3.6: The temporal variations of the magnitude of difference of Ca, Mg and P concentrations in the river simulation experiment. The negative bars indicate the decrease of concentration than the previous sampling time and the positive bars indicate the increase of concentration than the previous sampling time.

considered as an experimental error associated with this experiment. Also another possible experiment error can be taking initial samples after 1 week from experimental set up. The concentration variations at the three tiers at initial sampling may have been caused by the water running through the trays for a week. In natural river systems, the transport and storage of elements are controlled by many physical (e.g. temperature, particle size), chemical (e.g. pH, Eh) and biological (particularly microorganisms, organic matter?) parameters in the environment (Gibbs 1973, Pojasek and Zajicek 1978, Tessier and Campbell 1987, Fórstner 1990, Gadd 2004, Hochella et al. 2005). In the experiment conducted here, these factors identical for all compartments. For example, temperature in the greenhouse varied over the course of the experiment, but was the same for all compartments at any given point in time. On the other hand, by necessity, this experiment lasted 13 weeks, whereas in natural rivers, the time spans over which the processes studied here occur continue for decades and centuries.

3.6. Conclusion

This research showed the presence of water can increase the mobility of some elements. The results of these laboratory studies verified the assumption that the elements are mixing conservatively. Most elements showed a spatial and temporal variation of the element concentration in the sediments indicating depletion of soluble elements and re-disposition for less mobile Ca, Mg and P. Therefore, the results agree with the hypotheses that the soluble elements are mobilized by water and that for some elements the upstream sediments are acting as sediment sources for the downstream sediments.

CHAPTER 4. A MULTI-ELEMENT FINGERPRINTING APPROACH TO IDENTIFY PHOSPHORUS CONTRIBUTION TO THE SOURIS RIVER SEDIMENTS.

4.1. Abstract

Phosphorus, a key element in biological systems and often a limiting nutrient, is found frequently in water-bodies. In this study the potential for tracing sediments acting as phosphate sources to the Souris River, North Dakota, was assessed using the 'multi-element fingerprinting' technique (53 elements). Organic matter content or particle size of the sediments did not play an important role in determining the element concentrations in Souris River sediments. Most elements showed similar mixing ratios between tributary and upstream sediments, which were calculated assuming linear mixing. The tributaries were identified as major contributors of sediments to the river and contributions varied among sites. The sediment contribution from the tributaries and the phosphorus concentrations were used to calculate the phosphorus contribution from the tributary sediments to the main river. The larger tributaries of the lower Souris River showed higher phosphorus contribution compared to the smaller tributaries of the Upper Souris River. The differences in phosphorus contributions may be related to land use, underlying geology, and the size of the watersheds of the tributaries.

4.2. Introduction

Phosphorus is considered to be a limiting nutrient in the environment due to its slow rate of weathering under natural conditions. Increased use of fertilizers in agriculture has resulted in additions of excess amounts of phosphorus to the environment. Phosphorus can bind with soil particles and enter water bodies through surface runoff. The presence of

excess phosphorus in water can lead to eutrophication, resulting in over-production of algae and other plants. This may lead to both ecological and social problems. Ecological problems include increased production of potentially toxic phytoplankton, decreased water transparency and depletion of dissolved oxygen (Chapra 1992, Newman 1995, Correl 1998, Reddy et al. 1999). Social problems include the high cost of water treatment, loss of aesthetic quality of the river and reduction of fish species, many of which are economically important (Chapra 1992, Newman 1995, Correl 1998, Reddy et al. 1999).

Phosphorus can be present in many forms in river sediments. These forms include soluble reactive phosphates, inorganic phosphorus or organic phosphorus. The soluble reactive phosphates (SRP) can be present as $H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-}. The inorganic phosphorus in the natural environment can be as particulate inorganic phosphorus (phosphate minerals, adsorbed on to clay particles, or complexed with solid matter) or non-particulate inorganic phosphorus (condensed forms of phosphorus similar to those found in detergents). Organic phosphorus in the natural environment can also be present as particulate organic phosphorus (in living plants, animals, bacteria and organic detritus) or non-particulate organic phosphorus (dissolved or colloidal organic compounds that contain phosphorus) (Earnshaw and Greenwood 1984, Chapra 1992, Correl 1998).

The amounts of phosphorus entering aquatic ecosystems vary depending on land use, the form of phosphorus in runoff waters, physical and chemical characteristics of soils and sediments, types of runoff events and the chemical, physical and biological characteristics of the receiving water bodies (Logan 1982, Gray and Kirkland 1986, Sharpley and Smith 1989, Sharpley et al. 1992, Abrams and Jarrel 1995). The concentration of phosphorus in sediments relies on the concentration of phosphorus in

water, transport of soluble phosphates, adsorption and absorption by sediments and biological uptake (Andersen 1975, Søndergaard et al. 1992, Koski-Vähälä and Hartikainen 2001, Koski-Vähälä et al. 2001, Valija and Culaj 2010). Many studies have focused on assessing the phosphorus concentrations and phosphorus speciation in lake and river sediments (Tiessen 1995, House and Denison 1998, 2002, Reddy et al. 1999, Kim et al. 2003, Li et al. 2003, Valija and Culaj 2010). None of these studies has focused on assessing the spatial variation of the phosphorus concentrations to identify possible sink and source areas. The current study addresses the spatial variation of phosphorus in the environmentally and politically sensitive Souris River, which repeatedly crosses the Canada-U.S.A. international border. There is concern regarding phosphate loading in the water and the cross-border consequences of phosphate transport. However, the geographic origin of the phosphate is undetermined. Pinpointing the sources of polluted suspended sediments is critical for pollution abatement and regulation. In this project the potential for tracing sediments acting as phosphate sources to the Souris River will be assessed using the 'multi-element fingerprinting' technique.

Multi-element fingerprinting identifies the distribution of elements within a matrix and thus defines a unique signature in comparison to similar matrices (Djingova et al. 2004). It provides a profile, which can then be used for direct sediment source tracing. This involves determining the 'fingerprint' concentration of many elements simultaneously. The technique provides quality and efficiency of analysis with Inductively Coupled Plasma spectrophotometry (ICP). Multi-element fingerprinting has been used in plants (Djingova et al. 2004, Otte and Jacob 2005, Kissoon et al. 2010) and in tracing suspended sediment sources in catchments and river systems (Walling 2005). This method

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has been widely used as a tool to define catchment areas and as a way to identify sediment and pollutant sources in a variety of environments, particularly in Europe e.g. salmon rivers and urban catchments. (Jordan et al. 1998, 2001, 2005, Russell et al. 2001, Jordan and Rippey 2003, Krause et al. 2003).

The aims of the present study were to use the multi-element fingerprinting technique to identify the potential source and sink areas of phosphorus and to study the spatial variation of phosphorus concentration in the Souris River sediments. It was hypothesized that upstream and tributary sediments are acting as sources to the downstream sediments, and the tributaries are the major contributors of sediments and phosphorus to the river compared to the upstream sediments. This would be evidenced by calculating the tributary contribution of phosphorus along the river at different tributary locations. It was also hypothesized that the organic matter content and the particle fraction < 63 μm of sediments can play a key role in determining the P concentration of the sediments.

4.3. Materials and methods

4.3.1. Study area

The Souris River originates in Saskatchewan, Canada, flows southeast across the international border into North Dakota, and then turns north and crosses the international border again back into Canada to join the Assiniboine River near Brandon, Manitoba. The river is perennial and contains many old oxbows, meander scars, and channel relicts. The basin area covers 63,714 Km^2. Three major reservoirs, Boundary, Rafferty, and Alameda are in the Canadian portions of the basin, while Lake Darling is in North Dakota. Very low mean flow rates are observed typically during the winter months. During the high flow

period in spring the rate is approximately 45 m^3 s^{-1} (ND Department of Health 2004, NRCS 2007).

The Souris River lies within the Northwestern climate division of North Dakota. This area experiences four distinct seasons, including warm summers and very cold winters. Temperatures reach below – 18 °C during the winter and reach above 38°C during the summer months. Precipitation is limited during winter months and the majority of rainfall occurs throughout the summer (NRCS 2007).

Land uses in the surrounding areas are mainly cultivated agricultural lands (64%) with some small pastures (1%) and open water areas (1%) (NRCS 2007).Canola, wheat, barley, sunflower, corn, flax, alfalfa, and pulse crops are among the most common cultivations. There are three major National Wildlife Refuges (NWR) located in the U.S. portion of the Souris River basin. They are the Upper Souris River NWR, the J. Clark Salyer NWR and the Des Lacs NWR (NRCS 2007).

4.3.2. Sample collection

Sediment samples were collected from two areas: 1) seven small tributaries between the Canadian border and Lake Darling (A- 48°57'56.30"N, 101°56'45.90"W; B - 48°55'34.70"N, 101°55'49.70"W; C - 48°55'6.40"N, 101°55'22.50"W; D - 48°52'29.30"N, 101°51'55.70"W; E - 48°48'52.42"N, 101°50'7.41"W; F - 48°48'53.78"N, 101°49'41.42"W; and G - 48°47'50.15"N, 101°48'56.26"W), and 2) from four large tributaries between Minot and Bottineau (H - Des Lacs River 48°16'47.87"N, 101°25'7.19"W; I - Oak Creek 48° 3'52.15"N, 100°57'42.34"W; J - Wintering River 48°11'48.27"N, 100°34'40.69"W; and K - Willow Creek 48°34'41.30"N, 100°32'30.79"W) (Figure 4.1).
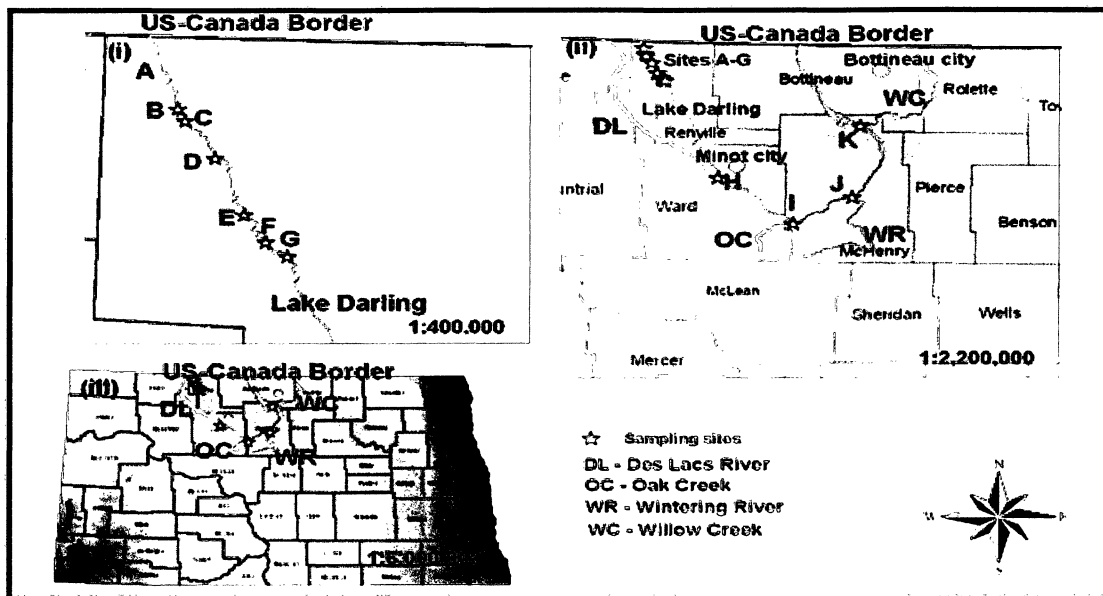
Figure 4.1: Souris River sampling sites: ((i) – Map showing Sampling sites in the upper Souris River area, (ii) – Map showing the four larger tributaries, (iii) – Map showing the general location of Souris River in ND, USA).

The seven small tributaries between the Canadian border and Lake Darling were

sampled in August 2008 and the four larger tributaries between Minot and Bottineau were

sampled in August 2009. The samples were collected in five replicates from the top layers

of sediment (maximum depth of sampling = 2 cm) proximal to the confluence of each

tributary to the main river channel. For the small tributaries (area 1), sampling consisted of

three locations: 1) in the tributary 50 m upstream from the confluence, 2) 50 m upstream

along the main river, and 3) 50 m downstream along the main river (Figure 4.2 a). At the

larger tributaries (area 2),sampling consisted of 11 locations: 1) at three 50 m intervals in

the tributary upstream from the confluence, 2) at three 50 m intervals in the main river

upstream, and 3) at five 50 m intervals in the main river downstream (Figure 4.2 b). When

sampling, eroding sites were sampled in the tributary and main river upstream locations

and depositing sites were sampled in the main river downstream locations because we

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expected that tributary and downstream sediments are acting as sediment sources to the downstream sediments.

4.3.3. Sample preparation and multi-element analysis

The samples were collected by inverting a plastic zip-lock bag as a glove to grab the sample, then folding it back over the sample. The sealed bags were stored in ice and transported to the laboratory. The samples were dried until they reached a constant weight at 60 °C, then homogenized in a mortar and pestle and sieved through a 180 μm sieve. These samples were sent to Acme Analytical Laboratories Ltd, Vancouver, Canada, to be analyzed for multiple elements using the group 1F MS-1F04 analytical package. At Acme Analytical Laboratories Ltd, a modified aqua regia solution of equal parts concentrated ACS grade HCl and HNO_3 and de-ionized H_2O was added to each sample (6 mlg^{-1}) to leach in a hot-water bath (~95°C) for one hour. After cooling, a 5% HCL solution was added to achieve a final volume with a 0.5 g per 10 mL sample weight-to-solution volume ratio. These solutions were aspirated into a Perkin Elmer Elan 6000 ICP mass spectrometer to analyze for 53 elements (detection limits as reported by Acme Analytical Laboratories Ltd in μg L^{-1}:Ag(2), As(0.1), Al(100), Au(0.002), B(20), Ba(0.5), Be(0.1), Bi(0.02), Ca(100), Cd(0.01), Ce(0.1), Co(0.1), Cr(0.5), Cs(0.02), Cu(0.01), Fe(100), Ga(0.1), Ge(0.1), Hf(0.02), Hg(0.5), In(0.02), K(100), La(0.5), Li(0.1), Mg(100), Mn(1), Mo(0.01), Na(10), Nb(0.02), Ni(0.1), P(10), Pb(0.01), Pd(0.1), Pt(0.002), Rb(0.1), Re(0.001), S(200), Sb(0.02), Sc(0.1), Se(0.1), Sn(0.1), Sr(0.5), Ta(0.05), Te(0.02), Th(0.1), Ti(10), Tl(0.02), U(0.1), V(2), W(0.1), Y(0.01), Zn(0.1) and Zr(0.1). Throughout the remainder of the paper molar units will be used.
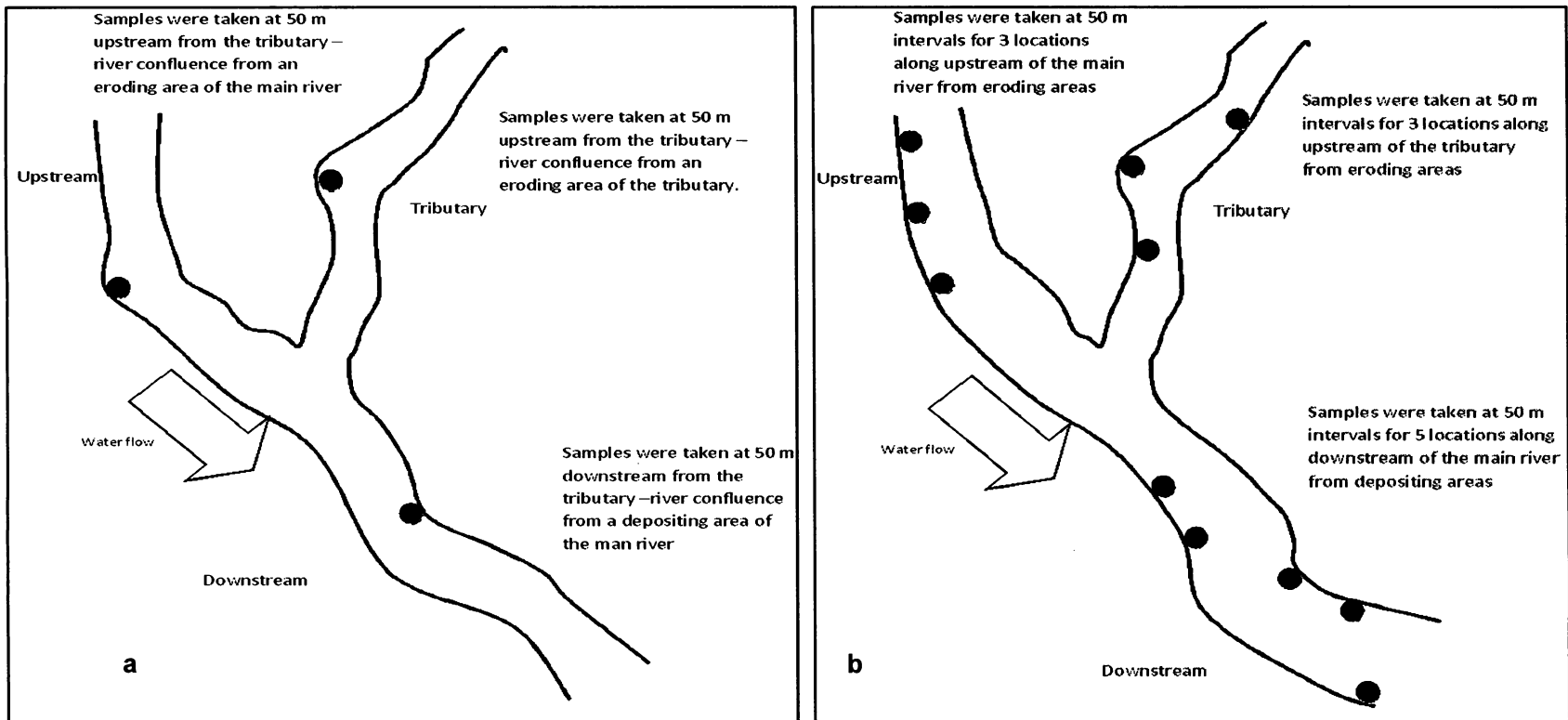
Figure 4.2: Sampling plan (a-Seven Small tributaries in the Upper Souris River; b- Larger tributaries in the Lower Souris River).

4.3.4. Loss-on-ignition

Loss-on-ignition (LOI) was used to determine organic matter content. About 15 g of dried homogenized samples were dried further at 105 °C in ceramic crucibles for 2 hours. The dry weight (W_d) of these samples was recorded. They were then ashed at 550 °C for 2 hours in a Sybron Thermoclyne muffle furnace and the weights of the remaining ash was recorded (W_a). The percentage LOI was calculated as ((W_d -W_a) / W_d) x 100.

4.3.5. Fraction of particles smaller than 63 µm (f<63)

The ash was then used for determination of the fraction of particles smaller than 63µm (f<63). The initial dry weight of the ash was recorded (W_i). These samples were wet-sieved through 63 µm sieve using distilled water. The material remaining on the sieve was collected onto a Whatman No. 1 filter paper, oven-dried at 60°C and dry weight of the ash recorded (W_r). The percentage f< 63 was calculated as ((W_i - W_r) / W_i) x 100.

4.3.6. Data analysis

Minitab 15 statistical software (Minitab® 15.1.30) was used for all statistical analyses. All data were $\log_{10}$ transformed before statistical analysis to obtain normal distribution and homogeneity of variance. Pearson correlation analysis was performed on element concentrations, f<63 and LOI. One-way ANOVA followed by Tukey's pair-wise comparison was used to analyze variation of element concentrations at each site.

The element concentrations upstream, downstream and tributary sediments at the tributary river confluence of each site were used for a series of calculations. I) A multi-element fingerprint was developed for each tributary, consisting of the concentrations for each element for confluence along with a fingerprint of the element concentrations along the river as it runs from upstream to downstream (e.g. Figure 4.3). II) The mean

contribution of sediment from each tributary was estimated from calculating the mean

overall percentage of contribution of elements from the tributary (see calculation below).

III) Because of the concerns of high phosphorous levels in this river, the contribution of P

from each tributary was calculated based on the concentrations of P in the sediments and

the relative sediment contributions to the river (see calculation below).

I) Multi-element fingerprint and concentration with river flow

Multi-element fingerprints for each tributary confluence were constructed by

plotting the sediment concentrations in the three sampling locations nearest to a tributary

confluence: in the tributary, the closest site upstream in the main river, and the closest site

downstream.

II) Contribution of sediment from each tributary

The contribution of the tributary (a_x) for the elements except phosphorus at each

sampling site was calculated assuming linear mixing between upstream and tributary

sediments, as follows.

$$[X]_D = a_x[X]_T + b_x[X]_U \qquad \text{Eq(4.1)}$$

$$\text{and} \quad a_x + b_x = 1 \qquad \text{Eq(4.2)}$$

and therefore

$$a_x = \frac{[X]_D - [X]_U}{[X]_T - [X]_U} \qquad \text{Eq (4.3)}$$

Where,

a_x-Mean contribution of tributary for element x

b_x- Mean Contribution of upstream for element x

$[X]_D$- Mean Concentration of element$x$ at the downstream location

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$[X]_U$- Mean Concentration of element x at the upstream location

$[X]_T$- Mean Concentration of element x at the tributary location

III) Contribution of P from each tributary

Elements with estimated contributions of more than 1 or less than 0 clearly did not meet the assumptions of conservative, linear mixing and so were not further taken into consideration for calculations. Most elements showed a tributary contribution between 0 and 1, or 0% and 100%, and the average value for a_x for those elements was considered the best estimate for the sediment contribution from the tributaries to the river.

The calculated mean sediment contributions from the tributaries were used to estimate the contribution of phosphorus from the tributary (C_p) at each site, as follows.

$$C_p = \frac{A_t*[P_t]}{(A_t*[P_t])+(A_u*[P_u])} \times 100 \qquad\qquad Eq(4.4)$$

Where,

A_t – Mean sediment contribution from the tributary

A_u – Mean sediment contribution from upstream of the main river

P_t – Mean measured phosphorus concentration in tributary sediments

P_u – Mean measured phosphorus concentration in the upstream sediments

4.4. Results

4.4.1. Correlation with f<63 and LOI and element concentrations

LOI ranged from 0.12 %- 18.4% with a mean of 3%. The percentage f< 63 ranged from 24.1 %- 98% with a mean of 84%. None of the elements showed a statistically significant correlation with LOI or f<63, nor did LOI correlate significantly with f<63.

Most of the elements did not show statistically significant correlations. Phosphorus

concentrations were significantly correlated to aluminum ($r^2 = 0.8$, $P = 0.000$), iron ($r^2 = 0.8$, $P=0.000$) and manganese ($r^2 = 0.6$, $P = 0.000$).

4.4.2. Analysis of elements and development of fingerprints

The element concentrations of Ag, Au, Ta, Te, W, B, Ba, In, Pd, Pt, Re, Ge and Hg

were below detection limit and will not be discussed further. The concentrations of other

elements were used to create multi-element fingerprints for each site. An example of a

fingerprint prepared for the Des Lacs tributary is given in Figure 4.3. Similar fingerprints

were prepared for all other sampling sites.
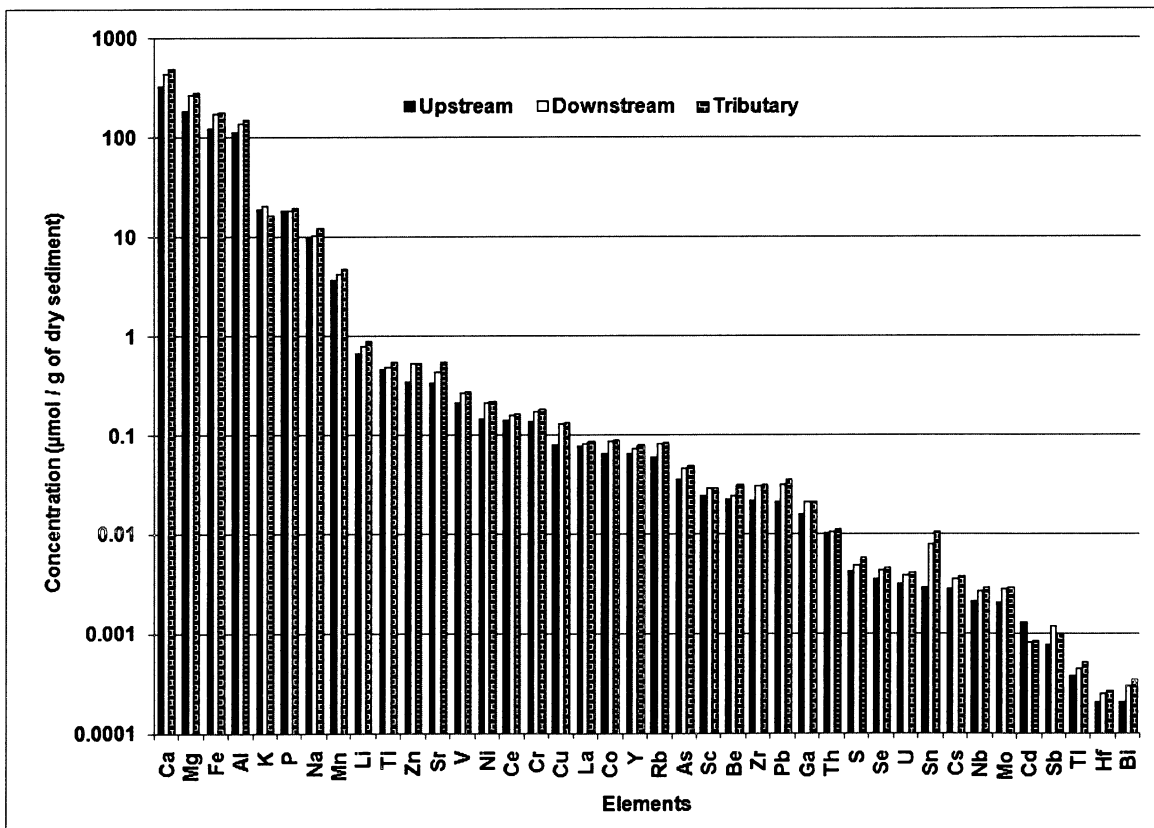
Figure 4.3: Multi-element fingerprint of sediments from the Des Lacs River tributary, and upstream and downstream locations of the Souris River (48°16'47.87"N, 101°25'7.19"W). Elements are ordered from high to low concentrations based upon the 'upstream' samples.

The mean concentration of elements in the near confluence, upstream, downstream

and tributary locations at each site are given in Table 4.1. In most sites, concentrations of

some elements (e.g. Mo, Cu, Na, Zn, Ni, Co, Fe, Cd, Mg, K, S) in the upstream locations

were significantly lower compared to the concentrations at the downstream and tributary

locations. The tributary concentrations of most elements were significantly higher

compared to both the upstream and downstream concentrations (Table 4.1). Hf, Tl, Sb and

U did not show significant concentration variations in the upstream, tributary or

downstream locations in any of the sites ($P \geq 0.05$). Therefore, those element concentrations

are not presented in Table 4.1.

Table 4.1: Mean concentration (± standard deviation)of elements (μmol g^{-1}dry sediment; unless otherwise stated) in the near confluence upstream downstream and tributary locations of the Souris River sampling sites. For each row, data presented by different superscripts are significantly different from each other (ANOVA, Tukey's pair wise comparison; $P<0.01$; $n=5$). (A-G – sites upstream of Lake Darling, DL-Des Lacs River, OC – Oak Creek, WR – Wintering River, WC – Willow Creek).

