

Technical Report No: ND12-05

**MULTI_ELEMENT FINGERPRINTING OF RIVER SEDIMENTS TO
IDENTIFY DIFFUSE POLLUTION SOURCES**

**Dimuthu Wijeyaratne
Marinus Otte
Dept. of Biological Sciences
North Dakota State University
Fargo, North Dakota**

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**North Dakota Water Resources Research Institute
North Dakota State University, Fargo, North Dakota**

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Dimuthu Wijeyaratne¹

Marinus Otte²

WRI Graduate Research Fellow¹ and Professor²

Department of Biological Sciences

North Dakota State University

Fargo, ND 58108

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The work upon which this report is based was supported in part by federal funds provided by the United States of Department of Interior in the form of ND WRI Graduate Research Fellowship for the graduate student through the North Dakota Water Resources Research Institute.

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Project Period: March 1, 2008 - February 28, 2011

Project Number: 2008ND170B and 2009ND189B

North Dakota Water Resources Research Institute

Director: G. Padmanabhan

North Dakota State University

Fargo, North Dakota 58108

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Abstract

The multi-element fingerprinting technique combines field data collection, laboratory analyses of sediments, and statistical modeling techniques to identify sediment sources in a watershed. It assumes linear mixing of elements, which was verified by two laboratory experiments. The main part of the study focused on two watersheds in North Dakota, the Souris River and the Turtle River, and aimed to assess the origin of pollutants. In the Souris River phosphate was the main pollutant of concern. The multi-element fingerprinting assessed the contributions of sediments from the tributaries to the river, which were in turn used to assess contributions of phosphorus. The highest phosphorus contribution to the river was recorded for Willow Creek (74.7%) and the lowest phosphorus contribution (39.3%) was from an unnamed tributary of the Upper 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 most likely related to land use, underlying geology, and the size of the watersheds of the tributaries in the Souris River watershed. A similar analysis was used for the Turtle River to calculate arsenic (As), cadmium (Cd) and selenium (Se) contributions. The highest contribution of these elements to the Turtle River was recorded from the Whiskey Creek (As 75.7%, Cd 75.8 % and Se 78 %).

Acknowledgements

We are very grateful to the North Dakota Water Resources Research Institute, North Dakota State Water Commission, ND INBRE, the North Dakota Department of Health, the Graduate School of North Dakota State University, NDSU Department of Biological Sciences, NDSU Environmental Conservation Sciences Graduate Program and the NDSU College of Science and Mathematics for assisting with funding throughout the project.

We gratefully acknowledge Dr. Donna Jacob for her help in analyzing samples with the ICP-OES. We would also like to thank Dr. Peter Oduor, Dr. Bernhardt Saini-Eidukat and Dr. Wei Lin for their expert help when needed. We are very grateful to Mr. Michael Ell of the North Dakota Department of Health, and Mr. Larry Swenson of the Soil Testing Laboratory of NDSU. Also special thanks to Alex Yellick, La Toya Kissoon, Sharmila Sunwar, Alex Stalboerger, Aida Asgary and Charith Chithraranjan.

1.0. Introduction

River sediments act both as sinks and sources of pollutants to the overlying water column and biota. 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. It is therefore very important to identify the spatial distribution and origin of a pollutant 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 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 the constraints associated with traditional studies on sediment transport and determination of 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, Kisson 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).

1.1. Study area and description of the problem

This project focused on two river basins. (1) The Souris River originates in Saskatchewan, passes through North Dakota to return to Canada in Manitoba is of international concern regarding phosphate and the cross-border consequences of pollution transport. (2) The watershed of the Turtle River is approximately 80 km long and about 30 km wide, and it is a tributary of the Red River. The Turtle River is of concern because of high concentrations of potentially toxic levels of metals and metalloids such as Cd, Se and As.

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 to assess the geographic origin of pollutants.

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

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.

2.0. Methodology

This project had 4 major parts.

1. Analysis of element concentrations in the sediments of the Souris River to identify the potential for using multi element fingerprinting technique for sediment tracking.
2. Laboratory study to simulate mixing and transport of chemical elements in river systems.
3. Multi element fingerprinting approach to identify phosphorus contribution from tributaries to the Souris River sediments.
4. Multi element fingerprinting approach to identify arsenic, selenium and cadmium contribution from tributaries to the Turtle River sediments.

2.1. Analysis of element concentrations in the sediments of the Souris River to identify the potential for using multi element fingerprinting technique for sediment tracking.

2.1.1. Study area and sample collection

The study was conducted in the Upper Souris River watershed. Sediment samples were collected in the summer of 2007 from four locations along the Upper Souris River. One sampling location was located in Canada and the other three locations 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.

2.1.2. Chemical analysis

Samples were oven dried at 60 °C, then homogenized using a mortar and pestle. About 0.5 g of each homogenized sample was acid digested and analyzed using a Spectro Genesis Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for 31 elements. 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).

2.1.3. 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 were recorded (W_a). The percentage LOI was calculated as $((W_d - W_a) / W_d) \times 100$.

2.1.4. 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 $((W_i - W_r) / W_i) \times 100$.

2.1.5. 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.

2.2. Laboratory study to simulate mixing and transport of chemical elements in river systems.

This part of the study consisted of two experiments. The sediment samples used in the laboratory experiments were top river bed sediment (maximum depth of sampling = 2 cm) samples collected from the Souris River of North Dakota in the summers of 2008 and 2009. 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.

2.2.1. Mixing of soil at different mixing ratios

Sediment from two different sites of Souris 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 water was added to the mixtures at 10 mL of 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).

2.2.2. 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 (30cm x 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 1).

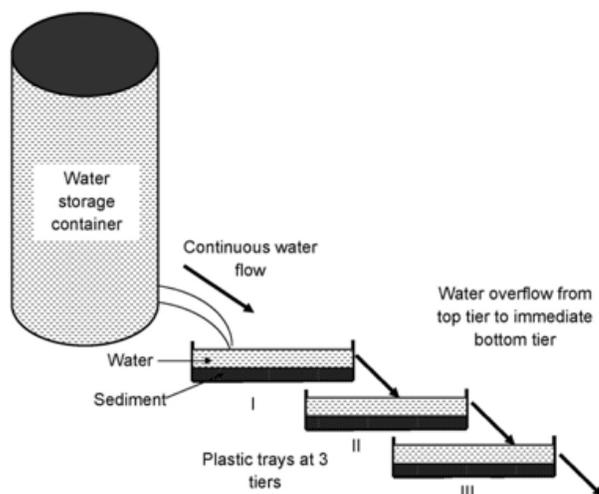


Figure 1: Experiment set-up of the river simulation experiment. The trays at different tiers were connected to each other in a way that all the overflowing water from the tray at the top tier (Tier I) entered to the tray at the immediate bottom tier (Tier II).

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.

2.2.3. 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 acid digested and then analyzed using a Spectro Genesis Inductively Coupled Plasma Optical Emission Spectrometer (ICP OES) for 34 elements

(instrument detection limits in μgL^{-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).

2.2.4. Loss-on-ignition

Same as 2.1.3.

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

Same as 2.1.4.

2.2.6. 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.

2.3. Multi element fingerprinting approach to identify phosphorus contribution from tributaries to the Souris River sediments.

2.3.1. Sample collection

Sediment samples were collected from two areas (Figure 2): 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)