Element	Site	Upstream	Downstream	Tributary	P Value
Al	A	88±23	122±20	149±10	0.032
	B	132±11[a]	143±2[a]	165±2[b]	0.004
	C	142±13[a]	151±8[a]	191±13[b]	0.005
	D	204±17[a]	230±7[b]	290±26[c]	0.003
	E	188±23	201±10	235±17	0.053
	F	221±2[a]	226±45[a]	337±30[b]	0.009
	G	307±18[a]	359±3[b]	425±54[c]	0.009
	DL	112±20	136±17	147±9	0.015
	OC	130±46	137±23	144±41	0.845
	WR	270±14	288±20	304±20	0.111
	WC	350±56[a]	357±73[a]	432±64[b]	0.009
As	A	0.023±0.004[a]	0.036±0.005[b]	0.039±0.003[b]	0.006

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	B	0.04±0.005	0.06±0.007	0.07±0.02	0.081
	C	0.04±0.007	0.06±0.023	0.06±0.001	0.103
	D	0.05±0.002[a]	0.05±0.002[a]	0.08±0.009[b]	0.000
	E	0.04±0.002	0.05±0.004	0.05±0.006	0.322
	F	0.05±0.008[a]	0.05±0.005[a]	0.09±0.006[b]	0.001
	G	0.06±0.007	0.07±0.004	0.1±0.03	0.106
	DL	0.03±0.005	0.04±0.005	0.04±0.01	0.036
	OC	0.05±0.01	0.05±0.006	0.05±0.01	0.430
	WR	0.06±0.006[a]	0.09±0.007[b]	0.09±0.005[b]	0.000
	WC	0.05±0.01	0.07±0.02	0.08±0.01	0.018
Be	A	0.02±0.00	0.03±0.006	0.03±0.03	0.075
	B	0.03±0.01	0.03±0.011	0.04±0.015	0.536
	C	0.02±0.001	0.03±0.006	0.033±0.011	0.238
	D	0.03±0.001[a]	0.04±0.006[b]	0.06±0.001[c]	0.001
	E	0.03±0.006	0.03±0.001	0.04±0.006	0.128
	F	0.04±0.01	0.05±0.01	0.05±0.01	0.225
	G	0.05±0.006	0.05±0.001	0.07±0.01	0.049
	DL	0.02±0.005	0.02±0.005	0.03±0.005	0.088
	OC	0.03±0.006	0.03±0.01	0.03±0.006	0.526
	WR	0.05±0.01	0.06±0.01	0.06±0.006	0.477
	WC	0.04±0.01	0.07±0.01	0.07±0.02	0.020
	A	0.2±0.02	0.3±0.01	0.6±0.01	0.026
Bi	B	0.3±0.1	0.4±0.1	0.5±0.1	0.035
(nmol / g)	C	0.3±0.1[a]	0.4±0.1[ab]	0.5±0.1[b]	0.013
	D	0.6±0.1[a]	0.6±0.1[a]	0.8±0.1[b]	0.040
	E	0.5±0.1	0.6±0.1	0.6±0.1	0.365
	F	0.7±0.1[a]	0.9±0.1[b]	0.9±0.1[b]	0.017

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	G	0.2±0. 1	0.3±0. 1	0.3±0. 1	0.203
	DL	0.2±0. 1	0.3±0. 1	0.4±0. 1	0.309
	OC	0.5±0. 1	0.7±0. 1	0.8±0. 3	0.037
	WR	0.2±0. 1	0.3±0. 1	0.4±0. 1	0.523
	WC	0.4±0. 1[a]	0.9±0. 1[b]	0.9±0. 1[b]	0.014
Ca	A	195±33[a]	463±52[b]	509±26[b]	0.000
	B	435±23	443±43	462±97	0.919
	C	431±24	443±21	555±99	0.063
	D	222±87[a]	493±11[b]	529±19[b]	0.004
	E	412±11	468±220	854±225	0.050
	F	595±249	856±118	1345±125	0.015
	G	309±10[a]	567±27[b]	670±33[b]	0.000
	DL	327±58	427±19	475±92	0.010
	OC	327±24	403±45	412±64	0.029
	WR	493±25[a]	582±66[b]	694±13[c]	0.000
	WC	308±76[a]	444±41[b]	469±70[b]	0.001
Cd	A	0.001±0.000001	0.001±0.00001	0.001±0.00001	0.016
	B	0.001±0.0001[a]	0.002±0.0001[b]	0.002±0.0001[b]	0.009
	C	0.001±0.001	0.002±0.001	0.003±0.001	0.021
	D	0.002±0.0001[a]	0.002±0.0001[a]	0.003±0.001[b]	0.006
	E	0.002±0.001	0.002±0.001	0.003±0.001	0.118
	F	0.002±0.001	0.003±0.001	0.004±0.001	0.008
	G	0.003±0.001[a]	0.003±0.001[a]	0.005±0.001[b]	0.000
	DL	0.001±0.0001	0.001±0.0001	0.001±0.0001	0.301
	OC	0.001±0.001	0.001±0.001	0.001±0.001	0.301
	WR	0.003±0.001	0.003±0.001	0.003±0.001	0.050
	WC	0.003±0.001[a]	0.003±0.001[a]	0.001±0.0001[b]	0.000

Table 4.1: (continued)

Ce	A	0.1±0.02	0.1±0.01	0.1±0.004	0.088
	B	0.1±0.014	0.1±0.005	0.2±0.004	0.037
	C	0.1±0.006[a]	0.1±0.005[a]	0.2±0.006[b]	0.001
	D	0.1±0.006	0.2±0.003	0.2±0.02	0.034
	E	0.1±0.006	0.1±0.008	0.2±0.009	0.757
	F	0.1±0.007[a]	0.1±0.003[a]	0.2±0.007[b]	0.002
	G	0.2±0.004	0.2±0.005	0.2±0.005	0.031
	DL	0.1±0.01[a]	0.1±0.008[a]	0.2±0.008[b]	0.009
	OC	0.1±0.008[a]	0.1±0.01[a]	0.2±0.01[b]	0.000
	WR	0.0±0.01	0.2±0.01	0.2±0.004	0.358
	WC	0.2±0.02	0.2±0.03	0.2±0.01	0.047
Co	A	0.052±0.005	0.068±0.009	0.07±0.004	0.019
	B	0.08±0.002	0.09±0.009	0.1±0.004	0.077
	C	0.07±0.01[a]	0.08±0.001[b]	0.1±0.006[c]	0.000
	D	0.1±0.008	0.1±0.002	0.1±0.008	0.014
	E	0.1±0.008	0.1±0.007	0.1±0.009	0.077
	F	0.1±0.02	0.1±0.004	0.1±0.005	0.018
	G	0.1±0.005	0.1±0.005	0.1±0.019	0.237
	DL	0.06±0.005 [a]	0.09±0.015[b]	0.09±0.006[b]	0.007
	OC	0.08±0.01	0.08±0.01	0.09±0.02	0.320
	WR	0.1±0.002	0.1±0.004	0.1±0.006	0.292
	WC	0.09±0.005[a]	0.1±0.02[b]	0.1±0.01[b]	0.000
Cr	A	0.1±0.02	0.1±0.02	0.2±0.01	0.018
	B	0.1±0.014[a]	0.2±0.004[b]	0.2±0.004[b]	0.001
	C	0.2±0.01	0.2±0.03	0.2±0.01	0.034
	D	0.2±0.02	0.3±0.009	0.3±0.04	0.051
	E	0.2±0.02	0.2±0.017	0.32±0.02	0.074
	F	0.2±0.04	0.3±0.002	0.3±0.02	0.010

	G	0.3 ± 0.008^a	0.4 ± 0.008^b	0.4 ± 0.039^b	0.007
	DL	0.1 ± 0.005^a	0.2 ± 0.01^b	0.2 ± 0.01^b	0.001
	OC	0.2 ± 0.01	0.2 ± 0.02	0.2 ± 0.03	0.067
	WR	0.2 ± 0.02	0.2 ± 0.02	0.2 ± 0.02	0.201
	WC	0.2 ± 0.02^a	0.4 ± 0.07^b	0.4 ± 0.04^b	0.000
Cs	A	0.002 ± 0.0001	0.003 ± 0.0001	0.004 ± 0.0001	0.018
	B	0.003 ± 0.0001^a	0.004 ± 0.0001^b	0.005 ± 0.0001^c	0.002
	C	0.003 ± 0.001^a	0.004 ± 0.001^b	0.005 ± 0.001^b	0.002
	D	0.005 ± 0.0001	0.005 ± 0.0001	0.006 ± 0.0001	0.019
	E	0.005 ± 0.001	0.005 ± 0.001	0.005 ± 0.001	0.096
	F	0.004 ± 0.001^a	0.005 ± 0.001^b	0.005 ± 0.001^b	0.004
	G	0.006 ± 0.001	0.006 ± 0.001	0.007 ± 0.001	0.107
	DL	0.003 ± 0.0001^a	0.003 ± 0.001^a	0.004 ± 0.0001^b	0.003
	OC	0.003 ± 0.001	0.004 ± 0.001	0.004 ± 0.001	0.120
	WR	0.004 ± 0.0001^a	0.005 ± 0.0001^b	0.006 ± 0.0001^c	0.000
	WC	0.004 ± 0.001^a	0.005 ± 0.001^b	0.006 ± 0.001^c	0.001
Cu	A	0.054 ± 0.015	0.105 ± 0.01	0.108 ± 0.021	0.011
	B	0.1 ± 0.013^a	0.1 ± 0.001^a	0.2 ± 0.005^b	0.001
	C	0.1 ± 0.01	0.1 ± 0.007	0.2 ± 0.05	0.016
	D	0.2 ± 0.01	0.2 ± 0.008	0.2 ± 0.04	0.051
	E	0.2 ± 0.02	0.2 ± 0.03	0.2 ± 0.04	0.065
	F	0.2 ± 0.04^a	0.2 ± 0.01^a	0.3 ± 0.01^b	0.009
	G	0.2 ± 0.01^a	0.3 ± 0.005^b	0.4 ± 0.01^c	0.000
	DL	0.08 ± 0.007^a	0.1 ± 0.02^b	0.1 ± 0.01^b	0.000
	OC	0.09 ± 0.02	0.1 ± 0.01	0.1 ± 0.04	0.501
	WR	0.1 ± 0.01^a	0.2 ± 0.002^b	0.2 ± 0.014^b	0.000
	WC	0.2 ± 0.07	0.3 ± 0.04	0.3 ± 0.01	0.024
Fe	A	93 ± 19	127 ± 19	150 ± 12	0.023

	B	159±4	167±14	189±6	0.028
	C	167±18	234±17	243±111	0.315
	D	207±21	230±3	273±27	0.017
	E	201±18	202±18	235±16	0.105
	F	205±40[a]	227±10[a]	328±14[b]	0.006
	G	287±13	348±2	382±52	0.020
	DL	120±10[a]	172±27[b]	175±25[b]	0.004
	OC	155±43	188±20	190±35	0.232
	WR	315±18	327±9	343±15	0.043
	WC	169±16[a]	364±24[b]	382±26[b]	0.000
Ga	A	0.01±0.004	0.01±0.004	0.02±0.001	0.055
	B	0.03±0.002[a]	0.02±0.0001[b]	0.03±0.0001[a]	0.004
	C	0.02±0.001[a]	0.02±0.002[a]	0.03±0.001[b]	0.001
	D	0.03±0.003	0.03±0.001	0.04±0.007	0.038
	E	0.03±0.003	0.03±0.003	0.03±0.002	0.141
	F	0.03±0.006[a]	0.03±0.001[a]	0.05±0.004[b]	0.005
	G	0.04±0.002[a]	0.05±0.002[b]	0.05±0.004[b]	0.001
	DL	0.02±0.002	0.02±0.001	0.02±0.003	0.303
	OC	0.02±0.002	0.02±0.001	0.02±0.003	0.303
	WR	0.038±0.002	0.038±0.003	0.039±0.003	0.671
	WC	0.02±0.003a	0.05±0.012[b]	0.05±0.002[b]	0.000
K	A	12±2	20±2	21±4	0.019
	B	19±1[a]	20±1[a]	26±1[b]	0.002
	C	19±1	21±1	24±2	0.052
	D	29±2[a]	35±2[b]	61±13[c]	0.002
	E	27±3	31±3	38±4	0.048
	F	34±1	35±7	50±3	0.016
	G	46±2[a]	55±1[b]	65±2[c]	0.000

	DL	18 ± 2^a	23 ± 4^b	15 ± 2^a	0.005
	OC	20 ± 3	20 ± 5	22 ± 5	0.699
	WR	35 ± 3^a	40 ± 4^{ab}	$42\pm1.^b$	0.001
	WC	37 ± 9	46 ± 4	50 ± 5	0.049
La	A	0.05 ± 0.01	0.05 ± 0.007	0.07 ± 0.003	0.087
	B	0.06 ± 0.003^a	0.08 ± 0.004^b	0.09 ± 0.002^b	0.000
	C	0.06 ± 0.007^a	0.08 ± 0.003^b	0.08 ± 0.003^b	0.006
	D	0.09 ± 0.002	0.1 ± 0.003	0.1 ± 0.01	0.046
	E	0.08 ± 0.006	0.09 ± 0.007	0.09 ± 0.004	0.562
	F	0.07 ± 0.003^a	0.09 ± 0.004^b	0.09 ± 0.002^b	0.001
	G	0.1 ± 0.002	0.1 ± 0.001	0.1 ± 0.004	0.021
	DL	0.07 ± 0.005	0.08 ± 0.006	0.08 ± 0.01	0.171
	OC	0.08 ± 0.007	0.09 ± 0.012	0.09 ± 0.007	0.042
	WR	0.1 ± 0.003	0.1 ± 0.003	0.1 ± 0.003	0.266
	WC	0.09 ± 0.01^a	0.1 ± 0.009^b	0.1 ± 0.01^b	0.009
Li	A	0.5 ± 0.098	0.6 ± 0.123	0.8 ± 0.063	0.054
	B	0.8 ± 0.06^a	0.8 ± 0.02^a	0.9 ± 0.02^b	0.006
	C	0.8 ± 0.04^a	0.8 ± 0.05^a	1.1 ± 0.04^b	0.001
	D	1.1 ± 0.08	1.3 ± 0.02	1.3 ± 0.1	0.134
	E	1 ± 0.1	1.1 ± 0.09	1.3 ± 0.08	0.085
	F	1.1 ± 0.2	1.3 ± 0.05	1.7 ± 0.1	0.019
	G	1.5 ± 0.04	1.7 ± 0.06	1.9 ± 0.2	0.034
	DL	0.6 ± 0.1	0.7 ± 0.1	0.8 ± 0.07	0.019
	OC	0.8 ± 0.09	0.9 ± 0.1	0.9 ± 0.2	0.828
	WR	1.5 ± 0.1	1.6 ± 0.05	1.6 ± 0.07	0.020
	WC	1.4 ± 0.08^a	1.9 ± 0.1^b	2 ± 0.4^b	0.008
Mg	A	148 ± 18^a	251 ± 45^a	352 ± 26^b	0.001
	B	286 ± 8	320 ± 66	336 ± 6	0.388

	C	276±11	278±14	296±10	0.199
	D	226±59[a]	381±8[b]	401±6[b]	0.005
	E	333±16	370±217	390±18	0.783
	F	349±62	451±8	457±22	0.031
	G	296±29[a]	457±12[b]	492±16[b]	0.000
	DL	181±24[a]	261±17[b]	275±29[b]	0.000
	OC	250±30	257±39	271±36	0.664
	WR	371±29	403±12	416±15	0.013
	WC	263±82	307±35	341±18	0.104
Mn	A	2.8±0.4[a]	3.9±0.09[b]	4.6±0.7[b]	0.009
	B	3.7±0.518	3.7±0.374	4.3±0.791	0.435
	C	2.4±0.6	4.2±1.13	5.1±0.5	0.016
	D	4.7±0.3[a]	5.9±0.2[b]	7.1±0.6[c]	0.001
	E	3.9±0.7	5.7±1.1	7.9±1.7	0.017
	F	5.5±2.6	7.9±1.7	14.3±1.9	0.015
	G	6.3±0.3	9.2±0.5	9.8±1.9	0.014
	DL	3.6±0.2	4.2±0.2	4.7±1.6	0.227
	OC	3.4±0.5	5.3±1.8	5.9±1.3	0.022
	WR	9.5±1	9.9±1.3	10.1±1.2	0.731
	WC	5.6±1.2[a]	11.6±1.6[b]	13.8±1.2[b]	0.000
Mo	A	0.001±0.00001[a]	0.002±0.0001[b]	0.002±000001[b]	0.007
	B	0.002±0.0001[a]	0.003±0.001[b]	0.005±0.001[c]	0.004
	C	0.002±0.001	0.004±0.001	0.005±0.003	0.119
	D	0.002±0.0001[a]	0.002±0.0001[a]	0.004±0.001[b]	0.003
	E	0.003±0.03[a]	0.004±0.001[a]	0.006±0.002[b]	0.008
	F	0.004±0.001[a]	0.007±0.001[b]	0.009±0.002[c]	0.012
	G	0.003±0.001[a]	0.004±0.001[a]	0.02±0.01[b]	0.007
	DL	0.002±0.001	0.003±0.001	0.003±0.001	0.093

	OC	0.001±0.0001	0.002±0.001	0.002±0.0001	0.141
	WR	0.002±0.001	0.002±0.001	0.003±0.001	0.149
	WC	0.002±0.0001[a]	0.004±0.001[b]	0.005±0.001[c]	0.000
Na	A	2±1[a]	6±1[b]	12±2[c]	0.002
	B	3±0.2[a]	14±1[b]	17±0.2[c]	0.000
	C	6±0[a]	6±0[a]	14±2[b]	0.000
	D	3±0[a]	14±2[b]	17±2[b]	0.000
	E	9±0[a]	14±1[b]	19±3[c]	0.001
	F	18±4	19±7	27±3	0.181
	G	18±1	18±1	19±2	0.739
	DL	9±0	10±2	12±1	0.183
	OC	10±1	13±3	16±2	0.016
	WR	21±2	24±2	24±2	0.020
	WC	26±3	32±3	32±4	0.087
Nb	A	0.002±0.0001	0.003±0.0001	0.003±0.001	0.142
	B	0.002±0.0001a	0.003±0.0001[b]	0.004±0.002[c]	0.000
	C	0.003±0.001[a]	0.003±0.001[a]	0.004±0.001[b]	0.009
	D	0.004±0.0001	0.004±0.0001	0.005±0.001	0.362
	E	0.003±0.001	0.004±0.001	0.004±0.001	0.033
	F	0.003±0.001	0.004±0.001	0.004±0.001	0.048
	G	0.003±0.001[a]	0.003±0.001[a]	0.004±0.001[b]	0.010
	DL	0.002±0.0001	0.003±0.001	0.003±0.0001	0.033
	OC	0.002±0.001	0.002±0.001	0.002±0.001	0.063
	WR	0.003±0.0001[a]	0.004±0.001[b]	0.005±0.001[c]	0.008
	WC	0.002±0.001	0.003±0.001	0.004±0.002	0.066
Ni	A	0.09±0.02[a]	0.1±0.02[b]	0.2±0.01[b]	0.007
	B	0.1±0.004[a]	0.2±0.01[b]	0.2±0.007[b]	0.004
	C	0.2±0.02[a]	0.2±0.021[a]	0.3±0.012[b]	0.003

	D	0.2 ± 0.03^a	0.3 ± 0.003^b	0.3 ± 0.025^b	0.006
	E	0.2 ± 0.03	0.2 ± 0.02	0.3 ± 0.02	0.186
	F	0.2 ± 0.01^a	0.3 ± 0.01^a	0.4 ± 0.02^b	0.007
	G	0.3 ± 0.02	0.4 ± 0.006	0.4 ± 0.03	0.011
	DL	0.1 ± 0.01^a	0.2 ± 0.01^b	0.2 ± 0.01^b	0.000
	OC	0.1 ± 0.01	0.2 ± 0.04	0.2 ± 0.01	0.127
	WR	0.3 ± 0.02	0.3 ± 0.01	0.3 ± 0.01	0.023
	WC	0.2 ± 0.01^a	0.4 ± 0.09^b	0.4 ± 0.03^b	0.000
P	A	15 ± 4	17 ± 2	19 ± 1.8	0.412
	B	13 ± 0.7^a	19 ± 0.8^b	20 ± 0.9^b	0.000
	C	18 ± 2	19 ± 0.5	20 ± 1	0.363
	D	23 ± 1	24 ± 0.8	24 ± 4	0.800
	E	20 ± 1	22 ± 0.1	24 ± 2	0.031
	F	19 ± 4	26.2 ± 1.3	32.8 ± 4	0.013
	G	26 ± 1	26 ± 0.4	29 ± 4	0.154
	DL	18 ± 1	18 ± 4	19 ± 1	0.815
	OC	17 ± 1	20 ± 1	20 ± 1	0.059
	WR	27 ± 2^a	28 ± 1^b	32 ± 1^b	0.003
	WC	15 ± 4^a	17 ± 0.4^a	21 ± 2^b	0.006
Pb	A	0.01 ± 0.002	0.02 ± 0.003	0.02 ± 0.001	0.010
	B	0.02 ± 0.002^a	0.03 ± 0.001^b	0.03 ± 0.001^b	0.003
	C	0.03 ± 0.002	0.04 ± 0.01	0.05 ± 0.04	0.610
	D	0.04 ± 0.002	0.04 ± 0.001	0.05 ± 0.007	0.023
	E	0.03 ± 0.003	0.03 ± 0.004	0.04 ± 0.002	0.254
	F	0.04 ± 0.001	0.05 ± 0.003	0.06 ± 0.04	0.600
	G	0.04 ± 0.003^a	0.06 ± 0.002^b	0.06 ± 0.003^b	0.000
	DL	0.02 ± 0.003	0.03 ± 0.006	0.03 ± 0.009	0.020
	OC	0.02 ± 0.007	0.02 ± 0.006	0.02 ± 0.007	0.516

	WR	0.05±0.001	0.05±0.006	0.05±0.001	0.054
	WC	0.02±0.002[a]	0.04±0.01[b]	0.05±0.009[b]	0.001
Rb	A	0.05±0.011	0.08±0.012	0.08±0.007	0.017
	B	0.08±0.01[ab]	0.09±0.001[a]	0.1±0.002[b]	0.010
	C	0.08±0.008[a]	0.09±0.009[ab]	0.1±0.004[b]	0.004
	D	0.1±0.009[a]	0.1±0.001[a]	0.2±0.02[b]	0.009
	E	0.1±0.011	0.1±0.013	0.1±0.011	0.087
	F	0.1±0.02	0.1±0.004	0.2±0.008	0.100
	G	0.1±0.006a	0.1±0.004[a]	0.2±0.014[b]	0.002
	DL	0.06±0.008[a]	0.08±0.008[b]	0.08±0.004[b]	0.000
	OC	0.07±0.021	0.07±0.013	0.08±0.012	0.673
	WR	0.1±0.01	0.1±0.007	0.1±0.007	0.320
	WC	0.1±0.03	0.1±0.01	0.1±0.02	0.028
S	A	8±1[a]	34±5[b]	38±9[b]	0.000
	B	7±1[a]	40±5[b]	97±18[c]	0.000
	C	88±16	90±11	91±20	0.975
	D	9±3[a]	41±7[b]	64±21[c]	0.001
	E	45±10[a]	72±13[b]	113±22[c]	0.006
	F	127±37[a]	130±23[a]	261±7[b]	0.006
	G	65±13	104±61	113±10	0.387
	DL	0.004±0.001	0.005±0.001	0.006±0.001	0.061
	OC	0.001±0.001	0.002±0.002	0.002±0.001	0.843
	WR	0.003±0.001	0.006±0.003	0.006±0.001	0.057
	WC	0.001±0.001[a]	0.002±0.001[b]	0.02±0.003[b]	0.000
Sc	A	0.01±0.003	0.02±0.003	0.03±0.001	0.017
	B	0.03±0.001[a]	0.04±0.002[b]	0.06±0.02[c]	0.000
	C	0.03±0.001[a]	0.04±0.002[b]	0.04±0.002[b]	0.001
	D	0.04±0.003	0.05±0.001	0.06±0.006	0.069

	E	0.04±0.003	0.05±0.005	0.05±0.004	0.076
	F	0.05±0.007	0.05±0.003	0.07±0.005	0.010
	G	0.06±0.002[a]	0.07±0.01a[b]	0.08±0.005[b]	0.001
	DL	0.02±0.003	0.03±0.004	0.02±0.005	0.124
	OC	0.03±0.006	0.03±0.005	0.03±0.004	0.776
	WR	0.05±0.004	0.05±0.004	0.05±0.005	0.190
	WC	0.06±0.01	0.06±0.015	0.07±0.004	0.077
Se	A	0.003±0.001	0.004±0.0001	0.005±0.001	0.037
	B	0.003±0.001	0.005±0.001	0.006±0.001	0.023
	C	0.005±0.001	0.005±0.001	0.008±0.001	0.044
	D	0.007±0.001	0.008±0.001	0.008±0.003	0.892
	E	0.005±0.001	0.005±0.001	0.01±0.002	0.005
	F	0.007±0.001[a]	0.008±0.003[a]	0.016±0.001[b]	0.008
	G	0.006±0.001[a]	0.008±0.001[b]	0.01±0.001[c]	0.001
	DL	0.004±0.001	0.004±0.001	0.004±0.001	0.479
	OC	0.003±0.001	0.004±0.002	0.005±0.001	0.065
	WR	0.007±0.001	0.008±0.001	0.008±0.001	0.152
	WC	0.004±0.002[a]	0.007±0.002[b]	0.008±0.002[c]	0.005
Sn	A	0.001±0.0002	0.001±0.0001	0.004±0.005	0.296
	B	0.001±0.0001	0.002±0.001	0.004±0.003	0.422
	C	0.002±0.001	0.003±0.001	0.005±0.003	0.307
	D	0.003±0.001	0.004±0.001	0.006±0.003	0.111
	E	0.002±0.001	0.003±0.001	0.004±0.002	0.422
	F	0.003±0.001	0.003±0.001	0.004±0.001	0.010
	G	0.003±0.001	0.003±0.001	0.006±0.003	0.028
	DL	0.003±0.001	0.008±0.004	0.01±0.007	0.056
	OC	0.002±0.001[a]	0.003±0.001[b]	0.003±0.001[b]	0.003
	WR	0.004±0.0001	0.004±0.001	0.004±0.0001	0.344

	WC	0.003±0.002	0.004±0.001	0.005±0.001	0.070
Sr	A	0.2±0.03	0.3±0.05	0.3±0.02	0.014
	B	0.2±0.01[a]	0.3±0.01[b]	0.3±0.03[b]	0.001
	C	0.3±0.026	0.4±0.01	0.4±0.01	0.017
	D	0.3±0.05[a]	0.4±0.03[b]	0.5±0.02[c]	0.005
	E	0.3±0.04[a]	0.4±0.03[a]	0.9±0.3[b]	0.003
	F	0.6±0.3[a]	0.9±0.2[a]	1.5±0.1[b]	0.002
	G	0.6±0.02	0.6±0.03	0.6±0.03	0.014
	DL	0.3±0.05	0.4±0.03	0.5±0.2	0.027
	OC	0.3±0.035	0.4±0.16	0.4±0.085	0.198
	WR	0.5±0.04[a]	0.6±0.04[b]	0.6±0.03[b]	0.004
	WC	0.4±0.1	0.5±0.4	0.6±0.2	0.555
Th	A	0.005±0.001	0.007±0.002	0.008±0.001	0.023
	B	0.006±0.0001[a]	0.01±0.001[b]	0.012±0.0001[c]	0.000
	C	0.008±0.0001[a]	0.009±0.0001[a]	0.012±0.001b	0.002
	D	0.01±0.001	0.01±0.001	0.01±0.001	0.200
	E	0.01±0.001	0.01±0.001	0.01±0.001	0.176
	F	0.01±0.001	0.01±0.001	0.01±0.001	0.036
	G	0.01±0.001[a]	0.02±0.001[b]	0.02±0.002[b]	0.000
	DL	0.01±0.001	0.01±0.001	0.01±0.001	0.579
	OC	0.01±0.001	0.01±0.001	0.01±0.003	0.059
	WR	0.01±0.001	0.01±0.001	0.01±0.001	0.065
	WC	0.01±0.002	0.01±0.002	0.01±0.002	0.010
Ti	A	0.4±0.03	0.4±0.05	0.6±0.2	0.412
	B	0.4±0.03[a]	0.5±0.02[b]	0.6±0.02[c]	0.001
	C	0.4±0.001[a]	0.5±0.028[b]	0.6±0.049[c]	0.003
	D	0.5±0.02	0.5±0.03	0.5±0.03	0.296
	E	0.5±0.03	0.5±0.001	0.5±0.001	0.010

	F	0.4±0.05	0.4±0.02	0.5±0.03	0.011
	G	0.3±0.02	0.3±0.04	0.4±0.07	0.197
	DL	0.5±0.04	0.5±0.02	0.5±0.06	0.023
	OC	0.5±0.01	0.5±0.04	0.5±0.02	0.723
	WR	0.4±0.02[a]	0.4±0.03[a]	0.5±0.02[b]	0.008
	WC	0.4±0.04	0.4±0.04	0.4±0.04	0.597
V	A	0.1±0.04	0.0±0.04	0.2±0.01	0.046
	B	0.2±0.02[a]	0.3±0.01[b]	0.3±0.01[b]	0.001
	C	0.2±0.01[a]	0.3±0.02[b]	0.4±0.01[c]	0.000
	D	0.4±0.03[a]	0.4±0.01[a]	0.5±0.06[b]	0.005
	E	0.3±0.04	0.4±0.02	0.5±0.04	0.021
	F	0.4±0.06[a]	0.4±0.02[a]	0.6±0.03[b]	0.008
	G	0.4±0.01[a]	0.5±0.01[b]	0.6±0.01[c]	0.000
	DL	0.2±0.02[a]	0.3±0.02[b]	0.3±0.01[b]	0.000
	OC	0.2±0.7	0.3±0.03	0.3±0.03	0.130
	WR	0.3±0.02	0.4±0.03	0.4±0.01	0.595
	WC	0.3±0.02[a]	0.6±0.02[b]	0.6±0.1[b]	0.001
Y	A	0.05±0.007	0.05±0.018	0.06±0.004	0.109
	B	0.05±0.002[a]	0.08±0.002[b]	0.08±0.001[b]	0.000
	C	0.06±0.008	0.07±0.005	0.08±0.002	0.046
	D	0.09±0.003	0.1±0.001	0.1±0.01	0.466
	E	0.08±0.009	0.09±0.003	0.09±0.003	0.204
	F	0.08±0.007[a]	0.09±0.002[b]	0.1±0.005[b]	0.002
	G	0.1±0.005	0.1±0.003	0.1±0.004	0.036
	DL	0.07±0.005[a]	0.07±0.004[a]	0.08±0.005[b]	0.002
	OC	0.07±0.008	0.08±0.007	0.08±0.004	0.349
	WR	0.1±0.004	0.1±0.002	0.1±0.006	0.502
	WC	0.08±0.007	0.1±0.01	0.1±0.006	0.001

Zn	A	0.3±0.065	0.4±0.068	0.4±0.051	0.022
	B	0.4±0.05[a]	0.5±0.004[a]	0.6±0.01[b]	0.003
	C	0.5±0.03	0.5±0.05	1.3±0.8	0.059
	D	0.7±0.05	0.8±0.007	0.9±0.1	0.024
	E	0.6±0.05	0.7±0.06	0.7±0.08	0.165
	F	0.7±0.1[a]	0.7±0.02[a]	1±0.04[b]	0.004
	G	0.9±0.05[a]	1±0.02[a]	1.3±0.05[b]	0.000
	DL	0.3±0.03[a]	0.5±0.04[b]	0.5±0.04[b]	0.000
	OC	0.4±0.08	0.4±0.07	0.4±0.1	0.655
	WR	0.8±0.02	0.9±0.04	0.9±0.09	0.096
	WC	0.8±0.2	1±0.1	1±0.06	0.039
Zr	A	0.01±0.004	0.02±0.004	0.02±0.001	0.058
	B	0.02±0.001[a]	0.03±0.001[b]	0.03±0.001[b]	0.000
	C	0.02±0.002[a]	0.03±0.001[b]	0.04±0.001[c]	0.000
	D	0.03±0.001	0.04±0.002	0.04±0.008	0.337
	E	0.03±0.003	0.03±0.003	0.03±0.001	0.201
	F	0.03±0.004	0.04±0.003	0.05±0.009	0.039
	G	0.04±0.006[a]	0.05±0.005[a]	0.07±0.003[b]	0.008
	DL	0.02±0.002	0.03±0.008	0.03±0.003	0.016
	OC	0.025±0.004	0.027±0.003	0.029±0.003	0.122
	WR	0.04±0.004	0.04±0.004	0.04±0.004	0.732
	WC	0.04±0.006	0.06±0.01	0.06±0.01	0.017

4.4.3. Contribution of sediment from each tributary

The contributions of sediments from the tributaries to the river, based on the element concentrations at each site, are given in Table 4.2. Some elements in the four

Table 4.2: The percentage tributary contribution ± 95% Confidence interval of elements(A-G – sites upstream of Lake Darling, DL-Des Lacs River, OC – Oak Creek, WR – Wintering River, WC – Willow Creek).

Element	Site A	Site B	Site C	Site D	Site E	Site F	Site G	DL	OC	WR	WC
Al	56±0.6	33±0.3	18±0.4	30±0.2	28.9±0.8	4.3±0.8	44.23±0.8	68±0.8	52.6±0.8	53.3±0.5	9±0.4
As	82.9±0.3	55.7±0.8	-26.5±1.2	11.9±0.1	69.2±0.2	8±0.3	43.8±0.6	76.6±0.7	31.2±0.2	77±0.6	54.3±0.3
Be	31.8±0.2	21.9±0.2	66.7±0.2	16.7±0.2	33.3±1.0	90.1±0.2	40±0.5	23.1±0.2	50±0.2	75±0.5	78.6±0.3
Bi	30.8±0.2	85.7±0.3	27.3±0.5	25±0.4	80±0.4	61.1±1.5	66.7±0.3	71.4±0.3	75±0.3	72±0.6	84.5±0.8
Ca	85.4±0.2	30.3±0.4	10.1±0.7	88.4±0.7	12.6±0.8	34.8±0.5	71.4±0.1	67.5±0.2	90.5±0.5	44.3±0.2	84.5±0.5
Cd	95.4±0.2	12.5±0.3	9.4±0.3	9.3±0.1	20.7±0.8	22±0.3	32±1	102±1	45±0.3	41.7±0.8	-8.1±0.3
Ce	24.8±1.6	72.6±0.3	70.4±0.3	60.8±0.7	30±0.6	46.7±0.2	42.5±0.4	68.5±0.6	64.5±0.6	45±0.4	36.7±0.5
Co	80.6±0.5	52.2±1.3	113±0.2	31.5±0.3	6.7±0.3	25.9±0.3	90±0.7	91.5±0.2	38.3±0.3	50±0.3	74.4±0.4
Cr	49.5±0.4	53.8±0.2	2.6±0.3	43.8±0.7	44.9±0.5	20.7±0.3	55.2±1.2	88.1±1.2	4.2±0.3	57.3±0.3	83.1±0.8
Cs	21.1±0.6	51.1±0.2	53.5±0.4	67.9±0.4	18.5±0.8	91.3±0.8	44±0.3	73.3±0.8	32.6±0.3	70.9±0.8	82.8±0.6
Cu	94.5±0.3	34.5±0.2	15.9±0.3	19.1±0.1	44.9±0.9	34±0.4	34.9±0.3	96.5±0.6	60.7±0.6	32±0.3	82.3±0.2
Fe	60.4±0.5	26.5±0.7	89±0.8	35.5±0.3	1.8±0.3	17.6±0.2	63.5±0.60	94.7±0.8	92.9±0.8	43.4±0.2	91.4±0.3
Ga	44.4±0.9	57.1±1.2	30.8±0.3	43.5±0.5	18.2±0.8	5.3±0.3	54±0.2	106±1	-16.7±0.6	40±0.3	97.9±0.8
Hf	58.6±0.3	12.5±0.4	-38.9±0.6	12.5±0.6	54.9±0.7	56±0.1	12.5±0.1	80±0.8	66.7±0.5	75±0.8	58.3±0.6
K	90±0.1	11.3±0.2	33.3±0.6	16.2±0.2	38.5±0.7	5.3±0.4	45.5±0.7	-83±0.8	20±0.2	69.2±0.3	66.7±0.6
La	16.4±0.2	72.4±2.1	74.4±0.3	51.3±0.8	85±0.6	96.8±0.4	26.2±0.2	54.9±0.6	70.5±0.6	59.1±0.2	88.8±0.9
Li	41.8±0.8	9.1±0.3	14.6±0.2	64.3±0.6	17.3±0.8	25.7±0.4	52.2±0.8	66.2±0.8	52.4±0.2	96±0.7	81.3±0.9
Mg	50.3±0.3	66.7±1.2	7.1±0.2	88.3±0.4	64.3±0.6	93.7±0.3	82.5±0.4	85.2±0.4	36±0.3	70.9±0.7	56.8±0.8

Table 4.2: (Continued)

Mn	63.5±0.3	4±0.6	65.1±0.6	50.4±0.2	45±0.9	27.3±0.1	83.1±0.2	57.3±0.8	74.9±0.1	70.9±0.2	73.1±0.3
Mo	87±0.2	60.7±0.7	89.2±0.1	15.4±0.3	29.1±0.5	53.9±0.6	6.3±0.5	92.3±0.4	121±1	21.4±0.3	70.4±1.4
Na	40.3±0.2	73.9±0.1	1.9±0.1	78.9±0.1	50±0.3	3.5±0.2	25±0.5	25±0.6	54±0.8	83.3±0.3	98.5±0.8
Nb	90±1.2	22.1±0.2	26.1±0.3	22.2±0.	60±0.8	78.8±0.4	4.3±0.2	77.1±0.6	72.5±0.6	42.0±0.5	75.7±0.3
Ni	67.2±0.3	64.4±0.6	25.6±0.1	29±0.3	19±0.8	16.7±0.3	50±0.6	96.9±0.8	117±2	52.6±0.3	84.1±0.6
Pb	82.6±0.5	55.3±0.5	159±3	34.9±0.6	37.9±0.8	53±0.3	64.1±1.2	70.4±0.3	69.3±0.8	30.8±0.5	84.1±0.9
Rb	75.6±0.4	50.8±0.3	40±0.5	43.9±0.2	37.1±0.4	51±0.6	50±0.6	99±0.3	44.7±1.2	64.3±0.8	32.7±0.3
S	86.2±0.3	37.4±0.1	137±3	58.5±0.6	38.5±0.8	2.3±0.2	80.4±0.4	44±0.4	85.7±0.8	95.4±0.9	2.4±0.2
Sb	84.6±0.5	50±0.3	-28±0.4	7.1±0.3	30±0.2	65±0.6	37.1±0.4	186±2	-64.3±0.8	-25±0.5	91.2±0.3
Sc	20±0.7	23.4±0.1	25±0.5	53.8±0.3	61.5±0.6	22.2±0.3	65.2±0.4	110±1.2	60±0.6	66.7±0.3	13.9±0.8
Se	33.3±0.3	50±0.3	16.7±0.3	88.2±0.3	16.7±0.7	9.1±0.3	23.5±0.6	79.2±0.8	75±0.8	80±0.5	83.3±0.3
Sn	23.8±0.6	38.8±0.6	35.9±1.2	5.6±0.3	48±0.4	20±0.2	8.3±0.1	66.7±1.2	85.7±0.8	66.7±0.5	75±1.3
Sr	82.2±0.5	72.1±0.1	97.8±0.3	96.5±0.2	11±0.6	30.3±0.5	21.2±0.2	47.9±0.8	85.7±0.8	132±2	48.1±0.3
Th	56±0.5	65±0.2	30.8±0.2	61.5±1.2	30±0.8	33.3±0.3	45.8±0.6	25±0.3	80.6±2.3	70±0.3	76.9±0.8
Ti	14.2±0.4	45.4±0.4	44.4±0.4	50±0.4	25±0.5	10±0.4	80±0.8	33.3±0.3	50±0.8	57.1±0.2	66.7±0.8
Tl	45.4±0.8	31.1±0.9	9.1±0.3	90.9±0.6	44.4±0.6	11.1±0.1	45±0.2	50±0.3	50±0.6	41.7±0.3	92±0.4
U	54.9±1.3	50±0.6	33.3±1.2	33.3±0.6	5.3±0.8	85.7±0.9	9.5±0.2	72.7±1.2	75±0.3	57.1±0.9	59.1±0.8
V	50±0.7	28.6±0.3	19±0.2	33.3±0.2	5.9±0.6	41.4±0.2	45.5±0.4	93.3±0.2	56.2±0.6	75±0.8	75±0.8
Y	43.7±1.3	69.8±0.1	58.3±1.2	78.6±0.4	81.4±1.2	70.1±1.3	47.3±0.8	53±0.5	56.2±0.8	82.7±0.6	61.9±0.6

Zn	99.7±0.7	53.3±0.2	7.4±0.6	26.6±0.	61.2±0.8	21.4±0.3	41.9±0.4	95.7±0.6	47±0.6	29.1±0.2	75.4±0.5
Zr	58.3±0.9	46.9±0.1	21.2±0.2	12.5±0.2	41.7±0.6	28.2±0.8	21.4±0.8	88.6±0.4	55±0.6	-12.5±0.8	66±0.6

major tributaries and the sites C and H in the Upper Souris River area showed clear enrichments and depletions for some elements, because their values were either below 0 or greater than 100%. For example, the graphical presentation of the contribution of the elements from the Des Lacs River to the Souris River shows that there is a depletion of K and enrichment of Cd, Ga, Sb, and Sc (Figure 4.4a). The elements that showed enrichment and depletion were different among the sites. For example, Site C showed depletions for As, Hf, and Sb and enrichments for Co, Pb, and S (Table 4.2). In Site H, Ca, Sr, and Ti showed depletion while Cs, Na, and S showed enrichment. In the Oak Creek there was a depletion of Ga and Sb, and an enrichment of Mo and Ni. Willow Creek did not show enrichment of elements, but it showed a depletion of Cd. In the Wintering River there was a depletion of Sb and Zr, and an enrichment of Sr (Figure 4.4b).

The mean percentage contribution of sediment from the tributary at each sampling site is presented in Figure 4.5. The highest contribution resulted from the Des Lacs River (71.6%±11.9) and lowest tributary contribution was at Site E (37.1%±6.8).

4.4.4. Percent contribution of phosphorous from each tributary

Contribution of phosphorus from the tributaries to the main river was calculated using the mean sediment contribution from the tributary and the phosphorus concentration in the upstream and tributary sediments (Table 4.3). The percentage contribution of phosphorus from the tributary at each sampling site is presented in Figure 4.6. The highest phosphorus contribution was recorded from Willow Creek (74.7%) and the lowest phosphorus contribution (39.3%) was at Site C (Figure 4.6).
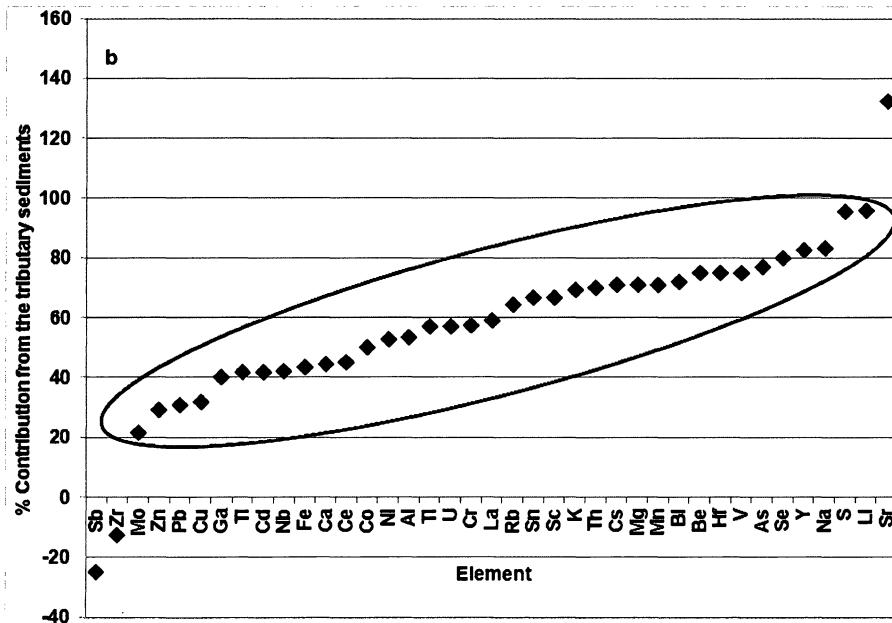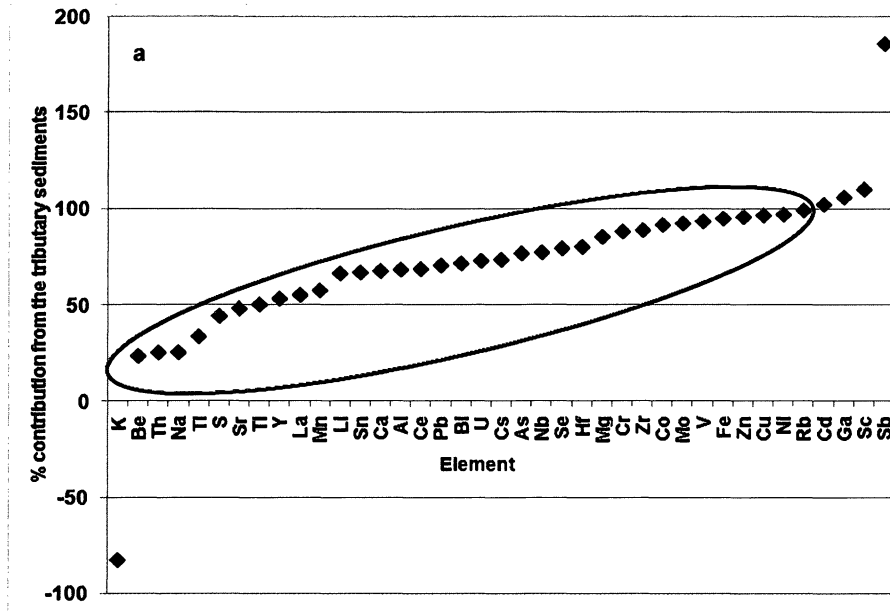
Figure 4.4: Example showing the percentage contribution of elements from the tributary sediments (a- Des Lacs River, b – Wintering River). The elements circled had calculated contributions between zero and 100% and were used for estimating the average contribution of sediments.
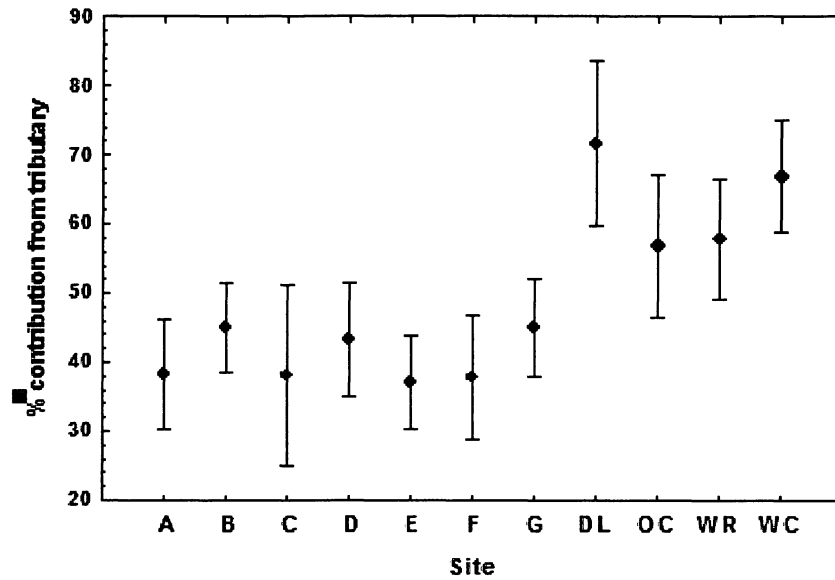
Figure 4.5: Average percent contribution (± 95% Confidence intervals) of sediments from the tributaries to the Souris River (n=40). (A-G – sites upstream of Lake Darling, DL-Des Lacs River, OC-Oak Creek, WR – Wintering River, WC- Willow Creek).
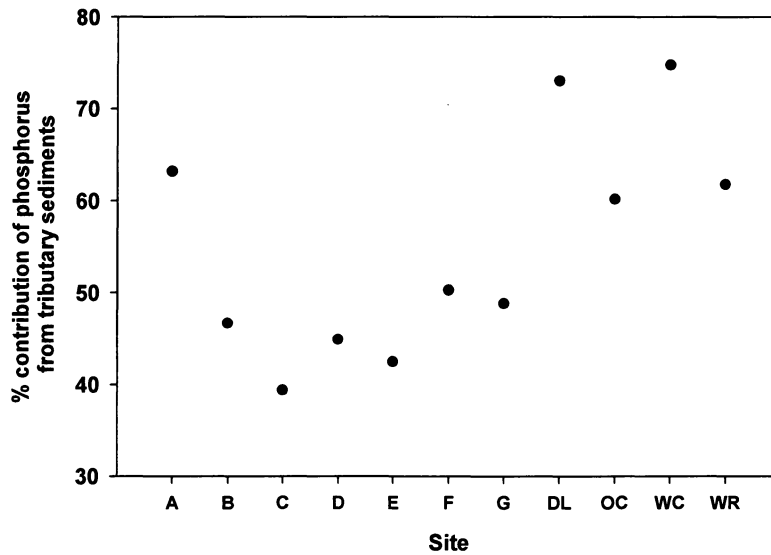
Figure 4.6: Percent contribution of phosphorus from the tributaries to the Souris River (A-G – sites upstream of Lake Darling, DL-Des Lacs River, OC-Oak Creek, WR – Wintering River, WC- Willow Creek).

Table 4.3: Sediment contribution, phosphorus contribution and mean concentrations of phosphorus in the near-confluence sediments of Souris River sites. (A-G – sites upstream of Lake Darling, DL – Des Lacs River, OC- Oak creek, WR – Wintering River, WC – Willow Creek).

Site	Sediment contribution from Tributary (%)	Mean concentration of P in tributary sediments (μmol / g of dry sediment)	Mean concentration of P in upstream sediments (μmol / g of dry sediment)	Contribution of P from Tributary (%)
A	58.3	19.5	15.9	63.1
B	44.9	19.9	18.6	46.6
C	38.1	19.8	18.8	39.3
D	43.3	24.5	23.0	44.8
E	37.1	24.5	19.7	42.4
F	37.8	32.8	19.8	50.2
G	45.0	29.8	25.6	48.7
DL	71.6	19.2	18.0	73.0
OC	56.9	20.5	18.0	60.1
WR	57.8	32.7	27.8	61.7
WC	66.9	21.6	14.8	74.7

4.5. Discussion

In this study, we expected significant variations in LOI and f<63 in Souris River sediments. LOI or f<63 did not show significant variations in sites or significant correlations with elements as expected. Often stream sediments contain high amounts of organic matter. Previous studies have revealed, in most wetlands and rivers, that phosphorus occurs in organic matter pools in sediments (Hesse 1962, Sommers et al. 1972, Stevenson 1982, Reddy et al. 1999). In the present study LOI was used as an indication of the organic matter content in the sediments (Boyer et al. 2003). Organic matter content did

not show significant variation among sites nor did it correlate with phosphorus or other element concentrations. This indicates that organic matter content in this river is not an important determinant of phosphorus concentrations in sediments. Studies have shown that often f<63 in stream sediments are enriched with chemical phosphorus and are important carriers of phosphorus compared to larger particles. The f<63 of sediments remain suspended for a longer period of time compared to coarse sediments and this promotes binding of phosphorus onto surfaces of f<63 (Lick 1982, Ongley et al., 1982, Logan, 1987, Santiago and Thomas 1992, Stone and English, 1993, Stone et al. 1995.). In this study f< 63 did not show significant correlations with phosphorus or other elements. This showed that f< 63 did not play an important role in determining phosphorus and other element concentrations in Souris River sediments.

The concentrations of the elements showed significantly higher concentrations in the tributary locations compared to the upstream and downstream locations in most of the sites. Also it was noted for many elements, concentrations of the downstream locations were intermediate between the upstream and tributary locations of the same site. These observations support the hypothesis that tributaries are the major contributors of most of the trace elements, and thus sediments, to the main river. Along the river, sediments are released from actively eroding sites, while they deposit downstream in areas of low flow rates. They may be released again and consequently sinks become sources for deposition further downstream. The sediments tend to deposit immediately downstream from a tributary river confluence due to flow convergence (Fairbridge 1978). Therefore the upstream and tributary sediments can act as sediment sources to the downstream sediment sink areas (Fairbridge 1978, Rosgen 1996, Leopold 2006, Charlton 2008).

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The elements that showed deviations from patterns consistent with conservative mixing varied between sites. The concentration of elements in the sediments can vary depending on geology, climate, and land-use of the surrounding area (Evans 2001, Jain 2004, Jain et al. 2005). Trace elements are introduced into the river as a result of natural weathering of soil and rocks and from a range of human activities, including mining and agriculture (Gibbs 1973, Salomons and Fórstner 1984, Tessier and Campbell 1987, Drever 1988). Trace elements that enter the aquatic environment from natural or anthropogenic sources become part of the water-sediment system and their distribution in water and sediment phase is controlled by a dynamic set of physical–chemical interactions and equilibria. These processes include sorption, precipitation, and complexation (Gibbs 1973, Salomons and Fórstner 1984, Tessier and Campbell 1987, Drever 1988, Fórstner 1990, Evans 2001, Jain 2004, Jain et al. 2005, 2008). Main factors that control trace element speciation and mobility are pH, types and concentration of ligands, redox potential of the environment, and oxidation states of the minerals in sediments (Fórstner 1990, Evans 2001, Jain 2004, Jain et al. 2005, 2008). These conditions can be different from place to place depending on the biological, chemical, and physical properties of the environment. Therefore, the elements that behave conservatively in one location can show depletions or enrichments in another location (Anazawa et al. 2004, Botes and Staden 2005).

The sediment contributions from tributaries of the Souris River ranged between 37.1% and 71. 6%.The seven small tributary sites had a relatively lower sediment contribution to the main river compared to the sediment contribution from the larger tributaries (Figure 4.6). The contribution of tributaries to the main river and the deposition of sediments in downstream sink areas can rely on many local factors, including decrease

in slope, increase in cross-sectional area, increase in boundary resistance, flow separation and occurrence of obstructions to flow (Fairbridge 1978, Rosgen 1996). In addition to these factors, the changes in the supply of sediment yield can affect the deposition of sediments in sink areas (Fairbridge 1978, Rosgen 1996, Leopold 2006, Charlton 2008).

In this study the concentration of phosphorus measured in upstream and tributary sediments and the sediment contribution of tributaries were used to assess the contribution of phosphorus from each tributary. The smaller tributaries showed a lower phosphorus contribution compared to the phosphorus contribution from larger tributaries. The smaller tributaries in the Upper Souris River area drain land within the Upper Souris River wildlife refuge. The land-use in the watersheds of the larger tributaries (Des Lacs River, Oak Creek, Willow Creek and Wintering River) was mostly dominated by agriculture. More than 99% of the land in the Lower Souris River watershed is used for agricultural activities (US EPA 2004, NRCS 2007). Approximately 80% of the land used for agricultural activities is used for cropping practices. Some potential nonpoint-source agricultural threats in the Lower Souris River area are livestock grazing, and chemical, fertilizer and manure application. When these activities occur collectively in a significant portion of the watershed it can lead to adverse effects on the associated water bodies (Saskatchewan Watershed Authority, 2004). Application of phosphorus fertilizer in agriculture has contributed to a large increase in crop yield and maintains adequate soil fertility for crop planting in later periods. However, a high concentration of phosphorus in the soil increases the risk of phosphorus loading to water-bodies through runoff and soil erosion. This is one possible explanation for the higher contributions of phosphorus from the larger tributaries compared to the smaller tributaries.

The tributaries in the Lower Souris area drain a larger proportion of land compared to the tributaries in the Upper Souris River area (Saskatchewan Watershed Authority 2004). The larger watersheds can carry more total phosphorus compared to smaller watersheds. This does not mean that the concentration of P in a gram of sediment would be higher because the concentration of P in sediments depends on the sediment type, organic loading from the external sources, and types of vegetation (Reddy et al. 1999, Walling et al. 2008).

Phosphorus can be accumulated in sediments over a long period of time and these sediments can act as pollutant sources to the overlying water column and downstream sink areas. The transfer of phosphorus between sediments and water is controlled by many factors. Phosphorus can be transferred from the water column to sediment through many biochemical and physical processes including ion exchange, adsorption, and precipitation (Abrams and Jarrell 1995, Stumm and Morgan 1996, Kim et al. 2003). Also the phosphorus accumulated in the sediments can be released to the water column as a result of molecular diffusion, ion exchange, and microbial metabolic activities (Reddy et al. 1999, Walling et al. 2008). The characteristics of the sediments and the overlying water column can affect the rate of deposition of phosphorus and the rate of reintroduction of phosphorus to the water column (Lijklema et al. 1993, Masunaga et al. 1993, Abrams and Jarrell1995, Kim et al. 2003). Also, an increase in pH can enhance the release of phosphorus from sediments because of the competition between hydroxyl anions and phosphate anions to the sorption sites of sediments (MacPherson et al. 1958, Andersen1975, Rippey 1977, Ryding and Forsberg 1977, Lijklema 1980, Bostrom et al. 1982, Jacoby et al. 1982, Koski-Vähälä et al. 2001, Kim et al. 2003).

Iron, aluminum, and manganese can bind with phosphorus in highly aerobic conditions forming precipitates with metal hydroxides (Hieltjes and Lijklema 1980, Fukushima et al. 1984, Bostrom1988, Abrams and Jarrell 1995, Stumm and Morgan 1996, Kim et al. 2003).In this study, the iron, aluminum, and manganese concentrations in the tributary sediments were significantly higher compared with the downstream sediments. Phosphorus concentrations were significantly correlated to aluminum, iron, and manganese. Each of these metals were present in concentrations of at least ten times those of P (Table 4.1), which suggests that these sediments have ample binding capacity to bind P and transport it over long distances.

4.6.   Conclusion

The multi-element fingerprints provided unique signatures at the tributary – river confluences of the Souris River. These multi-element fingerprints can be used to identify patterns of sediment loading from the tributaries. The multi-element fingerprints developed for the sediments of the main river and tributaries, and the patterns of sediment can be used to predict the phosphorus loading and transport in the Souris River. The phosphorus contribution of tributaries varies with land-use patterns of the watershed. The Lower Souris River tributaries contribute more phosphorus to the Souris River resulting in higher phosphorus concentrations in the Lower Souris River sediments compared to the Upper Souris sediments.

CHAPTER 5. A MULTI-ELEMENT FINGERPRINTING APPROACH TO ASSESS CONTRIBUTIONS OF ARSENIC, SELENIUM AND CADMIUM FROM TRIBUTARIES TO THE TURTLE RIVER SEDIMENTS

5.1. Abstract

The multi-element fingerprinting technique was used to assess the enrichment of As, Se and Cd in sediments of the Turtle River, North Dakota, U.S.A. The element concentrations of the top riverbed sediments from upstream and downstream locations of the main river and from inside tributaries were analyzed to develop multi-element fingerprints. The mixing ratios between upstream and tributary sediments of the river were calculated assuming linear mixing. The tributaries were identified as major contributors of sediments As, Se and Cd to the main river. The particle size and the organic matter content were very important in determining the element concentrations in the Turtle River sediments. The element concentration of sediments decreased as they moved away from the tributary-river confluence. The enrichment of As, Se and Cd in the Turtle River sediments may be related to the underlying geology and enrichment from the Dakota aquifer.

5.2. Introduction

Metals are natural constituents of rocks, soils, sediments and water. Metals can enter the water bodies as a result of natural or anthropogenic actions. When metals are released into the environment in higher than natural concentrations they can be toxic and cause major disruptions in aquatic ecosystems. The amounts of metals released to the natural environment have increased in the past decades as a result of developing industries,

increased mining activities, tanning activities etc. (Gibbs 1973, Fórstner 1990, Yong et al. 1992, Evans 2001).

Sediments and water play an important role in transport and storage of metals in the aquatic environment. Metals entering into aquatic ecosystems can be either in the form of dissolved cations or can be attached to sediments or organic matter (Fórstner 1990, Evans 2001, Dhakal et al. 2005).Metals entering into water-bodies can partition among different compartments within the aquatic ecosystem. This process is known as chemical speciation. There are several different chemical mechanisms involved in speciation and transport of metals in aquatic systems, including; 1) dissolution as ionic and inorganic compounds, 2) complex formation with organic molecules, 3) precipitation, 4) incorporation with biological components, and 5) incorporation with crystalline structures (Gibbs 1973, Pojasek and Zajicek 1978, Tessier and Campbell 1987, Fórstner 1990, Gadd 2004, Hochella et al. 2005).

Many studies have assessed the metal concentrations (Cr, Cd, Zn, Pb, Cu, Mn and Ni)in river sediments in many parts of the world (Cahill and Unger 1993, Bertin and Bourg 1995, Sin et al. 2001,Zhang and Wang 2001,Begand Ali 2008, Cardellicchio et al. 2009). Some studies have used sediment quality assessment values such as pollution risk indices and sediment quality guidelines to assess and compare the risks of metal contamination in river sediments (Covelli and Fontolan 1997, Peterson and Zelt 1999, Pekey et al. 2004, Cardellicchio et al. 2009, Chakravarty and Patgiri 2009, Harikumar et al. 2009). There are some studies that have used rare earth metal concentrations to quantify sediment sources and sinks of metals (Liu et al 2004, Polyakov and Nearing 2004, Lei et al. 2006, Stevens and Quinton 2008, Deasy and Quinton 2010).

This study uses the multi-element fingerprinting technique to study the spatial variation of As, Se and Cd in the Turtle River of North Dakota and contributions from its tributaries. The Turtle River is fed by the Dakota aquifer and is itself a tributary of the Red River of the North in northeastern North Dakota. There is concern regarding enrichment of As, Se and Cd in the Turtle River (ND Department of Health 2010).

Low concentrations of As, Se and Cd are naturally present in the environment, but enrichment of these elements can cause environmental and health issues. These elements may have originated from both natural and anthropogenic sources. They enter aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition, direct discharge from industrial operations, leakage from landfills and contaminated sites, and the dispersive use of sludge and fertilizers in agricultural practices (Elrick and Horowitz 1986, Wu 1995, Peters et al. 1999 [a], Peters et al. 1999 [b], Chowdhuri et al. 2003, Ghrefat and Yusuf 2006, Wong et al. 2006, Whitmore et al. 2008, Chapman et al. 2009, Rauf et al. 2009). Arsenic, selenium and cadmium entering into fresh waters from a variety of sources may be rapidly adsorbed by particulate matter and thus sediments may act as significant sinks of these elements. Many studies have been done to assess the concentrations of As, Se and Cd and other trace elements in various environments (Elrick and Horowitz 1986, Wu 1995, Peters et al. 1999 [a], Peters et al. 1999 [b], Chowdhuri et al. 2003, Ghrefat and Yusuf 2006, Wong et al. 2006, Whitmore et al. 2008, Chapman et al. 2009, Rauf et al. 2009).

In this study the potential for tracing sediments acting as As, Se and Cd sources to the Turtle River were assessed using the multi-element fingerprinting technique. A similar

multi-element fingerprinting approach was successfully used to assess the phosphorus loading to the Souris River in North Dakota (Chapter 4).

The multi-element fingerprinting technique can define unique signatures by identifying the distribution and concentrations of elements in similar matrices (Djingovaet al.2004). The unique profile obtained from multi-element fingerprinting can be used for tracing sediments in river systems. Multi-element fingerprinting is a tool used in studying element uptake in plants (Djingova et al. 2004, Otte and Jacob 2005, Kissoon et al. 2010) and in tracing suspended sediment sources in catchments and river systems (Walling 2005).

The objective of this study was to use the multi-element fingerprinting technique to determine the contribution of sediments, As, Se, and Cd from tributaries to the Turtle River. It was hypothesized that the tributary sediments are the major contributors of As, Se and Cd to the Turtle River compared to the upstream sediments.

5.3.   Materials and methods

5.3.1. Study area

The Turtle River is a tributary of the Red River of the North in northeastern North Dakota (Figure 5.1). The Turtle River begins as two streams, the North Branch, which begins as an intermittent stream in eastern Nelson County, and the South Branch, which begins as an intermittent stream in the southern part of the Nelson County. Both of these are fed by the Dakota aquifer. The north and south branches converge near the town of Larimore. The north branch of the Turtle River is about 60 km long and the south branch about 30 km. The total drainage area of the Turtle River is about 1645 Km^2. The total length of the Turtle River from the confluence of north and south branches to its confluence with the Red River is about 113 km (US EPA 2004). There are three major

tributaries to the Turtle River; Kellys Slough, Salt Water Coulee and Fresh Water Coulee

(US EPA 2004). The Turtle River is used for domestic and municipal purposes, recreation

activities, and as a source of fish and other aquatic biota (ND Department of Health 2010).

The river banks are mostly covered with grasses. The Turtle River watershed has an

extreme continental climate, distinguished by four very distinct seasons and great variation

in temperatures over very short periods of time. This area is known for long, cold, and

snowy winters and warm to hot, humid summers (US EPA 2004).
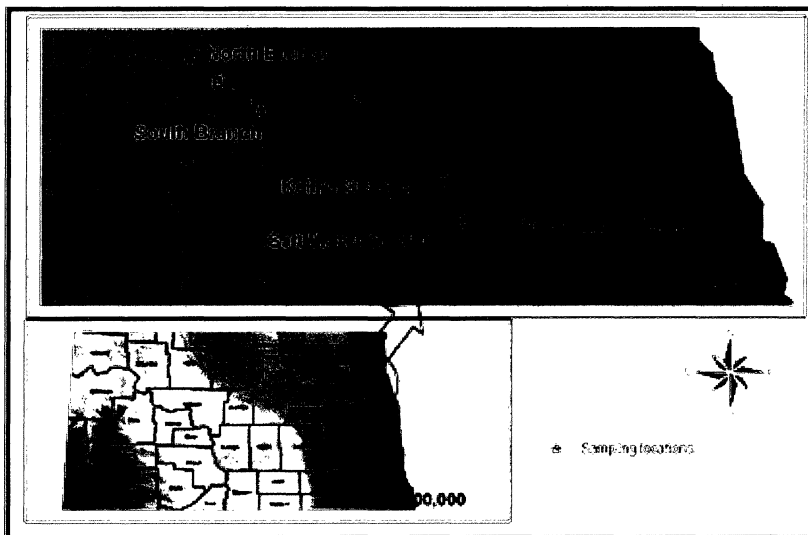
Figure 5.1: Turtle River sampling sites: ((i) – Map showing sampling sites in the Turtle River (ii) –Map showing the general location of Turtle River in ND, USA.

5.3.2. Sample collection

Sediment samples from the top layer of the riverbed were collected in August 2010,

from a tributary to the south branch (TSB) (Site A - 47°56'3.61"N, 97°36'57.67"W), a

tributary to the north branch (Whiskey Creek) (Site B - 48° 2'18.87"N, 97°42'1.93"W),

confluence of north branch and the south branch of the turtle river (Site C - 47°56'14.69"N,

97°35'2.40"W) and from three larger tributaries (Site D - Kellys Slough (48° 0'32.16"N, 97°13'22.69"W), Salt Water Coulee (Site E - 48° 0'30.20"N, 97°12'44.05"W) and Fresh Water Coulee (Site F - 48° 7'47.35"N, 97° 9'53.52"W) along the Turtle River (Figure 5.1). The samples were collected in five replicates from the top layers of sediment (maximum depth of sampling = 2 cm) proximal to the confluence of each tributary to the main river channel. sampling consisted of 11 locations: 1) at three 50 m intervals in the tributary upstream from the confluence, 2) at three 50 m intervals in the main river upstream, and 3) at five 50 m intervals in the main river downstream(Figure 5.2). In Site C, at the confluence of the north and south branches of the river, the south branch was considered as the tributary and the north branch was considered as upstream to maintain the consistency of sampling at the confluence site with the other sites.

5.3.3. Sample preparation and multi-element analysis

The samples were collected by inverting a plastic zip-lock bag as a glove to grab the sample, then folding it back over the sample. The sealed bags were stored in ice and transported to the laboratory. In the laboratory, samples were dried until they reached a constant weight at 60 °C, then homogenized in a mortar and pestle and sieved through a 180 μm sieve. These samples were sent to ACME analytical laboratories, Vancouver, Canada, to be analyzed for multiple elements using the group 1F MS-1F04 analytical package. At ACME analytical laboratories, a modified Aqua Regia solution of equal parts concentrated ACS grade HCl and HNO_3 and de-ionized H_2O was added to each sample (6 ml/g) to leach in a hot-water bath (~95°C) for one hour. After cooling, a 5% HCl solution was added to the sample to make it to the desired final volume which had a composition of

Samples were taken at 50 m
intervals for 3 locations
along upstream of the main
river from eroding areas

Samples were taken at 50 m
intervals for 3 locations along
upstream of the tributary
from eroding areas

Upstream

Tributary

Water flow

Samples were taken at 50 m
intervals for 5 locations along
downstream of the main river
from depositing areas

Downstream
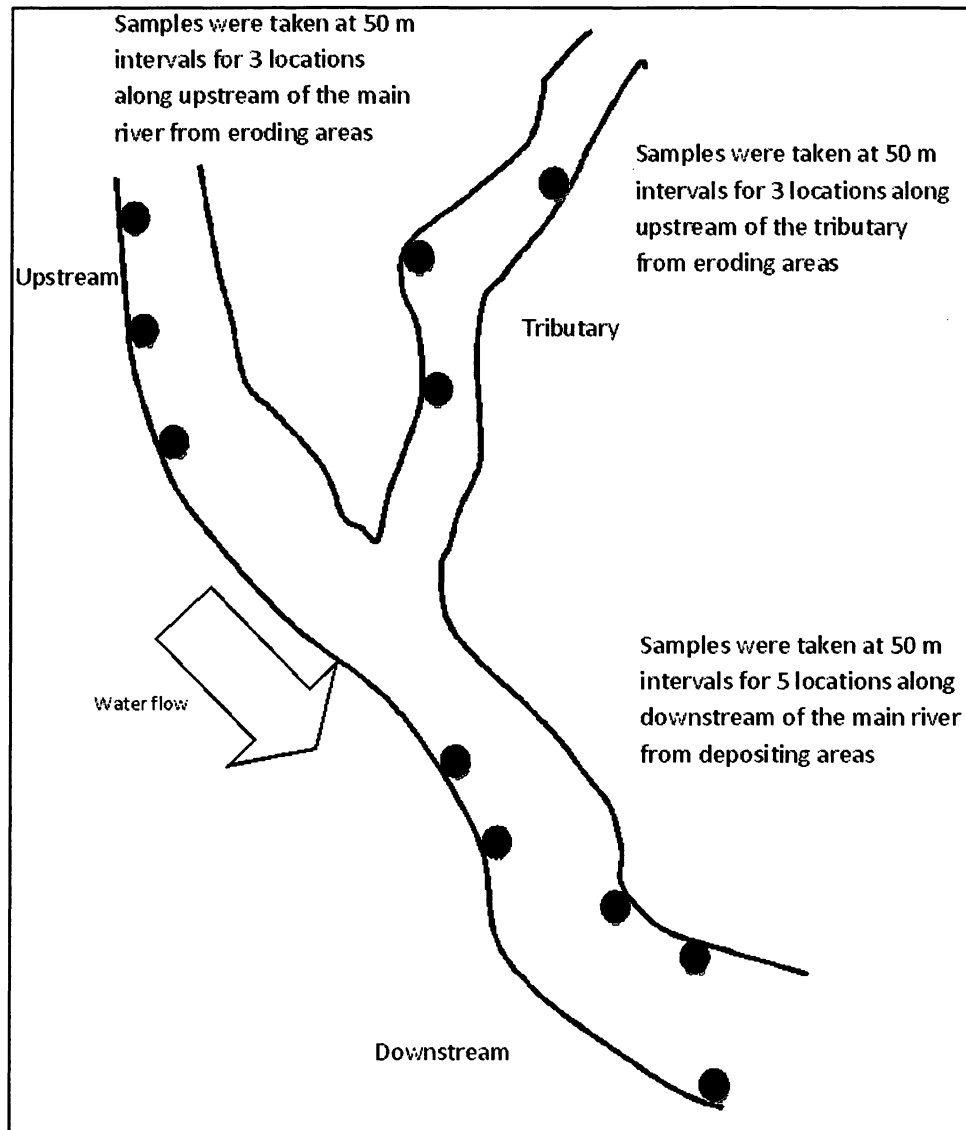
Figure 5.2: Sampling plan for the Turtle River.

0.5 g per 10 mL sample weight to solution volume ratio. These solutions were aspirated

into a Perkin Elmer Elan 6000 ICP mass spectrometer to analyze for 53 elements(detection

limits as reported by ACME analytical laboratories in $\mu g\ L^{-1}$ are given in brackets): Ag(2),

As(0.1), Al(100), Au(0.002), B(20), Ba(0.5), Be(0.1), Bi(0.02), Ca(100), Cd(0.01), Ce(0.1),

Co(0.1). Cr(0.5), Cs(0.02), Cu(0.01), Fe(100), Ga(0.1), Ge(0.1), Hf(0.02), Hg(0.5),

In(0.02), K(100), La (0.5), Li (0.1), Mg(100), Mn(1), Mo(0.01), Na(10), Nb(0.02), Ni(0.1),

P(10), Pb(0.01), Pd(0.1), Pt(0.002), Rb(0.1), Re(0.001), S(200), Sb(0.02), Sc(0.1), Se(0.1), Sn(0.1), Sr(0.5), Ta(0.05), Te(0.02), Th(0.1), Ti(10), Tl(0.02), U(0.1), V(2), W(0.1), Y(0.01), Zn(0.1) and Zr(0.1). Throughout the remainder of the paper molar units will be used.

5.3.4. Loss-on-ignition

Loss-on-ignition (LOI) is a measure of organic matter content. About 15 g of dried homogenized samples were dried further at 105 °C in ceramic crucibles for 2 hours. The dry weight (W_d) of these samples was recorded. They were then ashed at 550 °C for 2 hours in a Sybron Thermoclyne muffle furnace and the weights of the remaining ashes recorded (W_a). The percentage LOI was calculated as $((W_d-W_a) / W_d) \times 100$.

5.3.5. Fraction of particles smaller than 63 μm (f<63)

The ashes left after determination of LOI were used for determination of the fraction of particles smaller than 63 μm (f<63). The initial dry weight of the ash was recorded (W_i). These samples were wet sieved through 63 μm sieve using distilled water. The material remaining on the sieve was collected onto a Whatmann No 1 filter paper, oven-dried at 60°C and dry weight recorded (W_r). The percentage f< 63 was calculated as $((W_i - W_r) / W_i) \times 100$.

5.3.6. Data analysis

Minitab 15 statistical software (Minitab® 15.1.30) was used for all statistical analyses. The concentration of elements was used to develop multi-element fingerprints for each site. All data were log10 transformed before statistical analysis to obtain normal distribution and homogeneity of variance. Pearson correlation analysis was performed on

element concentrations, f<63, and LOI. One-way ANOVA followed by Tukey's pair-wise comparison was used to analyze variation of element concentrations at each site.

The un-normalized element concentrations in the upstream, downstream and tributary sediments at the tributary river confluence of each site were used for a series of calculations. I) A multi-element fingerprint was developed for each tributary, consisting of the concentrations for each element for each confluence along with a fingerprint of the element concentrations along the river as it runs from upstream to downstream. II) The mean contribution of sediment from each tributary was estimated from calculating the mean overall percentage of contribution of elements from the tributary (see calculation below). III) Because of the concerns of high arsenic, selenium and cadmium concentrations in this river, the contribution of enriched element (As, Se, and Cd) from each tributary was calculated based on the concentrations of these elements in the sediments and the relative sediment contributions to the river (see calculation below).

I)   Multi-element fingerprint and concentration with river flow

Multi-element fingerprints for each tributary confluence were constructed by plotting the sediment concentrations in the three sampling locations nearest to a tributary confluence: in the tributary, the closest site upstream in the main river, and the closest site downstream.

II)   Contribution of sediment from each tributary

The contribution of the tributary (a_x) for the elements except As, Se and Cd at each sampling site was calculated assuming linear mixing between upstream and tributary sediments, as follows.

$$[X]_D = a_x[X]_T + b_x[X]_U \qquad \text{Eq(5.1)},$$

$$\text{and} \quad a_x + b_x = 1 \qquad \text{Eq(5.2)}$$

and therefore

$$a_x = \frac{[X]_D - [X]_U}{[X]_T - [X]_U} \qquad \text{Eq (5.3)}$$

Where,

a_x-Mean contribution of tributary for element x

b_x- Mean Contribution of upstream for element x

$[X]_D$- Mean Concentration of element x at the downstream location

$[X]_U$- Mean Concentration of element x at the upstream location

$[X]_T$- Mean Concentration of element x at the tributary location

III)   Contribution of enriched element (As, Se and Cd) from each tributary

Elements with estimated contributions of more than 1 or less than 0 clearly did not meet the assumptions of conservative, linear mixing and so were not further taken into consideration for calculations. Most elements showed a tributary contribution between 0 and 1, or 0% and 100%, and the average value for a_x for those elements was considered the best estimate for the sediment contribution from the tributaries to the river.

The calculated mean sediment contributions from the tributaries were used to estimate the contribution of enriched elements (As, Se and Cd) from the tributary (C_p) at each site, as follows.

$$C_p = \frac{A_t*[P_t]}{(A_t*[P_t])+(A_u*[P_u])} \times 100 \qquad \text{Eq (5.4)}$$

Where,

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A_t – Mean sediment contribution from the tributary

A_u – Mean sediment contribution from upstream of the main river

P_t – Mean measured enriched element (As, Se or Cd) concentration in tributary sediments

P_u – Mean measured enriched element (As, Se or Cd) concentration in the upstream

sediments

5.4. Results

5.4.1. Correlation with f<63 and LOI

LOI ranged from 0.2 %-8.1 % with an average value of 2.7%. The percentage f<

63 ranged from 21.1 %-97.6% with an average of 47.6%.LOI was significantly correlated

with f<63 (r = 0.840) (Figure 5.3). Correlations were considered statistically significant if r

≤ 0.707. These correlations explain 50% or more variation (McClave and Sincich 2006).
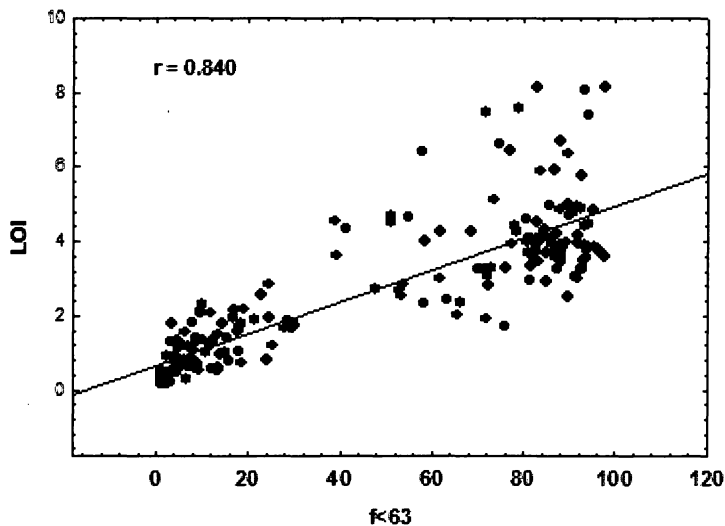
Figure 5.3: Correlation between LOI and f<63 in the Turtle River sediments.

Most elements showed statistically significant correlations with LOI and f<63. The

elements were categorized to four groups based on their correlations with LOI and f<63

(Table 5.1). Al, Bi, Cd, Co, Cs, Cu, Ga, K, Li, Ni, Pb, Rb, Sn, Tl and Zn showed

statistically significant correlations both with LOI and f<63. Nb and Zr were significantly

correlated with LOI, but not with f<63. Sr and Na were correlated only with f< 63, but not

with LOI. The remainder of the elements showed no significant correlations with either

LOI nor f<63 (Table 5.1).

Table 5.1: The correlation coefficients of elements based on Pearson's correlation analysis of element concentrations with LOI and f<63. The correlations in bold were considered significant at r $\geq$0.707 (n=330).

Element	Significant correlation (r value)	
	LOI	f<63
Al	**0.746**	**0.817**
As	0.446	0.448
Ba	0.453	0.432
Be	0.605	0.659
Bi	**0.774**	**0.839**
Ca	0.520	0.587
Cd	**0.804**	**0.834**
Ce	-0.166	-0.149
Co	**0.716**	**0.753**
Cr	0.297	0.358
Cs	**0.739**	**0.847**
Cu	**0.803**	**0.862**
Fe	0.493	0.513
Ga	**0.719**	**0.773**
K	**0.794**	**0.825**
La	-0.245	-0.244
Li	**0.833**	**0.914**
Mg	0.682	**0.792**
Mn	0.074	-0.021
Mo	-0.118	-0.184

Na	0.673	**0.807**
Nb	**0.718**	0.625
Ni	**0.736**	**0.813**
P	0.592	0.517
Pb	**0.772**	**0.816**
Rb	**0.822**	**0.873**
S	0.374	0.294
Sb	-0.036	-0.101
Sc	0.655	**0.744**
Se	0.200	0.197
Sn	**0.713**	**0.703**
Sr	**0.805**	**0.853**
Th	-0.479	-0.482
Ti	-0.506	-0.521
Tl	**0.742**	**0.879**
U	-0.099	-0.284
V	0.244	0.284
Y	0.444	0.520
Zn	**0.808**	**0.808**
Zr	**0.769**	0.640

5.4.2. Analysis for multiple elements and development of fingerprints

The element concentrations of Ag, Au, B, W, Hg, Te, Ge, Hf, Ta, In, Re, Pd, and Pt were below the detection limits and will not be discussed further. The mean concentrations of other elements in the near-confluence locations at each site are given in Table 5.2. The statistical analysis showed that concentrations of some elements (e.g. Al, Ba, Cd, Cr, Cu,

Fe, Mg, Mo, K) in the upstream locations of some sites were significantly lower compared to the concentrations at the downstream and tributary locations (Table 5.2). In some sites, the tributary concentrations of elements (eg: Al, Bi, As, Ca, Cd, K, Ce, Na, Cr, Cs, Fe, Mg, Mn etc.) were significantly higher compared to both the upstream and downstream concentrations (Table 5.2).

Table 5.2: Element concentration (mean ± SD) at the near-confluence upstream, downstream and tributary locations of the Turtle River sampling sites (μmol/g of dry sediment; unless otherwise stated).For each row, data presented by different superscripts are significantly different from each other (ANOVA, Tukey's pair-wise comparison; $P<0.05$; n=5). (TSB – Tributary to the South Branch of the Turtle River, WC – Whiskey Creek, C – Confluence of North and South Branch, KS – Kellys Slough, SWC – Salt Water Coulee, FWC – Fresh Water Coulee).

Element	Site	Upstream	Tributary	Downstream	Pvalue
Al	TSB	84±8[a]	163±1[b]	13±19[b]	0.001
	WC	103±9	190±5	153±14	0.050
	C	111±6[a]	247±5[b]	169±17[c]	0.000
	KS	255±7	271±7	261±7	0.336
	SWC	237±3	304±9	279±10	0.000
	FWC	259±7[a]	376±18[b]	352±26[c]	0.001
As (nmol/g)	TSB	4.8±1.8[a]	11.3±0.9[b]	7.7±2[b]	0.008
	WC	3.3±0.2	7.0±1.5	7.4±3.6	0.124
	C	3.9±0.5[a]	8.5±1.2[b]	6.7±0.3[c]	0.001
	KS	8.7±0.2[a]	10±0.4[b]	9.7±0.7[a]	0.052
	SWC	8.8±0.3	14.3±1.6	9.0±0.6	0.001
	FWC	7±0.9	23.5±8.6	9.3±0.6	0.013
Ba	TSB	0.6±0.1	1.2±0.1	0.7±0.3	0.016
	WC	0.5±0.01[a]	1±0.01[b]	0.7±0.01[b]	0.002
	C	0.5±0.02[a]	1.4±0.3[b]	1±0.1[b]	0.004
	KS	1±0.9	1.1±0.1	1.0±0.9	0.583
	SWC	0.8±0.1[a]	1.1±0.1[b]	1.0±0.02[b]	0.003

	FWC	0.6 ± 0.02^a	1.2 ± 0.3^b	1.2 ± 0.01^b	0.006
Be	TSB	0.03 ± 0.006	0.04 ± 0.006	0.03 ± 0.01	0.317
	WC	0.02 ± 0.0001	0.03 ± 0.0001	0.03 ± 0.006	0.027
	C	0.03 ± 0.006	0.04 ± 0.01	0.03 ± 0.006	0.072
	KS	0.04 ± 0.0001	0.06 ± 0.006	0.05 ± 0.006	0.031
	SWC	0.04 ± 0.01	0.06 ± 0.01	0.05 ± 0.006	0.422
	FWC	0.04 ± 0.01	0.07 ± 0.006	0.06 ± 0.0001	0.015
Bi	TSB	0.0003 ± 0.00002	0.0005 ± 0.0001	0.0004 ± 0.00007	0.082
	WC	0.0003 ± 0.00003	0.0006 ± 0.0002	0.0004 ± 0.00005	0.076
	C	0.0004 ± 0.00005^a	0.0008 ± 0.00003^b	0.0004 ± 0.00007^a	0.000
	KS	0.0008 ± 0.00001	0.0009 ± 0.00005	0.0008 ± 0.00003	0.022
	SWC	0.0008 ± 0.00002	0.001 ± 0.0002	0.0008 ± 0.00005	0.243
	FWC	0.0007 ± 0.00001^a	0.0009 ± 0.00005^b	0.0007 ± 0.00003^b	0.000
Ca	TSB	593 ± 40^a	721 ± 5^b	645 ± 8^c	0.002
	WC	909 ± 51	1147 ± 111	1027 ± 120	0.070
	C	993 ± 72^a	1265 ± 22^b	1053 ± 20^a	0.001
	KS	1268 ± 16	1316 ± 25	1308 ± 14	0.046
	SWC	1063 ± 147	1279 ± 25	1218 ± 18	0.055
	FWC	1183 ± 58^a	1566 ± 110^b	1226 ± 12^c	0.001
Cd (nmol / g)	TSB	1.8 ± 0.5	3.4 ± 0.2	3.2 ± 0.8	0.031
	WC	2.3 ± 0.3^a	5.1 ± 0.8^b	3.6 ± 0.6^a	0.005
	C	2.5 ± 0.1^a	5.1 ± 0.4^b	3.1 ± 0.2^c	0.000
	KS	4.9 ± 0.1^a	5.6 ± 0.1^b	5.4 ± 0.2^b	0.005
	SWC	5.2 ± 0.5	6 ± 1.1	5.6 ± 0.4	0.460
	FWC	4.8 ± 0.1^a	5.7 ± 0.4^b	5.2 ± 0.2^b	0.009
Ce	TSB	0.25 ± 0.07	0.4 ± 0.1	0.3 ± 0.1	0.193
	WC	0.2 ± 0.01	0.4 ± 0.2	0.3 ± 0.1	0.035

Table 5.2: (continued)

	C	0.2±0.04	0.3±0.1	0.2±0.01	0.121
	KS	0.2±0.002	0.2±0.01	0.2±0.009	0.430
	SWC	0.2±0.006	0.2±0.001	0.2±0.004	0.015
	FWC	0.2±0.003[a]	0.3±0.007[b]	0.2±0.001[a]	0.000
Co	TSB	0.04±0.006	0.1±0.02	0.07±0.002	0.010
	WC	0.06±0.005	0.1±0.03	0.08±0.007	0.019
	C	0.06±0.001[a]	0.1±0.005[b]	0.07±0.003[a]	0.000
	KS	0.1±0.004	0.1±0.003	0.1±0.003	0.023
	SWC	0.1±0.004	0.1±0.006	0.1±0.009	0.021
	FWC	0.07±0.006[a]	0.2±0.05[b]	0.1±0.004[c]	0.007
Cr	TSB	0.2±0.04	0.4±0.07	0.3±0.04	0.021
	WC	0.1±0.005[a]	0.4±0.05[b]	0.3±0.07[b]	0.003
	C	0.2±0.005[a]	0.3±0.006[b]	0.2±0.008[a]	0.000
	KS	0.3±0.009	0.3±0.007	0.3±0.006	0.062
	SWC	0.2±0.006[a]	0.3±0.01[b]	0.3±0.002[b]	0.000
	FWC	0.3±0.008[a]	0.4±0.02[b]	0.3±0.009[a]	0.000
Cs	TSB	0.003±0.0001	0.003±0.0003	0.003±0.0001	0.250
	WC	0.002±0.0001	0.004±0.001	0.003±0.0002	0.028
	C	0.003±0.0001[a]	0.006±0.0001[b]	0.003±0.0003[a]	0.000
	KS	0.005±0.0001	0.005±0.0002	0.005±0.0001	0.076
	SWC	0.005±0.0001	0.005±0.0002	0.005±0.0001	0.333
	FWC	0.005±0.0001[a]	0.006±0.0003[b]	0.005±0.0002[a]	0.005
Cu	TSB	0.07±0.02	0.1±0.007	0.1±0.02	0.049
	WC	0.06±0.005	0.2±0.06	0.09±0.02	0.015
	C	0.06±0.005[a]	0.1±0.01[b]	0.1±0.005[b]	0.000
	KS	0.2±0.009[a]	0.3±0.006[b]	0.3±0.003[b]	0.009
	SWC	0.3±0.02	0.3±0.008	0.3±0.01	0.494
	FWC	0.3±0.01	0.3±0.008	0.3±0.01	0.228

Table 5.2: (continued)

Fe	TSB	197±40	327±72	221±35	0.047
	WC	121.1±9.9[a]	282±47[b]	285±29[b]	0.001
	C	148±16[a]	223±3[b]	212±9[c]	0.000
	KS	246±5	255±4	251±14	0.539
	SWC	257±6	282±8	266±8	0.019
	FWC	239±8[a]	318±27[b]	288±22[c]	0.009
Ga	TSB	0.02±0.004	0.02±0.001	0.02±0.001	0.618
	WC	0.01±0.001	0.02±0.005	0.02±0.002	0.011
	C	0.01±0.001[a]	0.03±0.001[b]	0.02±0.001[c]	0.000
	KS	0.03±0.001	0.03±0.002	0.03±0.0003	0.317
	SWC	0.03±0.001[a]	0.04±0.0001[b]	0.03±0.001[b]	0.000
	FWC	0.03±0.002[a]	0.05±0.0002[b]	0.04±0.004[a]	0.002
K	TSB	14±3[a]	31±0.1[b]	26±5[b]	0.002
	WC	19.6±1	32±7	26±0.1	0.039
	C	23±0.01[a]	42±1[b]	29±1[c]	0.000
	KS	42±1	46±0.01	44±1	0.037
	SWC	43±1[a]	61±1[b]	53±2[c]	0.000
	FWC	45±1[a]	66±1.5[b]	56±0.02[c]	0.000
La	TSB	0.1±0.04	0.2±0.06	0.1±0.03	0.197
	WC	0.08±0.007	0.2±0.04	0.2±0.06	0.052
	C	0.1±0.02	0.2±0.05	0.1±0.009	0.121
	KS	0.1±0.004	0.1±0.005	0.1±0.003	0.892
	SWC	0.1±0.003	0.1±0.001	0.1±0.002	0.012
	FWC	0.1±0.001[a]	0.2±0.006[b]	0.1±0.002[a]	0.000
Li	TSB	0.6±0.1	0.8±0.02	0.6±0.08	0.110
	WC	0.6±0.05	1.2±0.5	0.8±0.07	0.107
	C	0.5±0.05[a]	1.3±0.04[b]	0.8±0.001[c]	0.000
	KS	1.7±0.05	1.8±0.06	1.8±0.08	0.429

Table 5.2: (continued)

	SWC	1.7±0.02[a]	2.1±0.06[b]	2±0.1[c]	0.001
	FWC	1.6±0.05[a]	1.9±0.05[b]	1.8±0.04[b]	0.002
Mg	TSB	218±18[a]	297±13[b]	285±15[b]	0.002
	WC	415±28	628±78	493±92	0.030
	C	466.2±34.9[a]	741.8±21.1[b]	529.3±23.4[a]	0.000
	KS	673±23	745±16	712±14	0.010
	SWC	709±14[a]	770±19[b]	745±2[c]	0.005
	FWC	471±39[a]	807±15[b]	761±21[c]	0.000
Mn	TSB	7.1±0.4[a]	27.8±1.3[b]	17.2±6.9[b]	0.020
	WC	12.7±2	20.2±2.9	20.1±7.2	0.160
	C	17.2±1.1[a]	75.6±15.6[b]	31.2±5.9[c]	0.001
	KS	21.7±0.5	24.4±0.7	22.4±1.3	0.028
	SWC	12.4±1.7[a]	27.6±2.5[b]	21.1±0.5[c]	0.000
	FWC	14.5±1.5[a]	49.2±13.8[b]	16.6±3.1[a]	0.003
Mo	TSB	0.004±0.001	0.006±0.001	0.005±0.0001	0.095
	WC	0.003±0.001	0.004±0.001	0.004±0.0001	0.107
	C	0.003±0.0001[a]	0.02±0.003[b]	0.009±0.001[c]	0.001
	KS	0.003±0.0002	0.004±0.0003	0.003±0.0004	0.068
	SWC	0.003±0.00001[a]	0.004±0.0003[b]	0.004±0.0001[b]	0.004
	FWC	0.003±0.00001	0.01±0.005	0.005±0.0005	0.037
Na	TSB	5.1±0.7	5.8±0.9	5.2±0.01	0.406
	WC	8.5±0.9	42.3±0.52	9.8±0.6	0.394
	C	7.8±0.7[a]	13.9±0.4[b]	10±0.7[c]	0.000
	KS	56±7	126±33	88±17	0.022
	SWC	52±2[a]	162±18[b]	102±18[c]	0.000
	FWC	51±3[a]	80±11[b]	52±0.9[a]	0.004
Nb	TSB	0.002±0.00001	0.002±0.0001	0.002±0.00003	0.026
	WC	0.002±0.00001	0.003±0.0001	0.002±0.00003	0.070

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	C	0.002±0.00001	0.002±0.0001	0.002±0.00003	0.108
	KS	0.002±0.00001	0.003±0.0001	0.003±0.00003	0.100
	SWC	0.003±0.00001[a]	0.004±0.0001[b]	0.004±0.00003[b]	0.000
	FWC	0.003±0.00001[a]	0.004±0.0001[b]	0.003±0.00003[a]	0.001
Ni	TSB	0.1±0.02	0.2±0.04	0.2±0.009	0.016
	WC	0.16±0.005[a]	0.3±0.05[b]	0.24±0.02[b]	0.004
	C	0.2±0.02[a]	0.4±0.03[b]	0.3±0.03[c]	0.000
	KS	0.3±0.007	0.4±0.009	0.4±0.003	0.011
	SWC	0.3±0.004[a]	0.4±0.01[b]	0.3±0.004[a]	0.002
	FWC	0.3±0.008	0.4±0.1	0.3±0.004	0.081
P	TSB	2.4±0.3	3.2±0.3	2.7±0.2	0.031
	WC	2.2±0.1[a]	2.8±0.1[b]	2.8±0.2[b]	0.005
	C	2.4±0.2[a]	2.9±0.1[b]	2.7±0.1[b]	0.009
	KS	2.9±0.02	3.1±0.05	3±0.1	0.104
	SWC	3±0.1	3.2±0.1	3.1±0.1	0.252
	FWC	2.7±0.3	3.4±0.3	2.8±0.05	0.019
Pb	TSB	0.02±0.001	0.03±0.007	0.03±0.001	0.179
	WC	0.02±0.001[a]	0.04±0.005[b]	0.03±0.003[b]	0.002
	C	0.02±0.003[a]	0.04±0.002[b]	0.03±0.001[c]	0.000
	KS	0.04±0.001	0.05±0.001	0.04±0.002	0.663
	SWC	0.05±0.002	0.05±0.005	0.05±0.004	0.310
	FWC	0.04±0.001	0.06±0.007	0.06±0.007	0.016
Rb	TSB	0.05±0.004[a]	0.1±0.002[b]	0.1±0.01[b]	0.000
	WC	0.07±0.006	0.1±0.03	0.1±0.008	0.022
	C	0.07±0.004[a]	0.1±0.02[b]	0.1±0.01[b]	0.000
	KS	0.2±0.006	0.2±0.007	0.2±0.007	0.282
	SWC	0.2±0.005[a]	0.2±0.004[b]	0.2±0.004[b]	0.001
	FWC	0.2±0.007[a]	0.2±0.004[b]	0.2±0.007[b]	0.000

S	TSB	26±1[a]	84±15[b]	63±9[b]	0.006
	WC	28±3	46±16	36±1	0.318
	C	31±3[a]	174±22[b]	58±2[c]	0.000
	KS	58±4	72±7	70±8	0.085
	SWC	59±5[a]	84±3[b]	68±8[a]	0.006
	FWC	44±13[a]	79±4[b]	46±5[a]	0.005
Sb	TSB	0.002±0.00001	0.002±0.0001	0.002±0.00001	0.075
	WC	0.001±0.00001[a]	0.002±0.0001[b]	0.002±0.00001[b]	0.008
	C	0.001±0.00001[a]	0.003±0.0001[b]	0.002±0.00001[b]	0.000
	KS	0.001±0.00001	0.002±0.0001	0.002±0.00001	0.152
	SWC	0.002±0.00001	0.002±0.001	0.002±0.00001	0.307
	FWC	0.002±0.00001	0.002±0.0001	0.002±0.00001	0.030
Sc	TSB	0.02±0.001[a]	0.03±0.001[b]	0.03±0.001[b]	0.000
	WC	0.02±0.001	0.03±0.005	0.03±0.005	0.021
	C	0.02±0.003[a]	0.05±0.003[b]	0.03±0.001[a]	0.000
	KS	0.04±0.003	0.05±0.001	0.04±0.001	0.035
	SWC	0.04±0.001	0.05±0.002	0.04±0.001	0.171
	FWC	0.04±0.003[a]	0.07±0.005[b]	0.06±0.003[b]	0.002
Se (nmol / g)	TSB	7.2±0.7	10.9±1.5	8±2.6	0.089
	WC	5.9±0.7[a]	14.3±1.9[b]	10.9±1.5[b]	0.001
	C	5.5±0.7[a]	24.9±3.9[b]	14.8±0.7[c]	0.000
	KS	10.9±0.7	11.4±1.3	11.1±0.8	0.857
	SWC	10.9±0.7	12.2±2.6	11.4±1.3	0.680
	FWC	4.2±0.7[a]	7.6±0.0001[b]	5.1±1.3[a]	0.007
Sn	TSB	0.002±0.001	0.003±0.001	0.002±0.0001	0.842
	WC	0.002±0.001	0.003±0.001	0.003±0.0001	0.111
	C	0.002±0.001	0.003±0.001	0.002±0.0001	0.296
	KS	0.03±0.0001	0.005±0.001	0.004±0.0001	0.125

	SWC	0.004±0.0002	0.007±0.003	0.006±0.004	0.570
	FWC	0.03±0.0001	0.004±0.001	0.003±0.0001	0.079
Sr	TSB	0.5±0.04	0.6±0.004	0.5±0.05	0.031
	WC	0.5±0.02	1±0.7	0.6±0.06	0.365
	C	0.6±0.01[a]	0.7±0.05[b]	0.6±0.04[a]	0.007
	KS	1.5±0.1	1.8±0.08	1.6±0.2	0.106
	SWC	1.6±0.06	2±0.5	1.7±0.04	0.297
	FWC	0.8±0.09[a]	1.3±0.2[b]	1.1±0.04[c]	0.008
Th	TSB	0.03±0.002	0.07±0.03	0.03±0.02	0.072
	WC	0.009±0.002	0.05±0.019	0.04±0.02	0.046
	C	0.01±0.002	0.04±0.02	0.02±0.002	0.183
	KS	0.011±0.001	0.012±0.001	0.012±0.001	0.464
	SWC	0.01±0.0001[a]	0.012±0.0001[b]	0.011±0.0001[b]	0.002
	FWC	0.01±0.0001[a]	0.024±0.003[b]	0.014±0.001[a]	0.000
Ti	TSB	0.5±0.05[a]	1.2±0.1[b]	0.9±0.1[b]	0.001
	WC	0.4±0.0001	0.9±0.1	0.8±0.2	0.041
	C	0.5±0.06	0.6±0.09	0.5±0.03	0.066
	KS	0.4±0.0001	0.44±0.0002	0.4±0.06	0.252
	SWC	0.4±0.0002	0.5±0.03	0.4±0.03	0.011
	FWC	0.4±0.0001	0.44±0.05	0.4±0.03	0.252
Tl (nmol / g)	TSB	0.5±0.001	0.8±0.001	0.7±0.001	0.033
	WC	0.5±0.001a	1.1±0.001b	0.8±0.001b	0.003
	C	0.4±0.001a	1.2±0.001b	0.7±0.001c	0.002
	KS	1.2±0.001	1.4±0. 01	1.3±0. 01	0.579
	SWC	1.1±0.1	1.4±0. 1	1.3±0. 1	0.020
	FWC	1.1±0.1[a]	1.6±0. 1[b]	1.3±0. 1[a]	0.000
U	TSB	0.008±0.001	0.01±0.0001	0.009±0.0001	0.062
	WC	0.007±0.0001[a]	0.008±0.0001[a]	0.01±0.001[b]	0.000

	C	0.007±0.0001[a]	0.012±0.001[b]	0.011±0.001[b]	0.002
	KS	0.007±0.0001[a]	0.008±0.0001[b]	0.007±0.0001[b]	0.002
	SWC	0.007±0.0001	0.008±0.0001	0.008±0.002	0.544
	FWC	0.008±0.002	0.01±0.001	0.009±0.0001	0.076
V	TSB	0.5±0.03	0.7±0.2	0.6±0.1	0.147
	WC	0.3±0.02[a]	0.7±0.1[b]	0.7±0.08[b]	0.002
	C	0.4±0.01[a]	0.6±0.01[b]	0.5±0.02[a]	0.000
	KS	0.5±0.02	0.6±0.02	0.6±0.02	0.090
	SWC	0.5±0.01[a]	0.6±0.03[b]	0.6±0.01[b]	0.005
	FWC	0.5±0.0002[a]	0.9±0.1[b]	0.7±0.02[c]	0.001
Y	TSB	0.12±0.004	0.14±0.0001	0.12±0.01	0.010
	WC	0.09±0.003[a]	0.13±0.003[b]	0.12±0.004[b]	0.000
	C	0.11±0.002[a]	0.13±0.004[b]	0.12±0.003[b]	0.001
	KS	0.12±0.003	0.13±0.004	0.13±0.002	0.127
	SWC	0.13±0.001	0.13±0.002	0.13±0.003	0.015
	FWC	0.12±0.002a	0.15±0.008b	0.14±0.001b	0.000
Zn	TSB	0.4±0.08	0.6±0.03	0.5±0.1	0.051
	WC	0.4±0.03[a]	0.8±0.09[b]	0.6±0.05[b]	0.001
	C	0.3±0.03[a]	0.9±0.05[b]	0.5±0.02[c]	0.000
	KS	0.9±0.02	0.9±0.02	0.9±0.03	0.366
	SWC	0.9±0.03	1±0.06	1±0.04	0.065
	FWC	0.8±0.01[a]	1.4±0.2[b]	0.9±0.05[a]	0.000
Zr	TSB	0.023±0.001	0.027±0.005	0.024±0.002	0.337
	WC	0.014±0.001	0.024±0.006	0.019±0.003	0.050
	C	0.02±0.002[a]	0.05±0.003[b]	0.02±0.002[a]	0.000
	KS	0.03±0.003	0.03±0.002	0.03±0.002	0.691
	SWC	0.03±0.001[a]	0.04±0.003[b]	0.04±0.001[b]	0.007
	FWC	0.03±0.002[a]	0.06±0.003[b]	0.05±0.005[c]	0.000

These element concentrations were used to create multi-element fingerprints for each site. An example of a fingerprint for Fresh Water Coulee is given in Figure 5.4. Similar fingerprints were prepared for all other sampling sites.
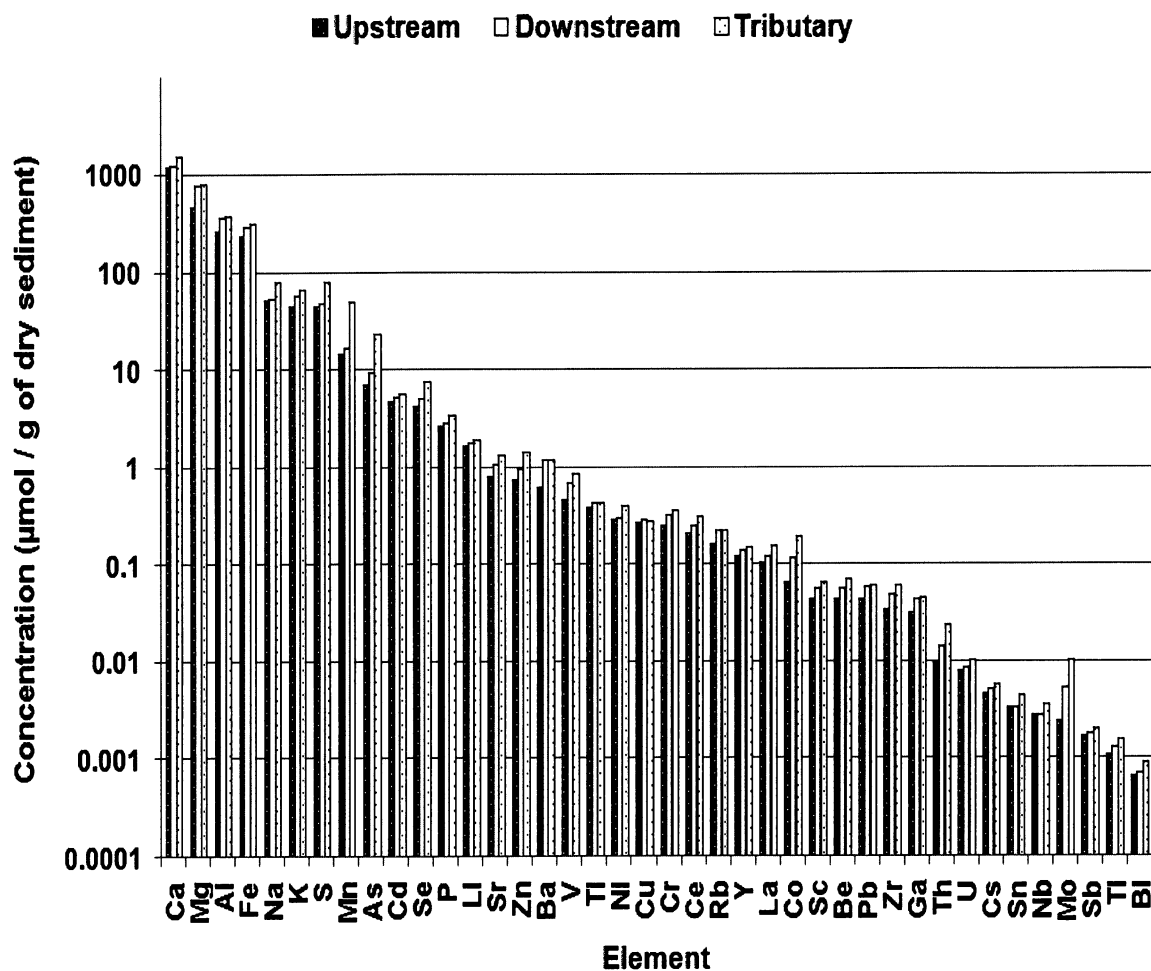
Figure 5.4: Multi-element fingerprint of sediments (concentrations) from the Fresh Water Coulee tributary, and upstream and downstream locations of the Turtle River (48° 7'47.35"N, 97° 9'53.52"W). Elements are ordered from high to low concentrations based upon the 'upstream' samples.

5.4.3. Contribution of tributary

The contributions of sediments from the tributaries to the river, based on the element concentrations at each site, are given in Table 5.3. Some elements at Whiskey Creek, Kellys Slough and Salt Water Coulee showed enrichments, because their contribution values were above 100%, meaning that the concentrations downstream were higher than those in the tributaries. None of the elements showed depletions at any site. The elements that showed enrichments were different among sites. For example, Whiskey Creek showed enrichments for Fe and U, while Kellys Slough showed enrichment of Ni and Fresh Water Coulee showed enrichment of Zn (Table 5.3, Figure 5.5).

Table 5.3: The percentage tributary contribution ± 95% Confidence interval of elements calculated using Eq5.3. (TSB – Tributary to the South Branch of the Turtle River, WC – Whiskey Creek, C – Confluence of North and South Branch, KS – Kellys Slough, SWC – Salt Water Coulee, FWC – Fresh Water Coulee).

Element	TSB	WC	C	KS	SWC	FWC
Al	65.6±5.5	57.1±0.5	42.7±0.2	38.5±1.2	63±3.2	78.9±7
Ba	28.9±0.4	47.5±0.3	54.3±0.5	78.6±0.6	74.7±0.2	95.3±0.4
Be	33.3±0.6	33.3±0.6	20±0.1	25±0.3	33.3±0.6	42.9±0.1
Bi	41.7±0.1	40±0.1	8.7±0.2	16.7±0.5	18.2±0.1	12.5±0.2
Ca	40.5±2.4	49.8±1.1	22.1±0.2	82.8±3.4	71.5±2.1	11.3±0.8
Cd	88.2±0.9	47.3±1.5	23.9±1.5	66.7±2.9	48.1±0.5	48.5±0.6
Ce	34.9±0.9	90.1±0.1	27.9±0.7	65.8±0.1	59.7±0.8	37.7±0.6
Co	43.8±0	43±0.3	21.9±0.4	17.6±0.8	70.3±0.1	37.8±0.7
Cr	19.8±0.9	91±0.1	45.2±0.3	96±0.2	84.3±0.4	56.3±0.6
Cs	60.9±0.3	50±1	21±0.2	12.5±0.3	72.7±0.2	35.6±0.6
Cu	83.1±0.2	20.2±0.8	66.9±0.5	88.3±0.1	74.6±0.8	71±0.8
Fe	18.3±0.4	101.9±0.3	84.9±5.9	53.3±1	37.2±1.7	60.9±4.3
Ga	50±0.1	75±0.7	37.5±0.9	66.7±0.2	52.9±0.5	79.3±0.8
K	75±1.1	46.7±0.3	30.4±1.4	50±0.5	61.9±1.2	54.2±1.6

La	32.6±0.5	97.7±0.6	25.5±0.4	83.3±0.6	73.5±0.5	34.9±0.3
Li	24.3±0.1	30.6±0.3	34.7±0.5	53.3±1	85.4±0.3	54.7±0.1
Mg	84.5±8.4	36.8±1.6	22.9±0.4	53.8±3.6	60±3.1	86.1±2.9
Mn	48.9±11.7	98±4.8	23.9±0.5	27±0.6	57.4±0.6	5.9±0.4
Mo	39.3±0.1	80.4±1	43.7±0.7	57.1±0.2	73.5±1	35.6±0.4
Na	20±0.4	3.9±0.7	35.7±0.5	45.4±0.4	45.3±2.5	4.5±0.5
Nb	96±0.6	55.6±0.7	85.7±0.2	75±0.1	93.8±0.7	4.3±0.5
Ni	94.2±0.5	50.4±0.8	41.8±0.1	102.7±0.2	67.2±0.2	10.4±0.7
P	42.3±0.5	93.1±0.4	58.1±0.3	58.8±1.6	82.4±0.1	20.3±0.4
Pb	68.4±0.4	63.6±0.1	37.3±0.1	5.9±0.3	38.5±0.3	87.1±0.1
Rb	74.6±0.3	49.7±0.4	38.3±0.3	41.7±1	86.1±0.2	94.8±0
S	64.3±3.4	44.4±0.6	19±0.6	85.7±3.2	37.5±1.3	6.1±0.8
Sb	53.6±0.4	80±0.4	68.5±0.9	80±0.9	66.7±0.3	30.8±0.2
Sc	58.3±0.5	88.2±0.8	27.3±0.1	57.1±0.3	50±0.2	53.6±0.1
Se	22.2±2.3	60±4.8	47.8±1	21±0.6	33.3±0.7	25±2
Sn	50±0.3	75±0.7	50±0.3	50±0.3	66.7±0.1	2±0.7
Sr	30.9±0.6	16.3±0.3	8.3±0.9	37.3±0.9	13.9±0.3	52.4±0.3
Th	16.9±0.3	80.2±0.2	30±0	66.7±0.6	33.3±0.7	30.7±0.8
Ti	64.1±0.4	76.9±0.3	50±0.9	33.3±0.3	80±0.5	66.7±0.3
Tl	50±0.8	46.2±0.4	35.2±0.5	50±0.8	63.6±0.2	41.4±0.7
U	35.7±0.1	110±0.3	85.3±0.3	71.4±0.4	83.3±0.5	25±0.1
V	45.2±0.1	96.7±0.3	52.4±0.8	57.1±0.3	69.2±0.5	50.8±0.2
Y	35.1±0.1	71.2±0.2	56.5±1	83±0.7	12.9±0.4	53.1±2.2
Zn	75.5±0.1	53.7±0.2	38.8±0.3	93.8±0.5	108.1±0.6	25.8±0.4
Zr	27.3±0.2	42.9±0.6	10.6±0.2	75±0.2	47.8±0.5	48.1±1.2
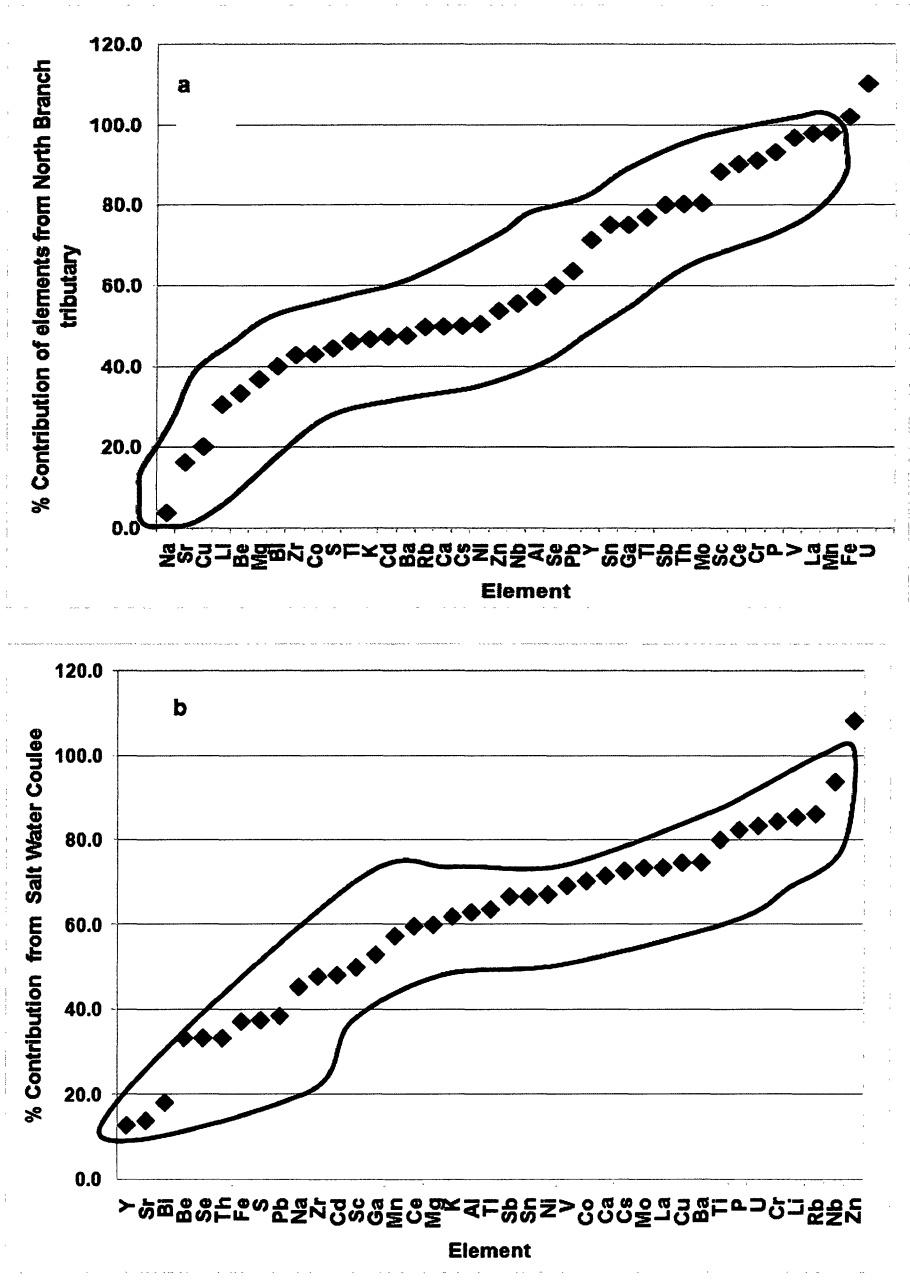
Figure 5.5: Example showing the percentage contribution of elements from the tributary sediments (a- Whiskey Creek; b – Salt Water Coulee) to the Turtle River. The elements circled had calculated contributions between zero and 100 % and were used for estimating the average contribution of sediments.

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The mean percentage contribution±95% confidence intervals of the tributary at each sampling site is presented in Figure5.6.The highest tributary contribution was shown in the Fresh Water Coulee (60.1%±21) and lowest was at the south branch of the Turtle River (39.3%±20.4).The tributary contributions at south branch of the Turtle River and Fresh Water Coulee were significantly lower than the contributions from other sites (Figure 5.6).
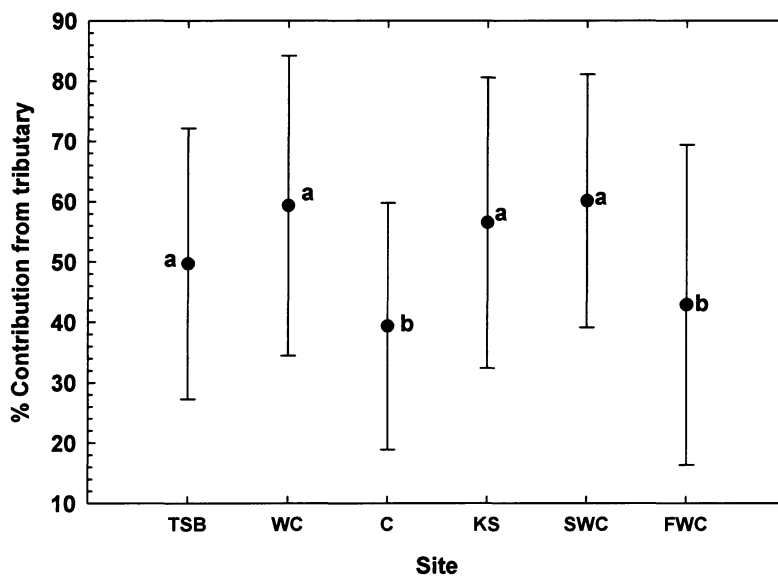
Figure 5.6: Percentage contribution of sediments ± 95% Confidence interval from the tributaries to the Turtle River (Different lowercase letters indicate significant differences in contribution). TSB – Tributary to the south branch of the Turtle River, WC – Whiskey Creek, C – Confluence of North and South Branch, KS – Kellys Slough, SWC – Salt Water Coulee, FWC – Fresh Water Coulee).

5.4.4. Percent contribution of As, Se and Cd from each tributary

Contributions of As, Se and Cd from the tributaries to the main river were calculated using the mean sediment contribution from the tributary and the concentration of

As, Se and Cd in the upstream and tributary sediments (Table 5.4) and are shown in Figure

5.7. Whiskey Creek showed the highest contributions of As, Se and Cd to the main river.

Lowest Se and Cd contributions were from Fresh Water Coulee, while the lowest As

contribution was recorded for the south branch of the Turtle River (Figure 5.7).
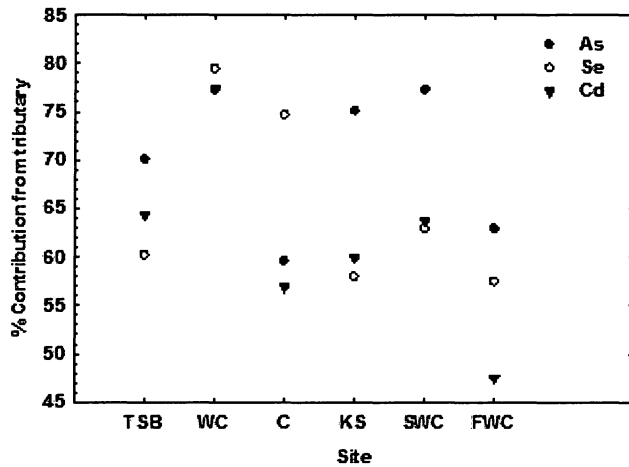
Figure 5.7: Percentage contribution of As, Se and Cd from the tributaries to the Turtle
River. TSB – Tributary to the south branch of the Turtle River, WC – Whiskey Creek, C –
Confluence of North and South Branch, KS – Kellys Slough, SWC – Salt Water Coulee,
FWC – Fresh Water Coulee).

5.4.5. Concentration variation along downstream locations

The element concentrations of the downstream locations from each tributary are

given in Table 5.5. The concentrations of most elements at all the sites decreased with

increasing distance from confluence, and at the furthest location downstream from the

confluence were significantly lower compared to near the confluence (Table 5.5). The

concentrations of Be, B, Cs, Nb, Sb, Sn and Tl did not show statistically significant

variations along the downstream sediments at any of the sites ($P \geq 0.05$). Therefore, the

concentration variation of these elements in the downstream sediments are not shown in

table 5.5.

Table 5.4: Sediment contribution, contribution and mean concentrations of arsenic, cadmium and selenium in the near confluence sediments of Turtle River sites. (TSB – Tributary to the South Branch of the Turtle River, WC – Whiskey Creek, C – Confluence of North and South Branch, KS – Kellys Slough, SWC – Salt Water Coulee, FWC – Fresh Water Coulee).

Site	Sediment contribution from Tributary (%)	Element	Concentration in upstream sediments (nmol / g of dry sediment)	Concentration in tributary sediments (nmol / g of dry sediment)	Contribution from Tributary (%)
TSB		As	4.8	11.3	70.0
	49.7	Cd	1.8	3.4	64.3
		Se	7.2	11.0	60.2
WC		As	3.3	7.0	75.7
	59.3	Cd	2.3	5.0	75.8
		Se	5.9	14.4	78.0
C		As	4.0	9.1	59.6
	39.3	Cd	2.5	5.1	56.9
		Se	5.5	24.9	74.6
KS		As	4.0	9.1	74.7
	56.5	Cd	5.0	5.6	59.4
		Se	11.0	11.4	57.4
SWC		As	3.8	8.4	77.1
	60.1	Cd	5.2	6.0	63.5
		Se	11.0	12.2	62.7
FWC		As	3.9	8.9	62.9
	42.9	Cd	4.8	5.8	47.5
		Se	4.2	7.6	57.5

Table 5.5: Element concentration (mean ± SD) along the downstream stretch of the Turtle River sampling sites (µmol/g of dry sediment; unless otherwise stated). For each row, data presented by different superscripts are significantly different from each other (ANOVA, Tukey's pair wise comparison; $P<0.05$; $n=5$). (TSB – Tributary to the South Branch of the Turtle River, WC – Whiskey Creek, C – Confluence of North and South Branch, KS – Kellys Slough, SWC – Salt Water Coulee, FWC – Fresh Water Coulee).

| Element | Site | Distance downstream from the tributary river confluence (m) | | | | | P value |
		50	100	150	200	250	
Al	TSB	135±19	127±7	117±18	116±21	96±9	0.113
	WC	153±14[a]	101±16[b]	80±5[b]	75±4[b]	67±7[b]	0.000
	C	169±17[a]	140±16[a]	122.3±7.4[a]	100±32[b]	85±6[b]	0.002
	KS	260±7	258±7	251±7	237±9	228±18	0.022
	SWC	279±10[a]	259±13[b]	253±7[b]	240.9±3[b]	233.5±11[b]	0.002
	FWC	352±26[a]	336±14[a]	248±3[b]	226±3[b]	226±6[b]	0.000
As (nmol / g)	TSB	8±	5±1	5±1	5±4	4±1	0.389
	WC	7±3	4±0	3±0.4	3±0.1	2±0.4	0.027
	C	6.8±0.3[a]	6.3±0.5[a]	5.3±0.6[a]	3.7±1.5[b]	2.8±0.2[b]	0.001
	KS	9.6±0.7	9.1±0.2	8.8±0.2	8.8±0.8	8.3±0.1	0.099
	SWC	9±0.6	8.8±0.6	8.4±0.21	7.2±1.2	7.2±0.1	0.024
	FWC	9.2±0.5[a]	9.1±0.4[a]	8.1±0.6[a]	4.4±0.4[b]	2.8±0.5[c]	0.000
Ba	TSB	0.7±0.3	0.6±0.02	0.5±0.07	0.4±0.06	0.4±0.0	0.117
	WC	0.6±0.1	0.6±0.1	0.6±0.08	0.5±0.06	0.4±0.04	0.086
	C	1.0±0.06[a]	0.6±0.06[b]	0.5±0.1[b]	0.5±0.1[b]	0.4±0.02[b]	0.001

	KS	1±0.03	1.0±0.03	0.9±0.06	0.9±0.03	0.9±0.02	0.017
	SWC	1±0.01[a]	0.9±0.03[b]	0.8±0.02[c]	0.7±0.007[c]	0.7±0.06[c]	0.000
	FWC	1.1±0.04[a]	0.8±0.01[b]	0.8±0.04[b]	0.8±0.05[b]	0.5±0.08[c]	0.000
Ca	TSB	645±8[a]	637±96[a]	555±18[a]	482±28[b]	472±5[b]	0.002
	WC	1028±120	943±38	925±65	832±59	793±76	0.026
	C	1054±21[a]	955±53[a]	936±174[a]	756±33[b]	667±51[b]	0.002
	KS	1308±14[a]	1267±16[b]	1262±27[b]	1222.5±40.1b[c]	1189.2±21.5[c]	0.002
	SWC	1218±18[a]	1138±39[b]	1119±21[b]	1032.1±29.9[c]	1003.8±14.6[c]	0.000
	FWC	1227±12[a]	1194±20[a]	984±18[b]	740±118[c]	633±85[c]	0.000
Cd (nmol / g)	TSB	3.1±0.8[a]	2.6±0.1[a]	2.4±0.4[a]	2.2±0.08[a]	1.2±0.2[b]	0.004
	WC	3.6±0.5	2.6±0.7	2.1±0.1	1.8±0.9	1.8±0.1	0.026
	C	3.1±0.2	2.5±0.2	2.4±0.8	2.1±0.08	1.6±0.1	0.014
	KS	5.3±0.1	5.2±0.2	5.1±0.1	4.4±0.4	4.7±0.2	0.015
	SWC	5.5±0.3[a]	5.5±0.2[a]	5.3±0.05[a]	4.8±0.1[b]	4.2±0.2[c]	0.000
	FWC	5.2±0.2[a]	5.2±0.3[a]	4.8±0.3[a]	3.3±0.6[b]	3.1±0.2[b]	0.000
Ce	TSB	0.3±0.07	0.2±0.02	0.2±0.03	0.2±0.009	0.1±0.06	0.143
	WC	0.3±0.1	0.2±0.01	0.2±0.01	0.2±0.01	0.1±0.01	0.015
	C	0.2±0.01[a]	0.2±0.02[a]	0.2±0.01[a]	0.1±0.01[b]	0.1±0.02[b]	0.002

Table 5.5: (continued)

	KS	0.2±0.009	0.2±0.005	0.2±0.007	0.2±0.006	0.2±0.015	0.123
	SWC	0.2±0.004[b]	0.2±0.004[b]	0.2±0.003[b]	0.2±0.004[b]	0.2±0.003[b]	0.000
	FWC	0.2±0.001[a]	0.2±0.008[a]	0.2±0.008[a]	0.2±0.006[a]	0.1±0.003[b]	0.000
Co	TSB	0.06±0.002	0.06±0.01	0.05±0.002	0.05±0.007	0.05±0.009	0.092
	WC	0.08±0.007[a]	0.07±0.012[a]	0.05±0.003[a]	0.05±0.002[b]	0.05±0.004[b]	0.001
	C	0.07±0.003[a]	0.06±0.004[a]	0.06±0.01[a]	0.05±0.001[b]	0.05±0.005[b]	0.003
	KS	0.1±0.003	0.1±0.005	0.1±0.002	0.1±0.004	0.1±0.009	0.010
	SWC	0.1±0.009[a]	0.1±0.003[a]	0.1±0.004[b]	0.1±0.004[b]	0.09±0.004[b]	0.000
	FWC	0.1±0.004[a]	0.1±0.006[ab]	0.1±0.001[b]	0.09±0.003[b]	0.08±0.004[c]	0.000
Cr	TSB	0.2±0.04	0.2±0.01	0.2±0.01	0.2±0.01	0.1±0.07	0.239
	WC	0.4±0.06[a]	0.2±0.03[b]	0.1±0.04[b]	0.1±0.01[b]	0.1±0.01[b]	0.001
	C	0.2±0.008[a]	0.1±0.009[b]	0.1±0.01[b]	0.1±0.01[b]	0.1±0.01[b]	0.000
	KS	0.2±0.006[a]	0.2±0.01[a]	0.2±0.009[ab]	0.2±0.005[b]	0.2±0.01[b]	0.004
	SWC	0.3±0.002[a]	0.2±0.01[a]	0.2±0.006[a]	0.2±0.008[b]	0.2±0.01[b]	0.000
	FWC	0.3±0.009[a]	0.2±0.01[b]	0.2±0.008[b]	0.2±0.005[c]	0.2±0.004[c]	0.000
Cu	TSB	0.1±0.01[a]	0.09±0.004[a]	0.07±0.006[b]	0.06±0.007[b]	0.04±0.008[b]	0.000
	WC	0.08±0.02	0.088±0.01	0.08±0.01	0.07±0.03	0.05±0.005	0.236
	C	0.1±0.005[a]	0.1±0.007[a]	0.09±0.01[a]	0.07±0.01[a]	0.2±0.004[b]	0.000
	KS	0.3±0.003[a]	0.2±0.004[b]	0.2±0.006[b]	0.2±0.007[c]	0.2±0.002[c]	0.000

	SWC	0.3 ± 0.01^a	0.3 ± 0.009^a	0.2 ± 0.005^{ab}	0.2 ± 0.01^b	0.2 ± 0.01^b	0.000
	FWC	0.3 ± 0.01^a	0.3 ± 0.01^a	0.3 ± 0.006^a	0.2 ± 0.036^b	0.2 ± 0.01^b	0.001
Fe	TSB	221 ± 35	209 ± 26	203 ± 3	181 ± 1	149 ± 58	0.137
	WC	285 ± 29^a	210 ± 45^b	148 ± 26^c	146 ± 13^c	109 ± 4^c	0.000
	C	211 ± 9^a	189 ± 38^a	151 ± 14^b	132 ± 31^b	114 ± 6^b	0.003
	KS	251 ± 14	250 ± 6	243 ± 1	239 ± 7	231 ± 22	0.057
	SWC	266 ± 8^a	258 ± 6^a	257 ± 6^a	244 ± 3^b	231 ± 3^c	0.000
	FWC	287 ± 21^a	215 ± 5^b	198 ± 2^b	195 ± 8^b	172 ± 2^c	0.000
Ga	TSB	0.02 ± 0.001^a	0.02 ± 0.001^a	0.02 ± 0^a	0.01 ± 0.003^b	0.01 ± 0.003^b	0.001
	WC	0.02 ± 0.001^a	0.02 ± 0.003^a	0.01 ± 0.002^b	0.01 ± 0.002^b	0.01 ± 0.001^b	0.000
	C	0.02 ± 0.001	0.01 ± 0.002	0.01 ± 0.001	0.01 ± 0.004	0.01 ± 0.001	0.024
	KS	0.03 ± 0.001	0.03 ± 0.001	0.03 ± 0.002	0.03 ± 0.001	0.02 ± 0.002	0.066
	SWC	0.03 ± 0.001^a	0.03 ± 0.002^b	0.03 ± 0.003^b	0.03 ± 0.002^b	0.02 ± 0.001^c	0.000
	FWC	0.04 ± 0.004^a	0.04 ± 0.006^a	0.04 ± 0.001^a	0.03 ± 0.001^b	0.03 ± 0.001^b	0.000
K	TSB	26 ± 5	24 ± 3	23 ± 0.01	21.3 ± 1.4	15 ± 4	0.026
	WC	26 ± 0.002^a	16 ± 4^b	12 ± 1^b	12 ± 1^b	9 ± 1^c	0.000
	C	29 ± 1^a	23 ± 0.003^b	21 ± 1^b	17 ± 1^c	16 ± 6^c	0.002
	KS	44 ± 1	44 ± 1	43 ± 4	41 ± 2	39 ± 3	0.171
	SWC	54 ± 2^a	50 ± 1^b	46 ± 0^b	46 ± 0^b	43 ± 1^c	0.000

Table 5.5: (continued)

	FWC	56±0[a]	55±3[a]	49±0[b]	47±1[b]	45±1[b]	0.000
La	TSB	0.1±0.03	0.1±0.01	0.1±0.01	0.1±0.009	0.09±0.03	0.163
	WC	0.2±0.05	0.1±0.008	0.1±0.009	0.1±0.01	0.08±0.007	0.020
	C	0.1±0.009	0.1±0.01	0.1±0.008	0.1±0.01	0.08±0.004	0.038
	KS	0.1±0.003	0.1±0.002	0.1±0.004	0.1±0.004	0.1±0.007	0.123
	SWC	0.1±0.002[a]	0.1±0.001[a]	0.1±0.004[a]	0.1±0.003[b]	0.1±0.001[b]	0.000
	FWC	0.1±0.002[a]	0.1±0.001[a]	0.1±0.005[a]	0.1±0.003[a]	0.09±0.002[b]	0.000
Li	TSB	0.6±0.08[a]	0.6±0.01[a]	0.5±0.06[a]	0.4±0.03[b]	0.4±0.02[b]	0.001
	WC	0.7±0.06[a]	0.4±0.1[b]	0.5±0.05[b]	0.4±0.05[b]	0.4±0.03[c]	0.001
	C	0.7±0	0.6±0.06	0.6±0.05	0.5±0.1	0.5±0.01	0.026
	KS	1.7±0.07	1.7±0.06	1.743±0.07	1.6±0.07	1.6±0.1	0.196
	SWC	2±0.1[a]	1.6±0.06[b]	1.6±0.04[b]	1.6±0.03[b]	1.6±0.14[b]	0.001
	FWC	1.7±0.04[a]	1.6±0.06[ab]	1.5±0.07b[c]	1.4±0.07[c]	1.4±0.04[c]	0.000
Mg	TSB	285±15[a]	260±10[b]	252±12[b]	249±4[b]	246±8[b]	0.009
	WC	494±92	429±27	429±30	416±49	352±45	0.103
	C	529±23[a]	503±34[a]	415±103[b]	396±23[b]	281±31[c]	0.001
	KS	712±14	701±4	695±23	691±32	684±35	0.023
	SWC	745±2[a]	718±12[a]	655±21[b]	612±21[b]	602±13[b]	0.000
	FWC	761±21[a]	706±10[a]	691±32[a]	673±39[a]	218±35[b]	0.000

Mn	TSB	17.2±6.9	17.2±9.4	10.3±0.5	9.5±0.7	8.3±0.8	0.160
	WC	20±7.2	17.3±6.2	13.2±3.3	10.2±3.1	8.6±0.3	0.000
	C	31±6	26±5	20±0.7	18±12	16±2	0.094
	KS	22±1	20±1	20±3	20±2	17±0.7	0.095
	SWC	21±0.4[a]	15±0.6[b]	14±2[b]	12±1[b]	8±0.7[c]	0.000
	FWC	16±3	12±7	9±3	6±0.8	3±0	0.020
Mo	TSB	0.005±0.0002[a]	0.005±0.0002[a]	0.005±0.001[a]	0.004±0.001[a]	0.002±0.001[b]	0.006
	WC	0.004±0.0004	0.003±0.001	0.003±0.0003	0.003±0.001	0.002±0.0002	0.143
	C	0.009±0.001	0.004±0.0001	0.003±0.001	0.003±0.001	0.002±0.0001	0.123
	KS	0.003±0.0001	0.003±0.0002	0.003±0.0001	0.003±0.0003	0.003±0.0003	0.234
	SWC	0.004±0.001	0.004±0.002	0.004±0.00006	0.003±0.0001	0.003±0.0002	0.136
	FWC	0.005±0.0004	0.005±0.001	0.004±0.001	0.004±0.001	0.001±0.0002	0.132
Na	TSB	5.2±0.002[a]	5±0.9[a]	4.9±0.2[a]	4.3±0.4[a]	2.7±0.2[b]	0.000
	WC	10±2	8±1	8±2	6±0.9	5±0.2	0.033
	C	10±0.7[a]	7±0.2[b]	8±1[b]	7±0.7[b]	5±0.4[c]	0.000
	KS	88±18	88±15	75±14	70±10	69±17	0.385
	SWC	102±18.5[a]	56.8±4.5[b]	49.2±1.5[b]	47.7±11.1[b]	42±6.2[b]	0.000
	FWC	52.7±0.9[a]	48.2±4.2[a]	46.2±4.8[a]	45.9±1.5[a]	29.8±2.2[b]	0.000
Ni	TSB	0.2±0.009	0.2±0.067	0.1±0.03	0.1±0.004	0.1±0.02	0.047

Table 5.5: (continued)

	WC	0.3±0.02^a	0.2±0.03^b	0.1±0.01^c	0.1±0.008^c	0.1±0.01^c	0.000
	C	0.2±0.02^a	0.2±0.008^b	0.1±0.01^b	0.1±0.05^b	0.1±0.004^c	0.007
	KS	0.3±0.003^a	0.3±0.007^a	0.3±0.005^b	0.3±0.01^b	0.3±0.03^b	0.002
	SWC	0.3±0.004	0.3±0.01	0.3±0.009	0.3±0.016	0.3±0.006	0.015
	FWC	0.2±0.004^a	0.2±0.005^a	0.2±0.01^b	0.2±0.02^c	0.1±0.01^d	0.000
P	TSB	2.7±0.2	2.7±0.2	2.5±0.2	2.4±0.05	2.3±0.3	0.243
	WC	2.7±0.2	2.6±0.3	2.5±0.1	2.5±0.1	2.1±0.09	0.045
	C	2.6±0.08^a	2.5±0.3^a	2.3±0.2^a	2.2±0.003^b	1.9±0.06^b	0.008
	KS	2.9±0.1	2.9±0.1	2.9±0.05	2.8±0.1	2.7±0.1	0.406
	SWC	3.1±0.1^a	3.1±0.08^a	2.9±0.08^b	2.9±0.03^b	2.7±0.09^c	0.006
	FWC	2.8±0.04	2.5±0.2	2.4±0.1	2.2±0.01	2.2±0.2	0.010
Pb	TSB	0.03±0.001^a	0.03±0.001^a	0.02±0.001^b	0.02±0.002^b	0.02±0.004^b	0.000
	WC	0.03±0.003^a	0.02±0.003^b	0.02±0.003^b	0.01±0.001^c	0.01±0.002^c	0.000
	C	0.03±0.001^a	0.03±0.004^a	0.02±0.002^b	0.02±0.006^b	0.02±0.001^b	0.005
	KS	0.04±0.002	0.04±0.003	0.04±0.002	0.04±0.003	0.04±0.002	0.514
	SWC	0.05±0.004	0.04±0.002	0.04±0.003	0.04±0.002	0.04±0.0004	0.020
	FWC	0.06±0.007^a	0.04±0.002^b	0.04±0.001^b	0.04±0.001^b	0.04±0.0003^b	0.000
Rb	TSB	0.09±0.01	0.08±0.003	0.08±0.01	0.07±0.01	0.06±0.01	0.060
	WC	0.1±0.008^a	0.07±0.013^b	0.05±0.004^c	0.05±0.005^c	0.04±0.009^d	0.000

Table 5.5: (continued)

	C	0.1 ± 0.01^a	0.08 ± 0.007^b	0.08 ± 0.004^b	0.07 ± 0.02^b	0.05 ± 0.001^c	0.006
	KS	0.1 ± 0.007	0.1 ± 0.006	0.1 ± 0.003	0.1 ± 0.007	0.1 ± 0.012	0.112
	SWC	0.2 ± 0.009^a	0.1 ± 0.005^b	0.1 ± 0.004^b	0.1 ± 0.002^b	0.1 ± 0.011^b	0.000
	FWC	0.2 ± 0.007^a	0.1 ± 0.005^b	0.1 ± 0.002^b	0.1 ± 0.004^b	0.1 ± 0.001^b	0.000
S	TSB	63 ± 9^a	58 ± 4^a	45 ± 17^a	37 ± 11^a	17 ± 2^b	0.002
	WC	36 ± 17	34 ± 0	32 ± 7	30 ± 4	27 ± 3	0.734
	C	58 ± 28	41 ± 14	31 ± 3	20 ± 4	16 ± 1	0.031
	KS	70.6 ± 7^a	67.5 ± 4^a	56 ± 3^{ab}	52 ± 4^b	49 ± 3^b	0.001
	SWC	68 ± 8	65 ± 24	60 ± 4	54 ± 4	37 ± 0	0.064
	FWC	47 ± 5	34 ± 16	33 ± 9	23 ± 1	18 ± 3	0.025
Sc	TSB	0.03 ± 0.001^a	0.03 ± 0.003^a	0.03 ± 0.003^a	0.03 ± 0.02^a	0.02 ± 0.003^b	0.001
	WC	0.03 ± 0.005^a	0.02 ± 0.003^b	0.02 ± 0.001^b	0.02 ± 0.001^b	0.02 ± 0.001^b	0.001
	C	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.005	0.02 ± 0.001	0.02 ± 0.001	0.017
	KS	0.04 ± 0.001	0.04 ± 0.003	0.04 ± 0.001	0.04 ± 0.002	0.04 ± 0.003	0.075
	SWC	0.05 ± 0.001^a	0.04 ± 0.03^b	0.04 ± 0.002^b	0.04 ± 0.001^b	0.03 ± 0.001^c	0.003
	FWC	0.06 ± 0.003^a	0.04 ± 0.001^b	0.04 ± 0.001^b	0.04 ± 0.001^b	0.03 ± 0.001^c	0.000
Se (nmol / g)	TSB	8 ± 2.6	7.5 ± 1.2	6.3 ± 1.2	5.9 ± 2.6	5.9 ± 1.4	0.572
	WC	10.9 ± 1.4^a	6.7 ± 1.9^b	4.6 ± 0.7^b	4.6 ± 0.7^b	3.3 ± 0.7^c	0.000
	C	14.7 ± 0.7^a	11.3 ± 1.2^a	8.4 ± 2.6^{ab}	5.4 ± 1.9^b	4.2 ± 1.4^b	0.000

		KS	11±0.8	10.5±1.4	10.5±0.7	10.5±0.7	10.1±1.2	0.872
		SWC	11.3±1.2	10.9±1.4	10.5±0.7	8.8±0	8.4±0.7	0.014
		FWC	5±1.2	4.6±0.7	3.7±1.2	4.2±0.7	2.9±0.7	0.162
Sr	TSB	0.4±0.04	0.4±0.05	0.4±0.01	0.4±0.005	0.3±0.02	0.040
	WC	0.5±0.05[a]	0.5±0.05[a]	0.5±0.03[a]	0.5±0.02[a]	0.4±0.03[b]	0.007
	C	0.6±0.04[a]	0.6±0.007[a]	0.5±0.007[b]	0.5±0.03[b]	0.4±0.03[c]	0.000
	KS	1.6±0.1	1.6±0.1	1.6±0.1	1.5±0.07	1.5±0.08	0.798
	SWC	1.6±0.03[a]	1.6±0.1[b]	1.5±0.07[ab]	1.4±0.02[b]	1.2±0.08[c]	0.001
	FWC	1.1±0.04[a]	1±0.02[b]	0.9±0.1[b]	0.9±0.1[b]	0.6±0.07[c]	0.002
Th	TSB	0.03±0.01	0.03±0.02	0.02±0.005	0.02±0.01	0.01±0.01	0.823
	WC	0.04±0.021	0.01±0.005	0.01±0.002	0.012±0.004	0.01±0.002	0.013
	C	0.02±0.002[a]	0.01±0.004[b]	0.01±0.004[b]	0.01±0.002[b]	0.008±0.002[b]	0.001
	KS	0.01±0.001	0.01±0.001	0.01±0	0.01±0	0.01±0	0.236
	SWC	0.01±0	0.01±0	0.009±0	0.009±0	0.009±0.001	0.023
	FWC	0.01±0.001[a]	0.01±0.003[a]	0.01±0.002[a]	0.01±0.001[a]	0.007±0.001[b]	0.000
Ti	TSB	0.9±0.1	0.6±0.04	0.6±0.1	0.4±0.1	0.4±0.08	0.001
	WC	0.7±0.21	0.5±0.04	0.5±0.05	0.4±0.02	0.4±0	0.037
	C	0.5±0.02	0.5±0.02	0.4±0	0.4±0.02	0.3±0	0.000
	KS	0.4±0.05	0.4±0.02	0.4±0.02	0.3±0	0.3±0	0.903

Table 5.5: (continued)

	SWC	0.4±0.02	0.4±0.02	0.4±0.04	0.4±0.02	0.4±0.02	0.239
	FWC	0.4±0.02	0.4±0.02	0.4±0.02	0.3±0	0.3±0.028	0.243
U	TSB	0.009±0.0002	0.009±0.001	0.009±0.001	0.008±0.00042	0.007±0.001	0.181
	WC	0.01±0.001[a]	0.01±0.003[a]	0.007±0.003[b]	0.007±0.001[b]	0.007±0.003[b]	0.001
	C	0.01±0.001	0.009±0.001	0.009±0.001	0.006±0.001	0.006±0.0004	0.136
	KS	0.007±0	0.007±0.0002	0.007±0	0.007±0.0004	0.006±0.0002	0.832
	SWC	0.008±0.002	0.008±0.0002	0.007±0.0004	0.006±0.0002	0.006±0.0004	0.076
	FWC	0.009±0.001	0.008±0.001	0.008±0.001	0.008±0.001	0.006±0.0002	0.083
V	TSB	0.5±0.09	0.5±0.01	0.5±0.03	0.5±0.01	0.3±0.1	0.050
	WC	0.7±0.08[a]	0.5±0.08[b]	0.3±0.03[c]	0.3±0.07[c]	0.2±0.02[d]	0.000
	C	0.5±0.0[a]	0.3±0.02[b]	0.3±0.07[c]	0.3±0.03[c]	0.3±0.02[c]	0.000
	KS	0.5±0.02	0.5±0.01	0.5±0.03	0.5±0.04	0.4±0.04	0.118
	SWC	0.5±0.01[a]	0.5±0.03[a]	0.5±0.01[a]	0.5±0.02[ab]	0.4±0.01[b]	0.000
	FWC	0.6±0.02[a]	0.5±0.01[b]	0.5±0.02[b]	0.5±0.02[b]	0.4±0.03[c]	0.000
Y	TSB	0.1±0.01	0.1±0.001	0.1±0.004	0.1±0.008	0.09±0.01	0.017
	WC	0.2±0.004[a]	0.1±0.011[b]	0.104±0.001[b]	0.09±0.002[c]	0.09±0.003[c]	0.001
	C	0.12±0.003[a]	0.11±0.002[b]	0.11±0.004[b]	0.09±0.004[c]	0.09±0.013[c]	0.007
	KS	0.1±0.002	0.1±0.001	0.1±0.001	0.1±0.006	0.1±0.005	0.032
	SWC	0.13±0.003[a]	0.13±0.002[a]	0.12±0.003[b]	0.12±0.003[b]	0.1±0.006[c]	0.001

	FWC	0.14 ± 0.001^a	0.13 ± 0.004^b	0.13 ± 0.002^b	0.12 ± 0.003^{bc}	0.1 ± 0.003^c	0.000
Zn	TSB	0.5 ± 0.1^a	0.5 ± 0.08^a	0.4 ± 0.02^b	0.3 ± 0.1^{bc}	0.2 ± 0.01^c	0.002
	WC	0.6 ± 0.05	0.4 ± 0.09	0.3 ± 0.1	0.3 ± 0.03	0.2 ± 0.01	0.029
	C	0.5 ± 0.02	0.5 ± 0.04	0.4 ± 0.02	0.4 ± 0.1	0.3 ± 0.03	0.102
	KS	0.8 ± 0.02	0.8 ± 0.01	0.8 ± 0.04	0.8 ± 0.01	0.7 ± 0.05	0.010
	SWC	1 ± 0.04^a	0.9 ± 0.06^b	0.8 ± 0.04^b	0.8 ± 0.004^b	0.7 ± 0.04^c	0.001
	FWC	0.9 ± 0.04^a	0.8 ± 0.03^{ab}	0.8 ± 0.01^b	0.7 ± 0.03^{bc}	0.7 ± 0.03^c	0.000
Zr	TSB	0.02 ± 0.002	0.02 ± 0.004	0.02 ± 0.003	0.0 ± 0.003	0.01 ± 0.002	0.201
	WC	0.01 ± 0.003	0.01 ± 0.003	0.01 ± 0.004	0.01 ± 0.001	0.01 ± 0.001	0.352
	C	0.01 ± 0.002	0.01 ± 0.001	0.01 ± 0.002	0.01 ± 0.003	0.01 ± 0.001	0.014
	KS	0.03 ± 0.002	0.03 ± 0.001	0.03 ± 0	0.03 ± 0.002	0.03 ± 0.003	0.058
	SWC	0.04 ± 0.001^a	0.03 ± 0.002^b	0.03 ± 0.002^b	0.03 ± 0.001^b	0.03 ± 0.002^b	0.000
	FWC	0.05 ± 0.005^a	0.03 ± 0.001^b	0.03 ± 0.003^b	0.02 ± 0.006^c	0.02 ± 0.003^c	0.000

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5.5. Discussion

In this study significantly higher concentrations of most elements were recorded in the tributary sediments indicating that the major contributors of elements to the Turtle River are its tributaries. None of the elements showed depletions at any of the sites, but Fe, U, Ni and Zn showed enrichments in some of the sites. The Turtle River is fed by the Dakota Aquifer. Water of the Dakota Aquifer is very saline and has a high dissolved solid content. The water generally contains excessive amounts of chloride, iron and sulfate (Kelly and Paulson 1970). In the present study enrichment of both Fe and U were recorded at the Whiskey Creek, which is a tributary of the North Branch of the Turtle River. In the Whisky Creek area of Nelson County ND, geological studies have revealed that there are Fe-containing minerals like amphiboles, ferromagnesian minerals, ferrous and ferric sulfides, oxides, and carbonates (ND Geological Survey 1975). The presence of Fe-containing minerals in the underlying geology may have caused enrichment in Fe in the Whisky Creek sediments. Studies on uranium speciation have revealed that U can be adsorbed to Fe oxides and Fe carbonates (Roden 2003, Sani et al. 2005, Kipp et al. 2009). Therefore the enrichment of Fe in Whiskey Creek sediments may have caused the enrichment of U in the sediments.

Ni and Zn are present as natural constituents of rocks, soil and sediments. Enrichment of Ni and Zn can result due to point and non-point sources. Diffuse Ni and Zn emissions can result from power plants, waste incinerators and metal industries (Lee et al. 2003, Tahri et al. 2005, Quinton and Catt 2007, Abe et al. 2010, Sarkar and Bhattacharya 2010). Enrichment of Ni was shown in the Kellys Slough tributary and of Zn in Salt Water Coulee respectively. The exact causes for enrichment of Ni and Zn in these tributaries are

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unknown. As this area does not have any metal related industries the enrichment could be possibly due to natural sources. These two tributaries are located in close proximity to each other. The web soil survey data indicates that the soil in this area of the watershed is silty loam in texture and the other parts of the watershed are dominated by silty clay soils. According to the USDA textural triangle, silty loam soil contains about 60 % silt and 40 % sand. This composition indicates high permeability of silty sand soil compared to the silty clay soils. Therefore, it is possible that diffusion of Ni and Zn from groundwater to the riverbed sediments in this area causes natural enrichment in the river sediments.

The lowest contribution of sediments was recorded at the confluence of north and south branches of the river. In this study, when sampling the confluence site near Larimore, the south branch of the river was considered as the tributary stretch and the north branch of the river was considered as the upstream stretch to maintain the consistency of sampling at that confluence with the other sites. In this case, sediment contribution of 39% came from the south branch of the river, which resulted in a contribution of 61% from the north branch of the river. Therefore, the contribution of sediments from the north branch was similar to the contribution from the Salt Water Coulee, which showed the highest contribution of sediments. This indicates that the north branch of the Turtle River was a more important sediment contributor compared to the south branch.

The highest contributions of As, Se and Cd were recorded in Whiskey Creek. Furthermore, the concentration of most elements (eg: Cr, Ni, P, Pb, Sb, V, Y, Zn) in this tributary showed significantly higher concentrations compared to upstream sediments (Table 5.2). This indicates that Whiskey Creek was a major contributor of trace elements and sediments to the main river.

The mean concentrations of As, Cd, and Se recorded in the Turtle River were, 5.2, 3.8 and 0.65 nmol/g of dry sediment. Arsenic compounds are abundant in the Earth's crust. Arsenic from weathered rocks and soils is dissolved in groundwater, and the prevalent forms of As in aquatic systems are, arsenic trioxide (As_2O_3), orpiment (As_2S_3), arsenopyrite (AsFeS) and enrealgar (As_4S_4) (Peterson and Carpenter 1986, Emsley 1989, Nikolaidis et al. 2004, Whitmore et al. 2008). Trace amounts of Cd can be present in surface and ground water as a natural constituent. It can exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulfates, or bound to organic complexes. Cadmium may enter aquatic ecosystems due to natural or anthropogenic sources. Most of the Cd entering into freshwater ecosystems can be adsorbed by particulate matter. Therefore sediments act as a major source of Cd to the overlying water column and biota in the fresh water ecosystems (OECD 1994, WHO 1992, Ghrefat and Yusuf 2006, Wong et al. 2006, Rauf et al. 2009). Selenium is also a natural component in soil, rocks and sediments. In water, Se can exist in dissolved, particulate or colloidal forms. They can be either deposited or re-suspended depending on the chemical, physical and biological conditions. Many studies have been done to assess the concentration and speciation of As, Cd and Se in aquatic environments (Wu 1995, Peters et al 1999 [b], Chowdhury et al. 2003, Ghrefat and Yusuf 2006, Wong et al. 2006, Whitmore et al. 2008, Rauf et al. 2009). The concentrations of these elements in the Turtle River were lower than the concentrations recorded in polluted sediments in other parts of the world (Wu 1995, Peters et al 1999 [b], Chowdhury et al. 2003, Ghrefat and Yusuf 2006, Wong et al. 2006, Whitmore et al. 2008, Rauf et al. 2009). Therefore, compared to those reports, the

Turtle River sediments show an enrichment of As, Se and Cd, but not to the extremes observed in some other systems.

The Turtle River is fed by the Dakota Aquifer and the water quality of the Dakota Aquifer is categorized as fair to poor for most parts. The water of the Dakota aquifer is rich in total dissolved solids (TDS), particularly carbonates and sulfates (Kelly and Paulson 1970, Rowden 2008). The carbonates and sulfates can form complexes and precipitates with metal ions and thereby can cause enrichment of metal ions. These metal ions may be subsequently released to the surface waters and may be deposited and re-suspended to and from the sediments, depending on the physical, chemical and biological characteristics in the environment (Gibbs 1973, Salomons and Fórstner 1984, Tessier and Campbell 1987, Drever 1988, Fórstner 1990, Ankley et al.1992, Maher and Aislabie 1992, Leivouri 1998, Evans 2001). Therefore the enrichment of As, Se and Cd in Turtle River sediments may be due to the enrichment of metal ions in the Dakota aquifer.

Accumulation of metals in the sediments is controlled by various complex physical and chemical reactions that take place in the environment. These include direct adsorption by fine grained clay particles in the sediments, adsorption by hydrated iron and manganese oxides, association with organic compounds and direct precipitation as new compounds (Gibbs 1973, Salomons and Fórstner 1984, Tessier and Campbell 1987, Drever, 1988, Förstner1990, Ankley et al.1992, Maher and Aislabie 1992, Leivouri 1998, Evans 2001, Jain 2004, Jain et al. 2005, Jain et al. 2008). These processes are influenced by various physico-chemical parameters such as, pH, dissolved oxygen, organic and inorganic carbon content, flow rate, oxidation states and presence of some anions and cations that can bind

or precipitate with the trace metals (Di Toro et al. 1991, Calmano et al. 1993, Wen and Allen 1999, Anazawa et al. 2004, Botes and Staden 2005).

In this study LOI was used as an indication of the organic matter content in the sediments (Boyer et al. 2003).Both LOI and f<63 showed significant variation among sites and they were correlated with most of the elements. Most elements did not show statistically significant concentration variations at some sites after normalizing for f< 63 and LOI. This indicates that binding of elements to both organic matter content and particle size play a role in determining the elemental concentrations in sediments at some areas in the Turtle River watershed.

The concentrations of almost all the elements at every site decreased with increasing distance from the tributary river confluence (Table 5.5). This shows that the elements tend to deposit immediately downstream from a confluence and subsequently decrease in deposition as they move away from the confluence. The concentrations of elements sorbed onto sediments and mobility of elements can be affected by the flow rate of water. The flow rate near the tributary river confluence tends to be higher due to flow convergence and it slows down as it moves away from the confluence. The lower flow rate can enhance the ability of sediments to release adsorbed trace elements to the water column because at low flow rates the contact time between sediments and water are high (Evans 2001, Dhakal et al. 2005, Leopold 2006, Charlton 2008). In turn, the retention and release of trace elements from the sediments to the water column is controlled by sorption characteristics of sediments, trace element concentrations in the water column, stream transport characteristic and residence times in bed sediments (Fairbridge1978, Fórstner 1990, Rosgen 1996, Evans 2001, Dhakal et al. 2005, Leopold 2006, Charlton 2008).

5.6. Conclusion

This research shows that there is a statistically significant variation of element concentrations in the Turtle River sediments. The Turtle River sediments are enriched with As, Cd and Se. The multi-element fingerprinting approach can be successfully used to identify possible sediment source and sink areas of the Turtle River and it can be also used to assess the spatial variation and transport of As, Cd and Se in the Turtle River sediments.

CHAPTER 6. GENERAL DISCUSSION

The sediments transported by a river or a stream are a mixture of sediments derived from different sources within the contributing catchment. Multi-element sediment fingerprinting is a valuable tool to assess the source, fate, and transport of sediments in a watershed. Large and complex combinations of parameters including physical, mineral–magnetic, chemical, radiometric, organic and inorganic properties are used in multi-element fingerprinting techniques (Yu and Oldfield 1989, Russell et al. 2001). The multi-element fingerprinting process can be used to measure temporal changes in sedimentation, to assess spatial information on the nature of the source material, to identify the selectivity of chemical properties in the erosion process and to estimate erosion under different land uses (Yu and Oldfield 1989, Owens et al. 2001, Russell et al. 2001). In multi-element fingerprinting studies, elements that have the potential to uniquely identify source materials are selected. These tracers are then used to represent sediment sources and sinks, and to assess the fate of the sediments (Walling 2005). Multi-element fingerprinting methods incorporated with river mixing models are applicable to larger river basins and they provide more accurate and precise information about potential source areas of sediments (Collins et al. 1997[a]). The multi-element sediment fingerprinting technique is highly site specific because tracer properties can vary among watersheds due to watershed variables, such as land use and management practices, geology of the parent material, and geomorphologic history (Collins and Walling 2002, Fox and Papanicolaou 2008). Therefore, no single type of natural tracer is globally applicable to allocate sediment sources in all watersheds. In multi-element fingerprinting studies, the selection of several elements with different origins and environmental behaviors helps to uniquely identify the

potential sediment sources and to quantify their relative contributions to the sediment load of a river (Davis and Fox 2009).

In this study the multi-element fingerprinting technique was used to assess the spatial variation and trends in element transport in two river basins in North Dakota, the Souris River and the Turtle River. It was hypothesized that tributaries were the major contributors of sediments and contaminants to the rivers, phosphorus in the Souris River, and several metals in the Turtle River.

The f< 63 in the Souris and Turtle Rivers varied in a similar range, but LOI in the Souris River sediments varied over a wider range compared to the Turtle River sediments. In the Turtle River sediments the LOI and f<63 were significantly correlated to each other but not in Souris River sediments. In Souris River sediments, none of the elements were correlated with either LOI or f<63, but in Turtle River sediments most of the elements showed statistically significant correlations with LOI and f<63. As an example, the correlations of Fe and Al with LOI and f<63 in the two rivers are shown in Figure 6.1.

In most other studies, clay and silt fractions of river sediments and organic matter have been considered to be the main adsorbing agents of trace metals (Bogen 1992, Stone et al. 1995, Jain and Ram 1997, Murray et al. 1999, Thayyen et al. 1999, Walling et al. 2000, Ranville et al. 2005, Puyate et al. 2007), showing strong correlations. The smaller size particles of river sediments are dominated by silicate minerals, which have a high surface affinity for metal ions due to their large surface area to volume ratio. The organic matter on the other hand, contains negatively charged surfaces which can bind positively charged metal ions in the solution phase (Coquerry and Welbourn 1995, Schorer 1997, Onstad et al. 2000, Rognerud and Fjeld 2001). The results of this study indicate that,
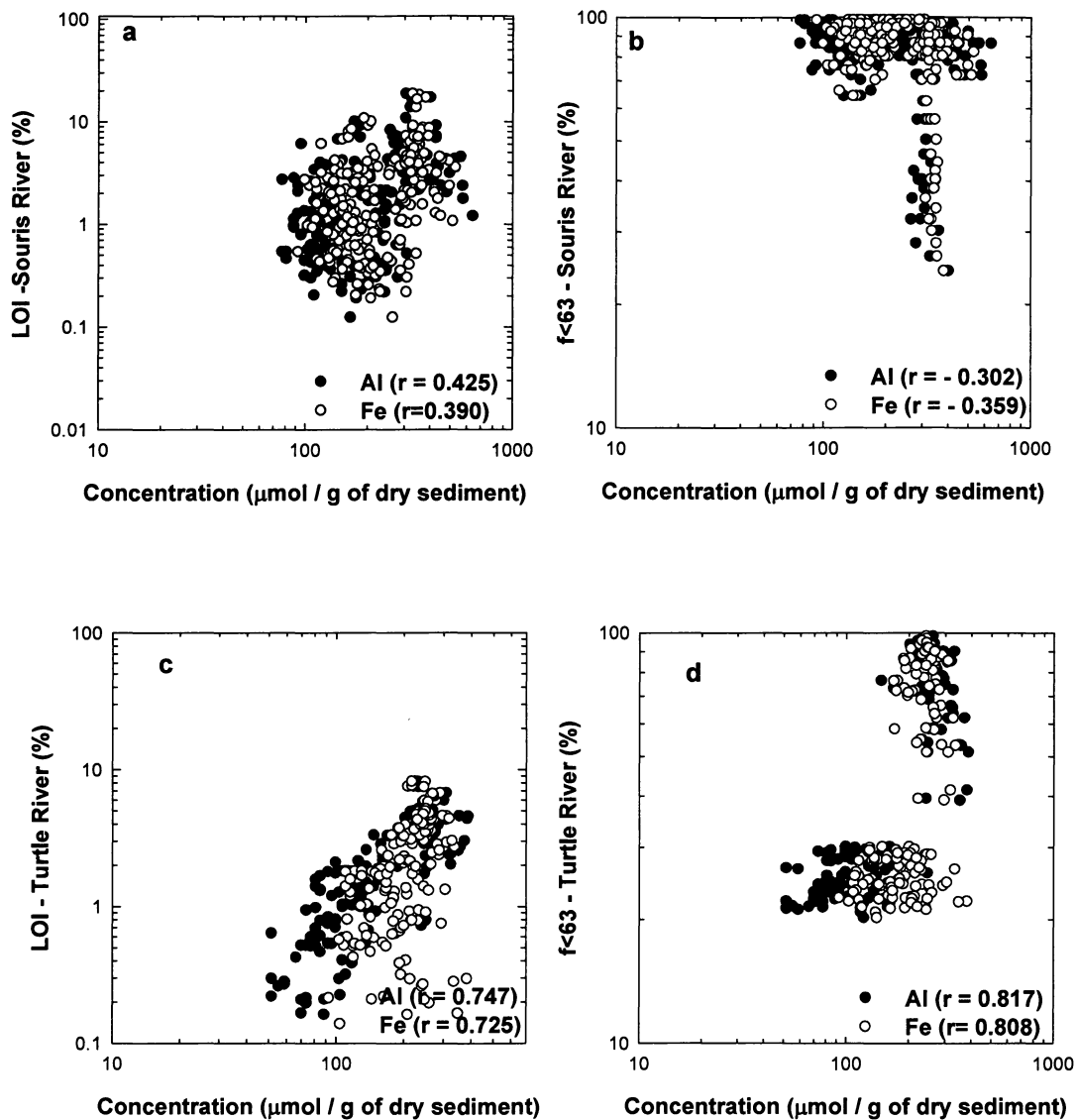
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Figure 6.1: Pearson's correlation of Fe and Al with LOI and f<63 in the Souris River and Turtle River sediments (a-Correlation with LOI- Souris River; b- Correlation with f<63-Souris River; c-Correlation with LOI- Turtle River; d- Correlation with f<63- Turtle River).

even though the ranges in f<63 were similar in both rivers, the compositions were different

and the binding capacities of the Turtle River sediments higher than those of the Souris

River sediments.

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In general, the concentrations of potential pollutant elements were low at upstream locations and increased at tributary river confluences. The concentration variation of phosphorus in sediments along the Souris River is given in Figure 6.2. Phosphorus concentrations of the sediments generally increased immediately after confluences of tributaries and decreased beyond that going downstream, away from the confluence (Figure 6.2). There is a noticeable decrease of phosphorus concentrations between the sites G and DL (Des Lacs River) (Figure 6.2). Site G is the last sampling site north of Lake Darling and site H is the first sampling site south of Lake Darling. Lake Darling is a reservoir created by constructing a dam across the Souris River and has an approximate surface area of 40 km^2. The damming across rivers can slow down the rate of water flow and can cause suspended sediment and associated nutrients to be retained within the reservoir. This results in decreasing the suspended sediment and nutrient loads to the sections downstream from the dam (Vörösmarty et al. 2003, Teodoru and Wehrli 2005, Mueller et al. 2010, Rao et al. 2010). In agreement with other studies on this type of situation, the results of the current study showed there is a large decrease in the phosphorus concentration at site H (downstream site from Lake Darling) compared to site G (upstream site from Lake Darling).

Similarly, As, Cd and Se in the Turtle River showed lower concentrations at the upstream locations and increased at the confluences of tributaries(Figures 6.3, 6.4 and 6.5).

Along rivers, sediments are released from actively eroding sites, while they deposit downstream in areas of low flow rates. They may be released again and consequently sinks become sources for deposition further downstream. The sediments tend to deposit immediately downstream from a tributary river confluence due to flow convergence
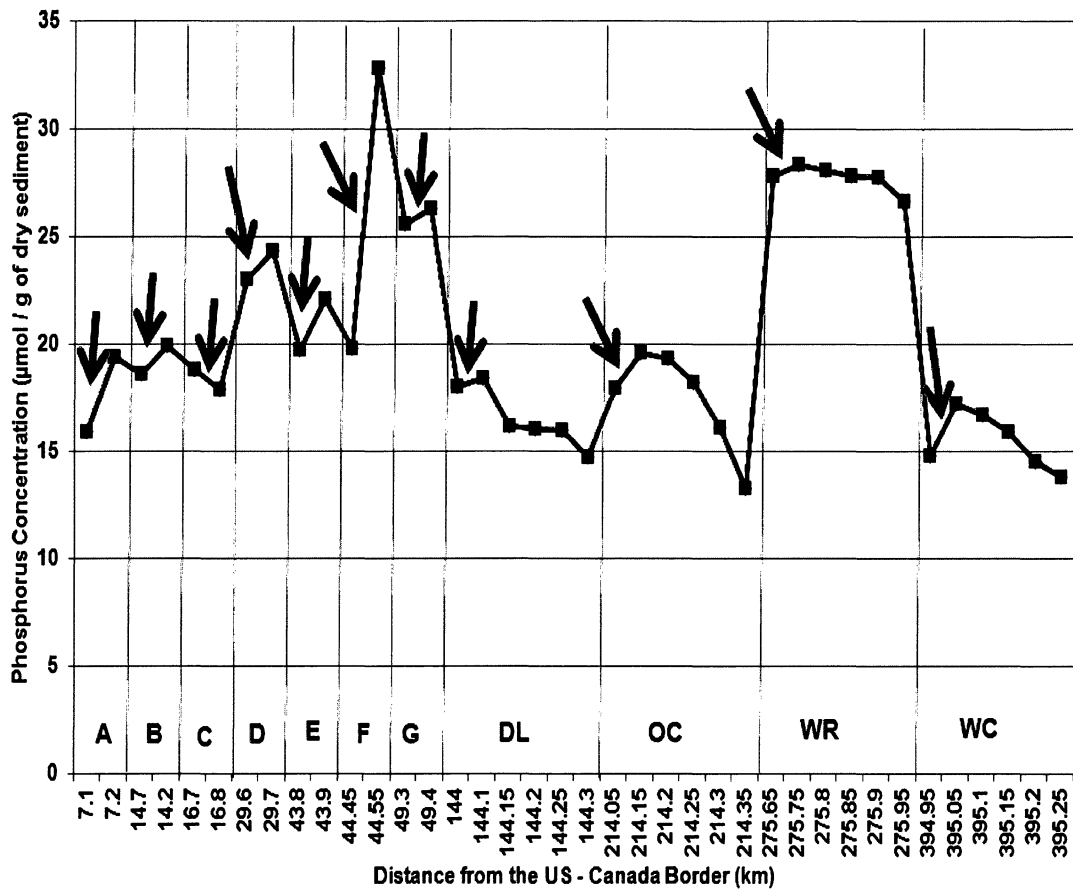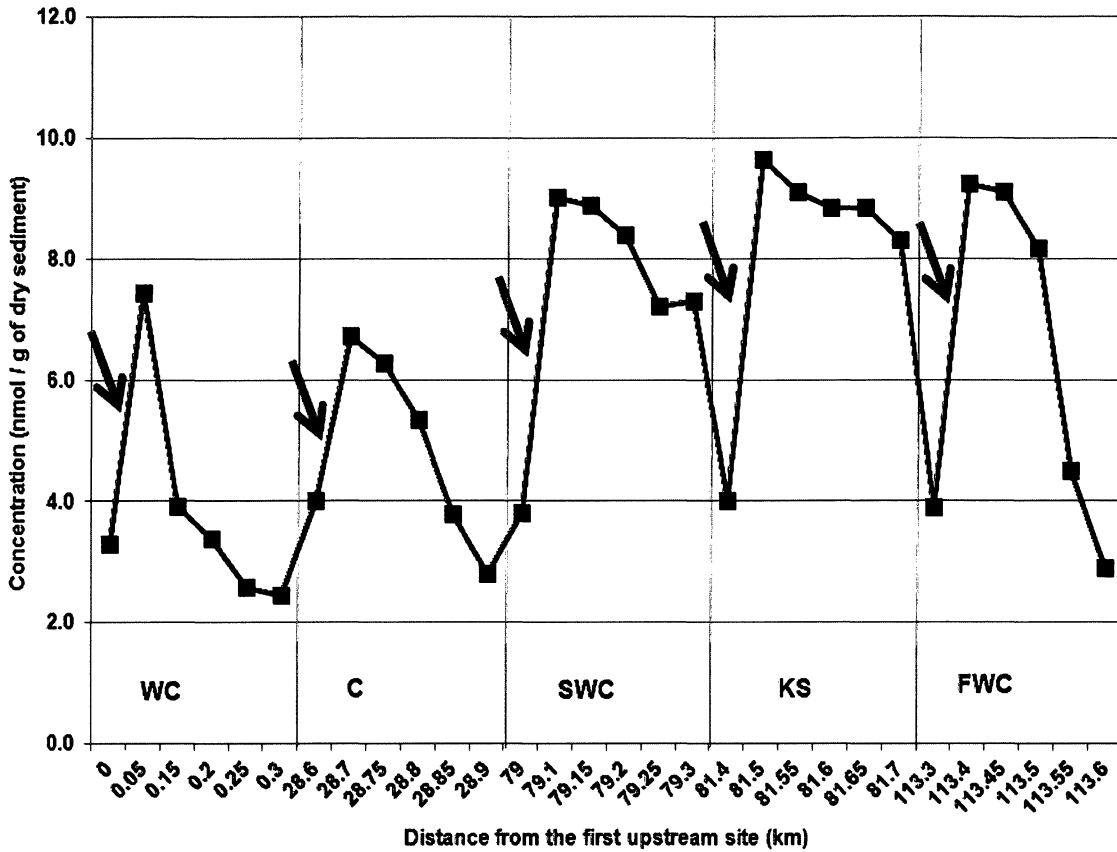
Figure 6.2: The variation of phosphorus concentrations along the Souris River. The blue arrows indicate the confluences of tributary (between upstream and downstream sites). The red vertical lines show the different watersheds(Sites A-G: smaller tributaries in the Upper Souris River north of Lake Darling, DL: Des Lacs River, OC: Oak Creek, WR: Wintering River, WC: Willow Creek).X-axis not to scale.

(Fairbridge 1978, Rosgen 1996, Leopold 2006, Charlton 2008). Therefore, upstream and tributary sediments can act as sediment sources to the downstream sediment sink areas. The results of this study showed, in most of the locations, the element concentrations along the main river spiked after the confluence of the tributary. In these locations the tributary sediments were the major sources of those elements for the
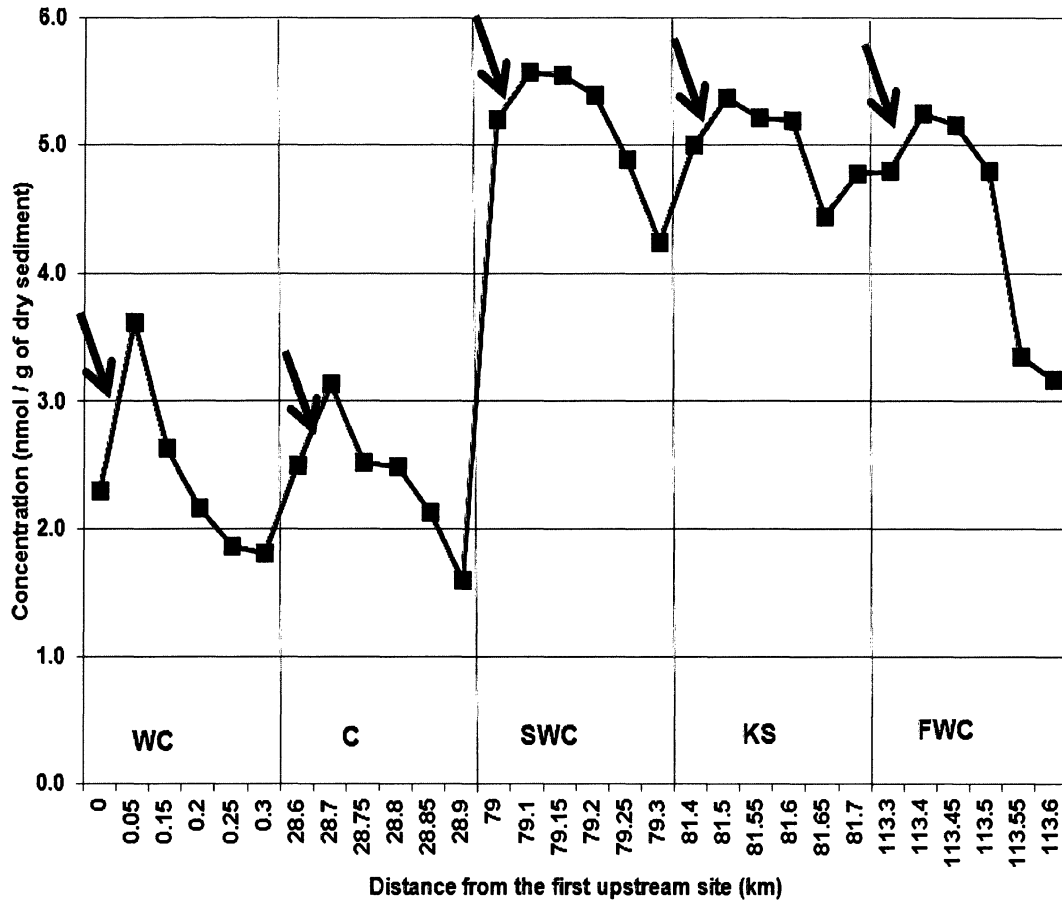
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Figure 6.3: The variation of arsenic concentrations along the Turtle River. The blue arrows indicate the confluences of tributary. The red vertical lines show the different watersheds. (WC – Whiskey Creek, C- Confluence of south and north branches, SWC – Salt Water Coulee, KS – Kellys Slough, FWC – Fresh Water Coulee). X-axis not to scale.

downstream sediments. In some locations the element concentration significantly increased

along the river even before the next confluence with another tributary. For example, the

concentrations of Fe and Al in the sediments along the Turtle River sediments at the

confluence of Salt Water Coulee (Figure 6.6) increased in the upstream stretch of the river

and it spiked after the confluence of the tributary.

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Figure 6.4: The variation of cadmium concentrations along the Turtle River. The blue arrows indicate the confluences of tributary. The red vertical lines show the different watersheds. (WC – Whiskey Creek, C- Confluence of south and north branches, SWC – Salt Water Coulee, KS – Kellys Slough, FWC – Fresh Water Coulee). X-axis not to scale.

In some sites the upstream locations showed higher concentrations than the downstream locations of the sites further upstream. This was observed both in the Souris River and Turtle River sediments. For example, in the Souris River, the phosphorus concentration of site J upstream was significantly higher compared to the concentration of downstream sediments of site I (Figure 6.2). A similar trend was observed in some sites
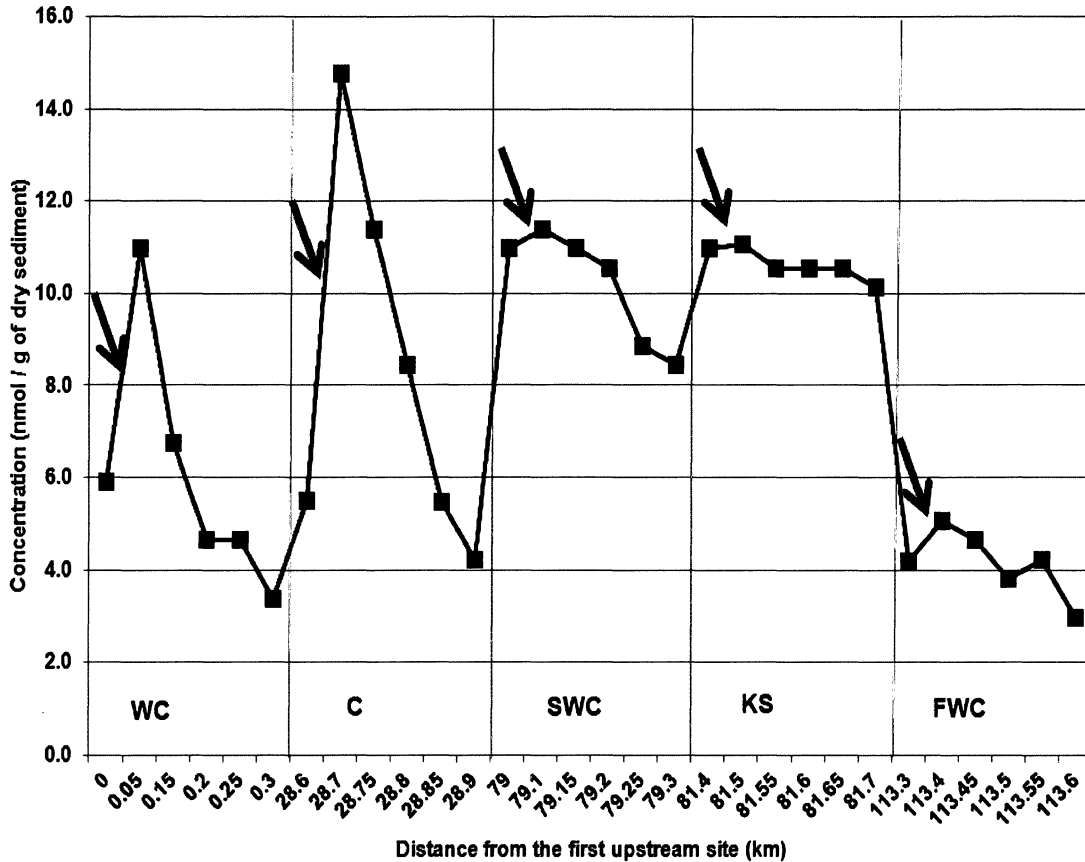
Figure 6.5: The variation of selenium concentrations along the Turtle River. The blue arrows indicate the confluences of tributary. The red vertical lines show the different watersheds. (WC – Whiskey Creek, C- Confluence of south and north branches, SWC – Salt Water Coulee, KS – Kellys Slough, FWC – Fresh Water Coulee). X-axis not to scale.

along the Turtle River; the Cd and As concentrations at the upstream location of site SWC in the Turtle River were significantly higher than in the downstream sediments of site C (Figure 6.3 and Figure 6.4). The concentration variation along the river sediments can be partly explained by differences in the organic matter and clay and silt fractions in the sediments, but in the Souris River the element concentrations did not show significant correlations with LOI or f < 63. As the element concentrations in the Turtle
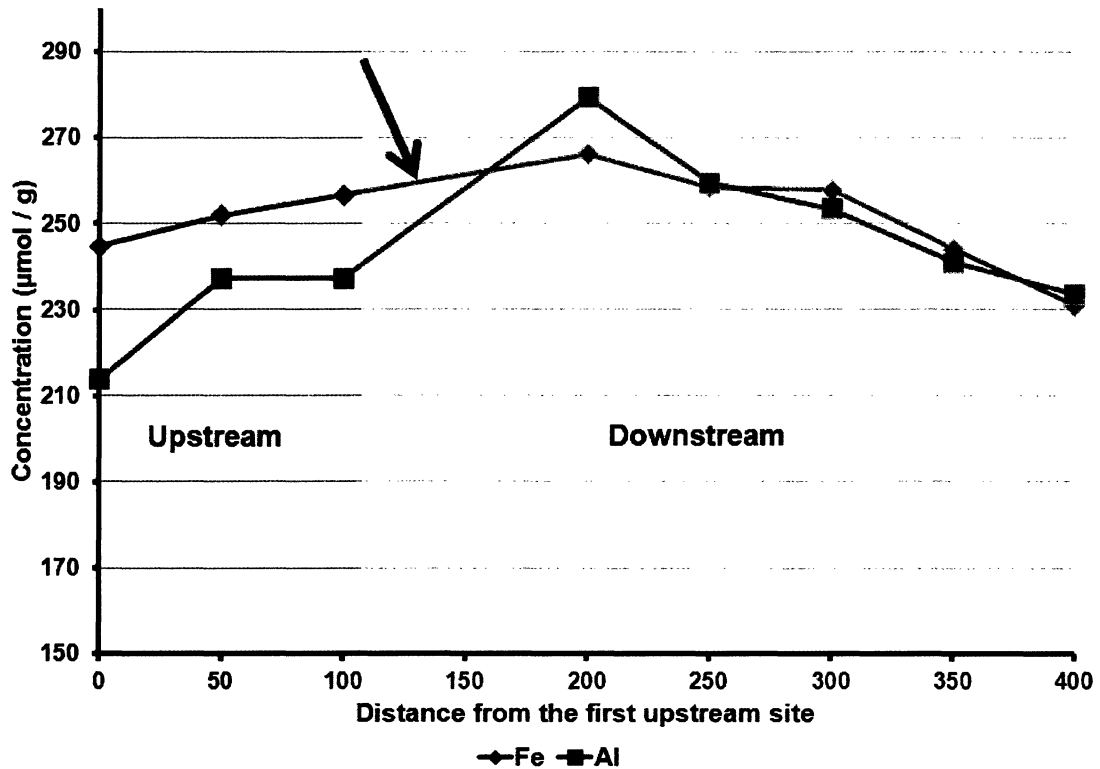
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Figure 6.6: Concentrations of Fe and Al along the Turtle River at the Salt Water Coulee confluence. The blue arrow indicates the confluence of Salt Water Coulee.

river were significantly correlated with f< 63 and LOI, the As and Cd concentrations were normalized for the LOI and f< 63 (Figure 6.7). The normalized concentrations also showed spiked concentration increases at the tributary confluences (Figure 6.7). In the normalized concentrations, a conspicuous concentration difference of As between the upstream location of site SWC downstream sediments of site C was still present while the difference of Cd is not prominent (Figure 6.7). This shows that there was a major unidentified source of As between the C and SWC sites. This is not necessarily a point source nor anthropogenic, but may be due to a diffuse natural source, such as upwelling of As-rich groundwater (Warner 2001, Holm et al. 2005).
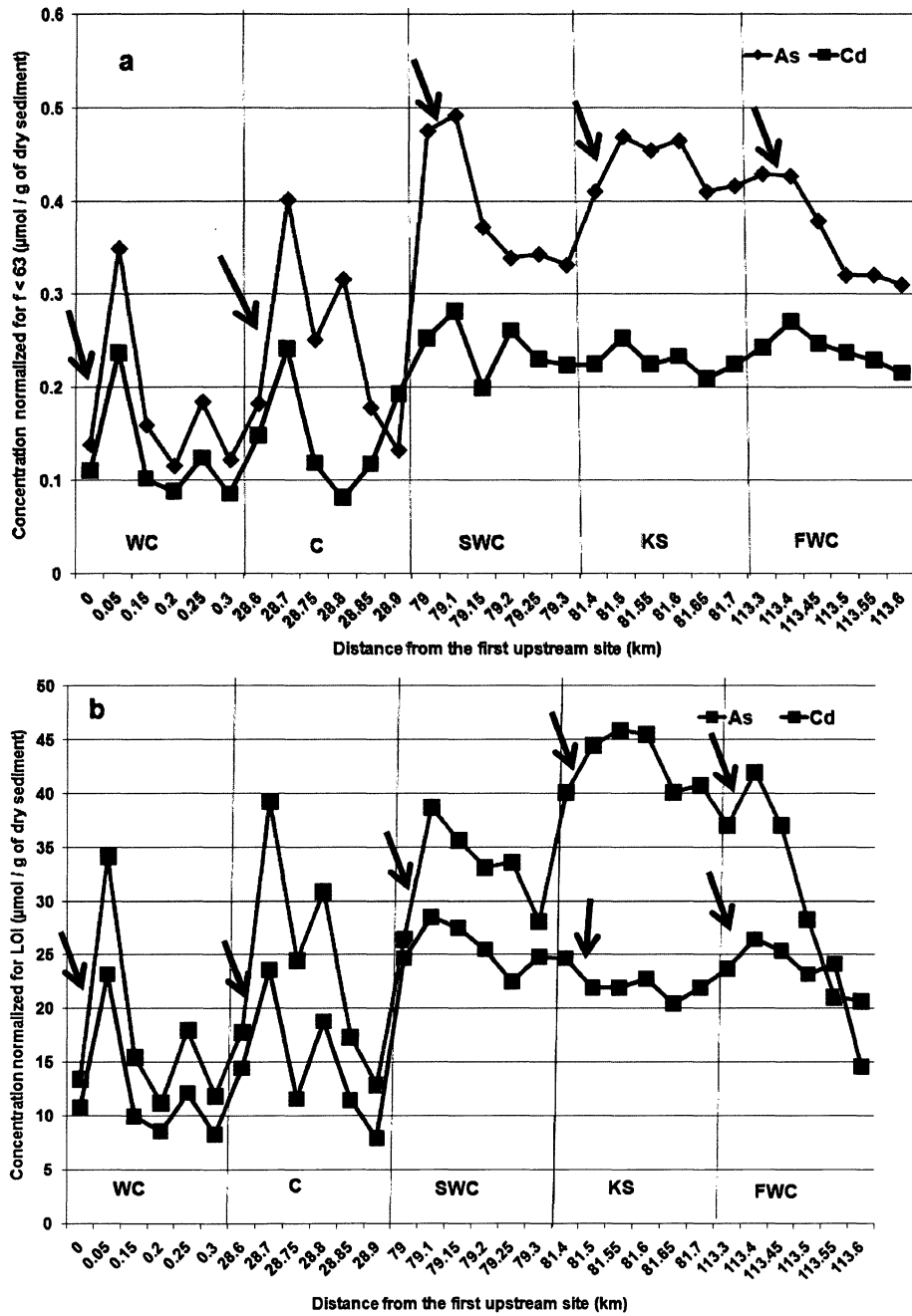
Figure 6.7: The normalized concentration variation of As and Cd along the Turtle River (a – normalized for f<63; b – normalized for LOI). The blue arrows indicate the confluences of tributary. The red vertical lines show the different watersheds. (WC – Whiskey Creek, C- Confluence of south and north branches, SWC – Salt Water Coulee, KS – Kellys Slough, FWC – Fresh Water Coulee). X-axis not to scale.

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Therefore, based on this information, three major source-sink relationships can be identified in river sediments, which are graphically presented in Figure 6.8, as follows:

1: Tributaries acting as the major sediment/pollutant sources to downstream sections of the main river (Figure 6.8 a)

2: Tributaries are minor sediment/pollutant sources to downstream sections (Figure 6.8 b).

3: Presence of unidentified diffuse and/or point sediment/pollutant sources from the surrounding areas   (Figure 6.8 c).

Sediment source-sink relationships similar to the field observations were also identified for Ca, P and Mg in the river simulation experiment conducted in the laboratory. Their concentrations increased in the bottom tier while they decreased in the top tiers over time. The increases in concentrations of these elements in the bottom tiers were smaller or equal to the decreases in concentrations in the top tiers, indicating a balanced mass balance between top and bottom tiers. This suggests that these elements were mobilized in the top tiers by running water and re-deposited in the lower tiers and agrees with what happens in the natural environment for most of the elements (eg: Ca, P, Mg, S).

The contribution of sediments from tributaries to the main river depends on many factors such as watershed size, flow rate, land uses, underlying geology and geomorphology. In the Souris River, the percentage contribution of sediments and the phosphorus from the Upper Souris River tributaries were lower compared to the contributions from the larger tributaries further downstream (Des Lacs River, Oak Creek, Wintering River and Willow Creek).
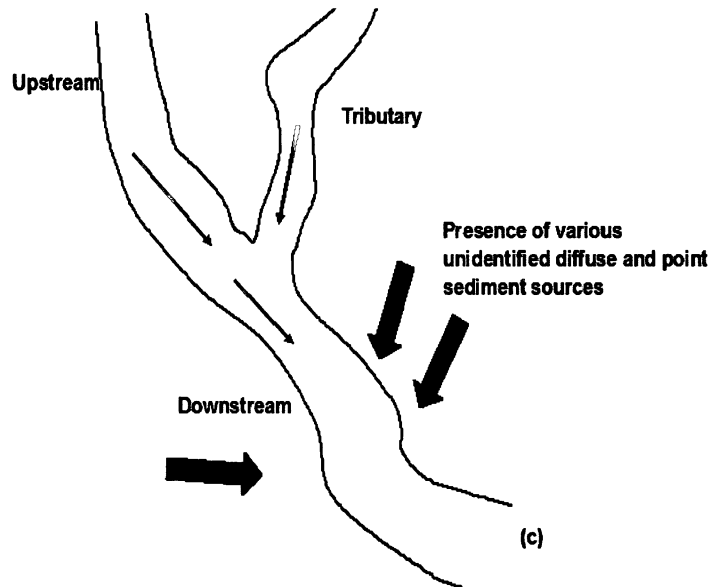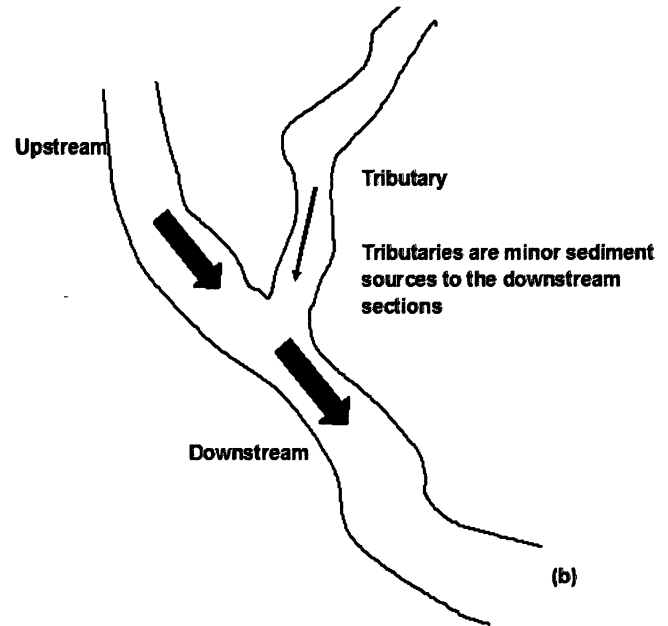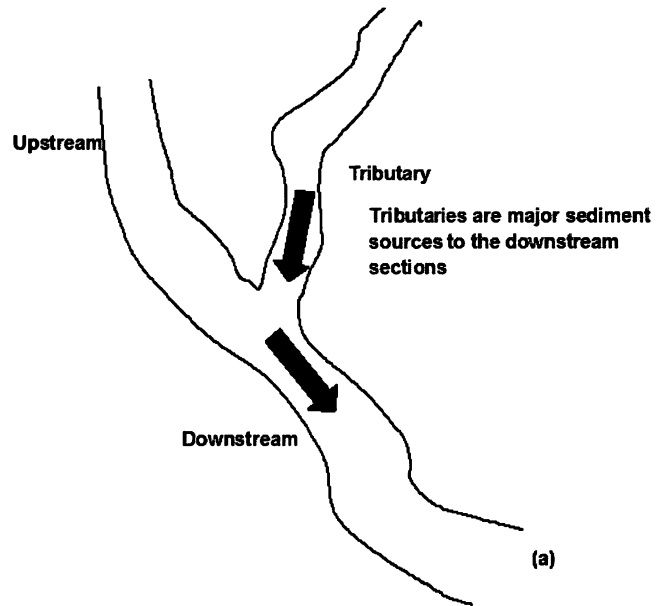
Figure 6.8: The sediment source – sink relationships in river systems. a: Tributaries are major sediment sources, b: The tributaries are minor sediment sources, c: Presence of unidentified diffuse and point sediment sources.

The relative sizes of the watersheds of the tributaries in the Souris River were calculated using topography maps of the area (Table 6.1). In this calculation, the surface area of the watershed of tributary A (which was the first site sampled and the site closest to the Canadian border) was used as the base value. The surface area of the Site A watershed was approximately 70 km^2. Therefore the sizes of the watersheds of the tributaries to the Souris River relative to tributary A were calculated as surface area of the watershed of tributary A (km^2) / 70 km^2, giving the watershed of tributary A, a value of 1. The relative watershed size of the Upper Souris River tributaries were smaller compared to the relative watershed size of the downstream tributaries in the Lower Souris River (Table 6.1). The correlation between the relative size of the Souris River watersheds and the contributions of sediment and phosphorus are given in Figure 6.9. In the Souris River watersheds, the sediment and phosphorus contributions of the tributaries were highly correlated with the relative sizes of the watersheds (Figure 6.9). The smaller watersheds contribute smaller amounts of sediments to the main river compared to the larger watersheds (Table 6.1). Therefore, it was concluded that in the Souris River, the tributaries of the Lower Souris River area, with larger relative watershed sizes, are the major contributors of sediments and phosphorus to the Souris River.

The smaller tributaries in the Upper Souris River area drain land within the Upper Souris River wildlife refuge. The land-use in the watersheds of the larger tributaries (Des Lacs River, Oak Creek, Willow Creek, and Wintering River) was mostly dominated by agriculture. Some potential nonpoint-source agricultural threats in the Lower Souris River area are livestock grazing, and chemical, fertilizer and manure application (Saskatchewan Watershed Authority, 2004). Draining of larger portions of land used by agricultural

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activities may also have resulted in higher phosphorus concentration in the Lower Souris

River tributaries.

Table 6.1: The relative size of the watersheds($1 = 70$ km^2), the percentage contributions of sediment and phosphorus from the Souris River tributaries (Sites A-G - the smaller tributaries in the Upper Souris River north of Lake Darling, DL – Des Lacs River, OC – Oak Creek, WR – Wintering River, WC – Willow Creek).

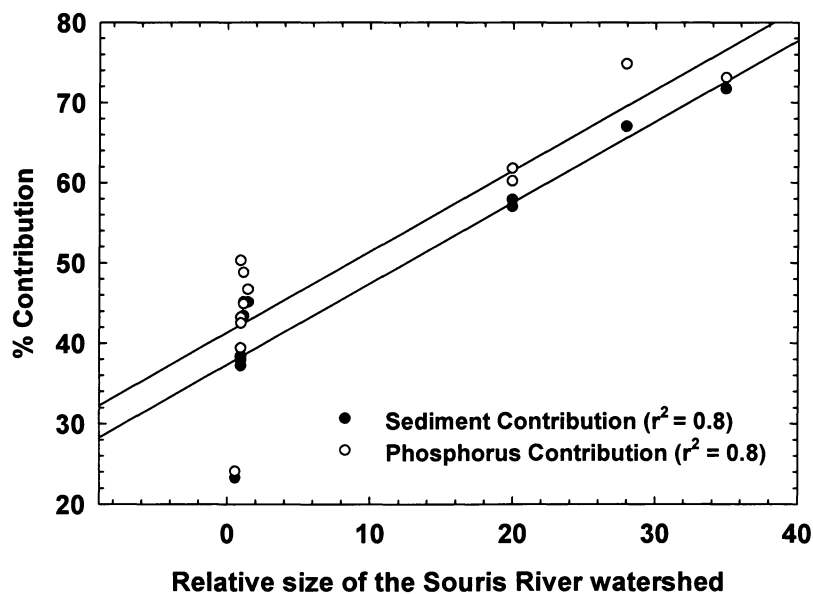| Site	Relative size of the watershed	Contribution (%) Sediment	Contribution (%) Phosphorus
A	1	58.3	63.1
B	1.5	45	46.6
C	1	38.1	39.3
D	1.2	43. 3	44.8
E	1	37.1	42.4
F	1	37.8	50.2
G	1.2	45	48.7
DL	35	71.6	73
OC	20	56.9	60.1
WR	20	57.8	61.7
WC	28	66.9	74.7

Figure 6.9: Correlation between the relative sizes of the Souris River watersheds and their sediment and phosphorus contributions.

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The Upper Souris River area, north of Lake Darling mainly consists of black organic clay and silt deposits, whereas in the Upper Souris River area north of Lake Darling most soils consist of sand fractions with variable amounts of shale and carbonates. The sand fraction is largely quartz and feldspars. Generally, the sand is loose and highly permeable (ND Geological Survey 1985). The clay soils have small pore sizes compared to sandy soils and this makes it difficult for water carrying nutrients and contaminants to pass into the watershed. The high permeability of the sandy soils may have permitted more nutrient runoff into the watershed. This may be another reason why the tributaries in the Lower Souris River area showed higher phosphorus contributions compared to the Upper Souris tributaries.

The relative sizes of the watersheds of the tributaries in the Turtle River were calculated using topographic maps of the area (Table 6.2). In this calculation, the surface area of the watershed of the tributary to the South Branch (TSB) of the river was used as the base value. The surface area of this watershed (TSB) was approximately 90 km^2. Therefore the relative sizes of the Turtle River watersheds were calculated as: Surface area of the watershed (km^2) / 90 km^2. The relative size of the tributaries of the Turtle River and their percentage contribution of sediments, As, Se and Cd are given in Table 6.2. The relative sizes of the watersheds in the Turtle River tributaries did not cover as wide a range as in the Souris River, and therefore there was no clear relationship between the size of tributaries of the Turtle River and their contributions (Table 6.2, Figure 6.10).Several studies investigated the effect of watershed characteristics on sediment loading, and have shown that not only the size of the watershed, but also the magnitudes of rainfall events, the water flow rate, peripheral land use characteristics, and the particle size of the

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sediments can play a key role in determining the contribution of sediments from the

watersheds (Trimble 1997, Lopes and Canfield 2004).

Table 6.2: The relative size of the watersheds($1 = 90$ km^2), the percentage contributions of sediment arsenic, cadmium, and selenium from the Turtle River tributaries (TSB – Tributary to the South branch, WC – Whiskey Creek, SB – South branch, NB North branch, KS Kellys Slough, SWC – Salt Water Coulee, FWC – Fresh Water Coulee).

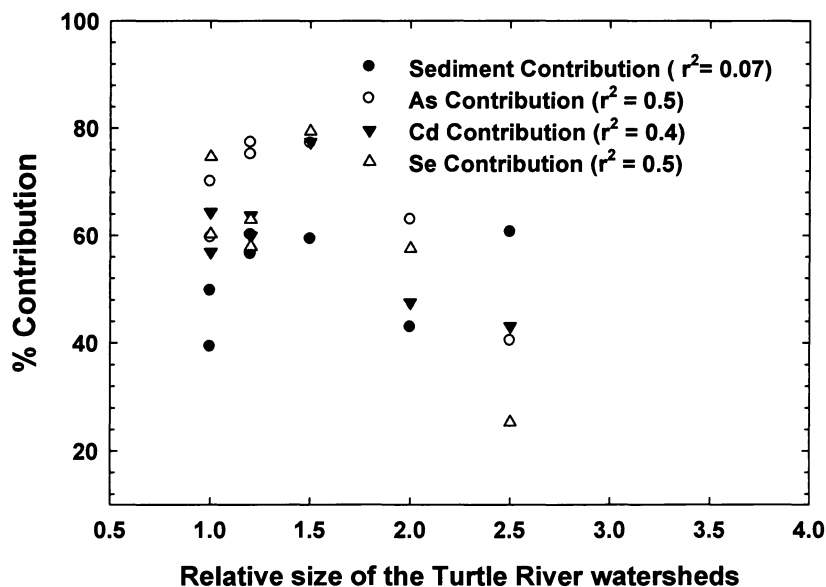| Site | Relative size of the watershed | Contribution (%) | | |
		Sediment	As	Cd	Se
TSB	1	49.7	70	64.3	60.2
WC	1.5	59.3	77.2	77.4	79.4
SB	1	39.3	59.6	56.9	74.6
NB	2.5	60.6	40.4	43.1	25.3
KS	1.2	56.5	75.1	59.9	57.9
SWC	1.2	60.1	77.29	63.7	62.9
FWC	2	42.9	62.9	47.5	57.5

Figure 6.10: The correlation between the relative size of the Turtle River watersheds and the sediment, As, Cd and Se contributions.

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In order to compare the two rivers, the mean concentrations of elements in the Souris River and the Turtle River are given in Table 6.3. The concentrations of Cu, Zn, Pb, Ni, Co, Bi, K, Tl, Ga, Cs, Rb, Y, Ce, Be and Li did not show statistically significant differences between the Souris River and Turtle River sediments. The concentrations of Al, Ba, Co, Fe, Hf, Mo, Nb, Sc, and Sn were significantly higher in the Souris River sediments compared to the Turtle River sediments ($P \leq 0.05$). The concentrations of Ca, Cr, La, Mg, Mn, Na, Sb, S, Sr, Th, and U showed significantly higher concentrations in the Turtle River sediments compared to the Souris River sediments ($P \leq 0.05$) (Table 6.3). The underlying geology of the area can play a key role in determining element concentrations in the surface sediments. For example, the Turtle River is fed by the Dakota Aquifer (Kelly and Paulson 1970, Rowden 2008). The underlying geology of the Turtle river area consists mainly of fine-grained quartzose sandstone that is interbedded with dark-gray shale (Kelly and Paulson 1970, Rowden 2008). Water from the Dakota Aquifer contains high dissolved solids, is very saline, and contains high sodium concentrations (Kelly and Paulson 1970, Rowden 2008). Carbonate minerals are also common in the area and contain high concentrations of Ca and Mg. Sulfur-bearing minerals like gypsum ($CaSO_4 \cdot 2H_2O$) and pyrite (FeS_2), are also present in the parent geologic material in the area. Other elements and compounds present include Fe, Mn, As, hydrogen sulfide (H_2S), ammonia (NH_3), methane (CH_4), and radioactive compounds like Ra and Rn (Kelly and Paulson 1970, Rowden 2008).Therefore, the presence of higher concentrations of Ca, Cr, La, Mg, Mn, Na, Sb, S, Sr, Th and U in the Turtle River sediments can be accounted for by the underlying geology of the Turtle River area.

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Table 6.3: Comparison of mean element concentrations (μmol / g of dry sediment) of the Souris River and Turtle River sediments. Data are presented as mean ± SD.

Element	Souris River	Turtle River	P value
Al	224±115	192±86	0.002
As	0.1±0.03	7±3.7	0.000
Ba	1.1±0.4	0.8±0.3	0.000
Be	0.04±0.02	0.04±0.01	0.012
Bi	0.0005±0.0003	0.001±0.0003	0.012
Ca	464±229	972±283	0.000
Cd	0.002±0.001	3.8±1.5	0.000
Ce	0.2±0.03	0.2±0.05	0.011
Co	0.1±0.04	0.09±0.04	0.007
Cr	0.23±0.09	0.25±0.06	0.009
Cs	0.004±0.001	0.004±0.001	0.014
Cu	0.2±0.09	0.2±0.1	0.115
Fe	240±98.4	216.2±55.7	0.003
Ga	0.03±0.01	0.03±0.01	0.014
Hf	0.0004±0.0002	0.0003±0.0001	0.000
K	30.5±12.9	34.1±16	0.010
La	0.09±0.02	0.1±0.03	0.000
Li	1.2±0.5	1.2±0.6	0.521
Mg	288±83.6	521.9±193.2	0.000
Mn	7.6±5.2	18.3±11.5	0.000
Mo	0.3±0.001	0.004±0.002	0.000
Na	18.8±9.3	37.8±37.3	0.000
Nb	0.003±0.001	0.002±0.001	0.000
Ni	0.3±0.1	0.2±0.09	0.391
P	21.6±6.6	2.7±0.3	0.000
Pb	0.04±0.01	0.04±0.01	0.376
Rb	0.1±0.04	0.1±0.06	0.012
S	0.01±0.003	48.51±26.3	0.000
Sb	0.001±0.0003	0.002±0.0004	0.000
Sc	0.04±0.02	0.036±0.01	0.000
Se	0.01±0.002	8.34±4	0.000
Sn	0.004±0.003	0.003±0.001	0.001
Sr	0.5±0.2	1±0.5	0.000
Th	0.01±0.004	0.02±0.01	0.000
Ti	0.5±0.1	0.5±0.2	0.196
Tl	0.001±0.0003	0.001±0.0004	0.010
U	0.004±0.001	0.008±0.002	0.000
V	0.4±0.1	0.5±0.1	0.000

Table 6.3 (Continued)

Y	0.1±0.02	0.1±0.02	0.012
Zn	0.7±0.3	0.7±0.3	0.644
Zr	0.04±0.02	0.03±0.01	0.000

Many studies have been done to assess the concentrations of elements in rivers. The concentration ranges in the present study were compared with mean element concentrations recorded in some polluted and unpolluted rivers as documented in other studies (many elements have not been evaluated by other researchers and thus no comparisons are possible) (Table 6.4). Of the 25 elements compared, the concentrations of most of the elements recorded in the Souris River and the Turtle River in this study were lower than the mean concentrations recorded in most of other rivers (Table 6.4). For example, the concentration ranges of Co, Cr, Cu, Mn, Ni, Pb, Ti, V and Zn in the Souris River and the Turtle River were lower than the mean concentrations of these elements recorded in rivers in the other parts of the world (Table 6.4). The concentration of Al, Ca, Fe, K, Li, Mg, Mn and Na in the Nestos River, Greece, which was considered to be a be a non-polluted river, lies within the concentration range of these elements in the Turtle River and the Souris River (Papastergios et al. 2009). The concentration of S in the Nestos River lies within the range of S concentration of the Turtle River, but is higher than the range of S concentration in the Souris River (Papastergios et al. 2009). The mean concentrations of all the other elements recorded in the Nestos River were higher compared to the concentrations recorded in the Souris River and the Turtle River (Table 6.4).These results indicate that there is no concern about metal pollution either in the Souris River or Turtle River compared to some other rivers.

Table 6.4: Element concentrations (μmol/g) in the Souris River, the Turtle River and some other rivers. a: Papastergios et al. 2009; b: Kronfeld and Navrot 1974; c: Lin et al. 2006; d: Singh et al. 2005[a]; e: Singh et al. 2002; f: Jain 2004; g: Mathis and Cummings 1973; h: Sakai et al. 1986; i: Uzairu et al. 2009

	Souris River (This study)	Turtle River (This study)	Nestos River Greece [a]	Qishon River, Israel [b]	Second Songhua River, China [c]	Gomiti River, India [d]	Ganges River, India [e]	Yamuna River, India [f]	Illinois USA [g]	Toyohira River Japan [h]	Kubabbi River, Nigeria [i]
Al	77.8 - 648.6	51.9 - 389. 2	0.3								
Ba	0.5-2.4	0.2 - 2	3.8								
Ca	104.8 - 1948.6	149.7 - 1691.6	0.2								
Ce	0.1 - 0.3	0.1-0.5	1.0								
Co	0.05 - 0.3	0.03-0.2	0.3	0.3	0.4		0.7				
Cr	0.09 - 0.6	0.1-0.4	0.9	7.1	1.8	0.8	8.9			1.2	1.1
Cs	0.002 - 0.008	0.001-0.007	0.1								
Cu	0.04 -0.4	0.03-0.4	0.7	0.6	0.9	1.6	5.8	0.8	0.7	0.8	1.9
Fe	93.1 -533.6	93.1-384.9	0.4								
Ga	0.01 - 0.08	0.01-0.05	0.2								
K	10.2-69.2	0.07-0.3	0.1								
La	0.05 - 0.1	0.07-0.3	0.1								
Li	0.4 -2.8	0.3-2.2	0.5								
Mg	139.9-452.5	172.8-818.6	0.2							25.2	
Mn	1.6 - 35.7	2.7-93.6	17.7		20.5						
Mo	0.0009 - 0.01	0.0009-0.02	0.01								
Na	4.3 - 59.1	2.6-173.6	0.03								
Ni	0.1 - 0.6	0.09-0.5	0.8	0.7	0.7	0.9	3.1				0.7
Pb	0.01 - 0.08	0.01-0.07	0.7	4.0	0.9	1.2	2.7	2.2	1.0	0.9	0.6
Rb	0.03 - 0.2	0.03-0.2	1.3								
S	0.0006 - 0.03	9.3-199.6	0.01								
Sb	0.0005- 0.002	0.0008-0.003	0.004								
Sn	0.0008 - 0.02	0.0008-0.01	0.01								

| Sr | 0.2 - 2.1 | 0.3-2.6 | 0.6 |
| Th | 0.005 - 0.03 | 0.005-0.09 | 0.3 |

The mean and the range of P concentrations in the Souris River, the Turtle River, and sediments of some other rivers reported worldwide are given in Table 6.5. The mean phosphorus concentration of the Souris River sediments were about tenfold higher compared to with the Turtle River sediments (Table 6.5).Both the Souris River and the Turtle River drain areas that are used by agriculture (US EPA 2004, NRCS 2007), but there is concern of phosphorus loading into the Souris River, not to the Turtle River (US EPA 2004). The results from this study agreed with this concern, showing higher phosphorus concentrations in the Souris River sediments compared to the Turtle River. No studies were available on phosphorus loading rates to the Souris River or the Turtle River. The Souris river drainage area is about 63,714 Km^2 and the Turtle river drainage area is about 1,645 Km^2 (US EPA 2004). Therefore, the Souris River watershed is about 40 times larger than the Turtle River watershed. The larger watersheds carry more sediment compared to smaller watersheds (Nichols and Renard 2003). Therefore, we can expect more sediment to be present in the Souris river watershed compared to the Turtle River sediments. As both watersheds are dominated by agricultural activities, we can assume the phosphorus loading rates to both watersheds to be similar for the purpose of comparison. Therefore, the presence of higher phosphorus concentrations in the Souris River watershed can be accounted for by higher sediment load in the Souris River compared to the Turtle River.

In the Souris River area, secondary minerals are sometimes found within primary minerals. These secondary minerals consist of calcite, gypsum, limonite, manganese dioxide, and dolomite (ND Geological Survey 1985). Inorganic phosphorus present in the pore water of sediments can be retained by oxides and hydroxyl oxides of iron and aluminum and by calcium carbonate (Khalid et al. 1977, Logan 1982, Sonzogni et al. 1982,

Richardson 1985). Therefore, the presence of secondary minerals may also be a reason for higher phosphorus concentration in the Souris River sediments compared to the Turtle River sediments.

The phosphorus concentrations recorded in the Souris River sediments are within the range of the phosphorus concentrations in many nutrient-polluted rivers in the US and other parts of the world (Table 6.5). The phosphorus concentration of the Turtle River sediments was lower than the phosphorus concentrations recorded in most of the other rivers (Table 6.5).

Table 6.5: Phosphorus concentrations (μmol / g) in the Souris River, the Turtle River and some other rivers.

River	Concentration range	Reference
Souris River	11.6 - 37.8	
Turtle River	1.9-3.7	
Nestos River, Greece	0.02	(Papastergios et al. 2009)
Thames River, UK	63	(House and Denison 2002)
River Adour, France	3.2 - 435.8	(Brunet and Astin 1998)
Maumee River, USA	15.4-40.7	(Mccallister and Logan 1978)
Mississippi 5 watersheds, USA	8.8-34.4	(Duffy et al. 1978)
Seven Great Lake rivers, USA	27.1-40.7	(Young et al. 1988)
Exe, UK	23.4-78.3	(Walling et al. 2001)
Severn, UK	17.4- 48.3	(Walling et al. 2001)
Avon, UK	18.3-74.2	(Walling et al. 2001)

Phosphorus entering rivers can be present as soluble reactive phosphate (SRP), dissolved inorganic P, dissolved organic P, particulate inorganic P, and particulate organic P (Logan, 1982, Gray and Kirkland 1986, Sharpley and Smith, 1989). The relative proportion of each form depends on soil, vegetation, and land use characteristics of the drainage basin. Phosphorus is incorporated in sediments in both inorganic and organic forms, including physically adsorbed onto sediment surfaces, chemically bonded in

minerals, biologically assimilated in cells, and in detritus originating from the sediments. Retention and release of phosphorus by riverbed sediments are controlled by sorption characteristics of bed sediments, soluble reactive phosphorus concentrations in the overlying water column and stream transport characteristics (Andersen 1975, Logan 1982, Gray and Kirkland 1986, Sharpley and Smith 1989, Sharpley et al. 1992, Søndergaard et al. 1992, Abrams and Jarrel 1995, Koski-Vähälä and Hartikainen 2001, Koski-Vähälä et al. 2001, Valija and Culaj 2010). These characteristics are different from one river basin to another depending on the biological, physical and chemical characteristics of the environment. The Souris River sediments can be considered as phosphorus enriched compared to the other nutrient enriched water-bodies (Table 6.5). The enrichment of phosphorus in the Souris River can be caused by either natural enrichment or anthropogenic influences. Natural enrichment of phosphorus in the Souris River sediments can be caused from sources such as weathering of phosphorus containing minerals in rocks and soils. The anthropogenic sources can be due to increased use of phosphorus containing fertilizer, agricultural runoff and cattle operations.

The concentrations of As, Se and Cd in the Souris River and Turtle River and in some other rivers are given in Table 6.6. The concentrations of As, Se, and Cd in Turtle River and Souris River sediments were not significantly different from each other ($P \geq 0.05$). These concentrations recorded in the Souris and Turtle Rivers were similar to the ranges of concentration of these elements recorded in other parts of the world (Table 6.6). The concentrations of As, Se, and Cd in the Turtle River and Souris River sediments can be due to natural enrichment as well as anthropogenic activities. As, Cd, and Se are present ubiquitously as natural constituents of rocks and sediments, and natural processes

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such as runoff and physical weathering may have led to high levels of these elements in the river sediments (Rowden 2008). The land use of the Turtle River and Souris River watersheds are dominated by agricultural activities (US EPA 2004, NRCS 2007). The fertilizer used in agricultural activities may contain trace amounts of As, Cd and Se and may therefore also have contributed to loading of the river. There are no records about element loading rates into the Turtle River or Souris River watersheds.

Table 6.6: Arsenic, Cadmium and Selenium concentrations (μmol / g) in the Souris River (SR), the Turtle River (TR) and some other rivers in the world.

	As	Cd	Se	References
Souris River	0.02-0.2	0.0005 -0.005	0.001-0.01	
Turtle River	0.002 – 0.03	0.0009-0.007	0.003-0.003	
Nestos River Greece	0.1	0.01		(Papastergios et al. 2009)
Lake Macquarie, NSW, Australia			0.1	(Peters et al. 1999)
Similkameen river BC	0.2-0.6	>0.003	>0.005	(Jhonson 1997)
Missippippi River	0.2		0.005	(Elrick and Horowitz 1986)
Yaharra river	0.03		0.001	(Elrick and Horowitz 1986)
River Ravi, Pakistan		0.0009- 0.03		(Rauf et al. 2009)
Wadi Al-Arab Dam, Jordan		0.007-0.013		(Ghrefat and Yusuf 2006)
Guiyu, China		0 -0.1		(Wong et al. 2006)
Qishon River, Israel		1.4		(Kronfeld and Navrot 1974)
Kubabbi River Nigeria		0.2		(Uzairu et al. 2009)
Fairbridge District	1.3-16			(Bombach et al. 1994)

In addition to the element concentrations, sediment quality assessment values are used in assessing the metal enrichment of the river sediments. These are the (1) 'contamination factor', (2) 'degree of contamination', (3) 'pollution loading index'(PLI), and (4) 'geoaccumulation index (I_{geo})'. These sediment quality assessment values are widely used to assess the metal enrichment of sediments in various environments. In the

present study these assessment values will be used to study the enrichment of metals in the Souris River and Turtle River sediments.

(1). A contamination factor (C_f^i) can be used to describe the contamination of a given substance in a particular location (Hakanson 1980).

$$C_f^i = \frac{C_{0-n}^i}{C_b^i}$$

where, C_{0-n}^i is the mean concentration of a given substance, C_b^i is the background concentration for the substance. Background concentrations used in the calculations of this study are the regional geochemical baselines recorded by US Geological Survey for the Western United States (Shacklette and Boerngeng 1984). These background concentrations were also similar to values recorded in Martin and Meybeck's study (Martin and Meybeck 1979) which have been widely applied to other studies (Loska et al. 1997, Pekey et al. 2004, Rath et al. 2005, Ahdy and Khaled 2009, Chakravarty and Patgiri 2009, Harikumar et al. 2009).

(2). The sum of contamination factors of all the elements is referred to as the degree of contamination (C_d) and it describes the contamination of a particular location by all examined substances (Hakanson 1980, Loska et al. 1997, Pekey et al. 2004, Ahdy and Khaled 2009, Chakravarty and Patgiri 2009, Harikumar et al. 2009). The categorization of level of pollution in sediments based on the contamination factor and the degree of contamination is given in Table 6.7.

(3). The pollution load index (PLI) is another simple method to assess the level of pollution in sediments (Tomilson et al. 1980). Sediment pollution load index can be determined from:

$$PLI = (C_{f1} \times C_{f2} \times \text{....} \times C_{fn})^{1/n}$$

where, C_{f1} is contamination factor of substance 1, C_{f2} is contamination factor of substance 2 and C_{fn} is contamination factor of substance n, with n as the total number of substances. If PLI < 1, then this indicates no pollution at a particular site and PLI > 1 indicates a polluted site (Tomilson et al. 1980, Satyanarayana et al. 1994, Chakravarty and Patgiri 2009, Harikumar et al. 2009).

Table 6.7: Categorization of sediments based on contamination factor and degree of contamination

Contamination factor (C_f^i)	Degree of contamination (C_d)	Description of level of contamination
$C_f^i < 1$	$C_d < 7$	Low degree of contamination
$1 < C_f^i < 3$	$7 < C_d < 14$	Moderate degree of contamination
$3 < C_f^i < 6$	$14 < C_d < 28$	Considerable degree of contamination
$C_f^i > 6$	$C_d > 28$	Very high degree of contamination

(4). I_{geo} also determines the extent of metal accumulation of sediments. This is widely used in assessing the metal contamination of sediments (Rubio et al. 2000, Loska and Wiechula 2003, Pekey et al. 2004, Singh et al. 2005[b], Lin et al. 2006, Wakida et al. 2008, Ahdy and Khaled 2009, Chakravarty and Patgiri 2009, Harikumar et al. 2009, Nasrabadi et al. 2010). I_{geo} can be calculated as follows:

$$I_{geo} = log_2 \frac{C_i}{1.5 \, C_b}$$

where, C_i is the concentration of the element and C_b is the background concentration of the element recorded by the US geological survey in Western United States. The I_{geo} scale consists of seven different grades (Table 6.8) and the according to this grade classification the level of pollution ranges from unpolluted to highly polluted.

Table 6.8: Categorization of sediments based on geoaccumulation index (*Igeo*).

Value of I_{geo}	Class	Description of level of Pollution
$I_{geo} \leq 0$	0	Unpolluted
$0 < I_{geo} < 1$	1	Unpolluted to moderately polluted
$1 < I_{geo} < 2$	2	Moderately polluted
$2 < I_{geo} < 3$	3	Moderately to strongly polluted
$3 < I_{geo} < 4$	4	Strongly polluted
$4 < I_{geo} < 5$	5	Strongly to extremely polluted
$5 < I_{geo}$	6	Extremely polluted

The contamination factor, degree of contamination, PLI and I_{geo} values for the Souris River and Turtle River sediments were calculated from the concentrations of Cu, Pb, Zn, Ni, Mn, Fe, Cd and Ni using the above formulas. The contamination factor, the degree of contamination, and the pollution loading index for the Souris River and the Turtle River are given in Table 6.9.

The contamination factor and degree of contamination values in Souris River and the Turtle River showed very low contamination with respect to Cu, Pb, Zn, Ni, Fe and Cr in all the sites (Table 6.9). Some sites of these watersheds showed moderate levels of Mn and Cd contamination (Table 6.9). The PLI also showed that both the Souris River and Turtle river sites were unpolluted with respect to metals (Table 6.9). The I_{geo} values for the

elements in the Souris River and Turtle River are given in Figure 6.11. The I_{geo} values of

the Souris River sediments were in the unpolluted range. The Turtle River sediments were

moderately enriched with respect to Mn concentration (Figure 6.11).

Table 6.9: The contamination factor, degree of contamination (Hakanson 1980), and the pollution loading index (PLI, Tomilson et al. 1980)for the Souris River and Turtle River sediments.

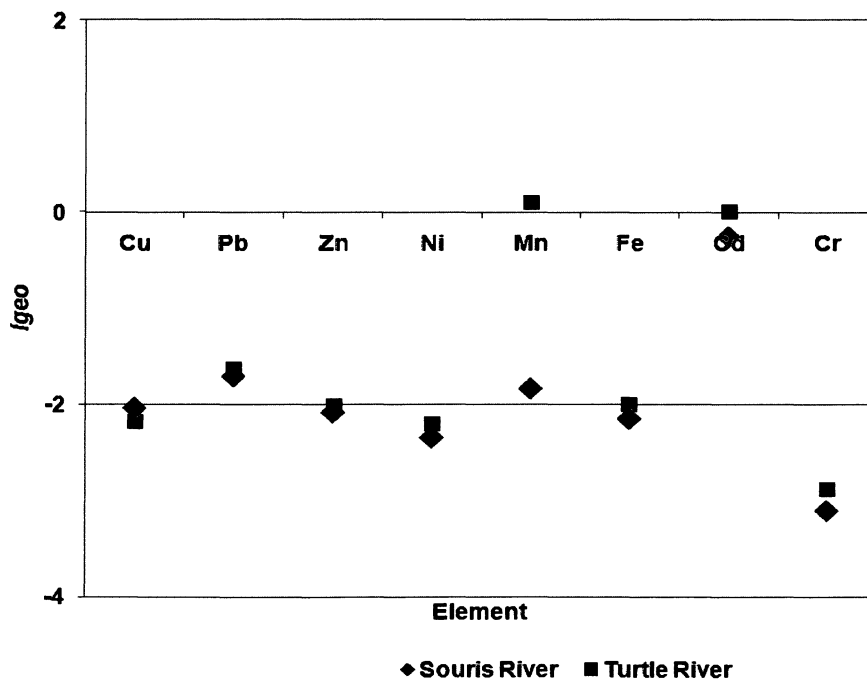| Element	Contamination factor	
	Souris River	Turtle River
Cu	0.1-0.7	0.2-0.6
Pb	0.2-0.8	0.3-0.7
Zn	0.1-0.7	0.3-0.5
Ni	0.1-0.5	0.2-0.4
Mn	0.2-1.1	1.3-3.2
Fe	0.1-0.6	0.3-0.4
Cd	0.4-2.6	1.6-3.1
Cr	0.1-0.3	0.2-0.3
Degree of contamination	1.4-6.9	1.0–3.4
PLI	0.1-0.8	0.2-0.8

Figure 6.11: Mean I_{geo} values for the Souris River and the Turtle River sediments.

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In conclusion, this study provides a detailed analysis of element concentrations along the Souris and Turtle Rivers in North Dakota and information about relative sediments and element loading rates from the tributaries to the main rivers. The multi-element fingerprints can be used to calculate the relative contribution of sediments from the tributaries to the main river and potential contamination, but this method does not help to calculate the actual loading rates for the watershed. Therefore, determination of sediment and element loading rates in the Souris River and the Turtle River may help to improve the results obtained in this study. As future improvements to this study, it is also recommended to repeat this study over time to study the temporal variation in the element concentrations depending on the variation of climatic factors. In addition this multi-element fingerprinting can be done on the suspended sediments and water of the Souris River and Turtle River to assess the changes of element concentrations over time. Use of the multi-element fingerprinting technique to the soils in the different land use areas around the watersheds may help to identify the potential source areas of elements of concern.

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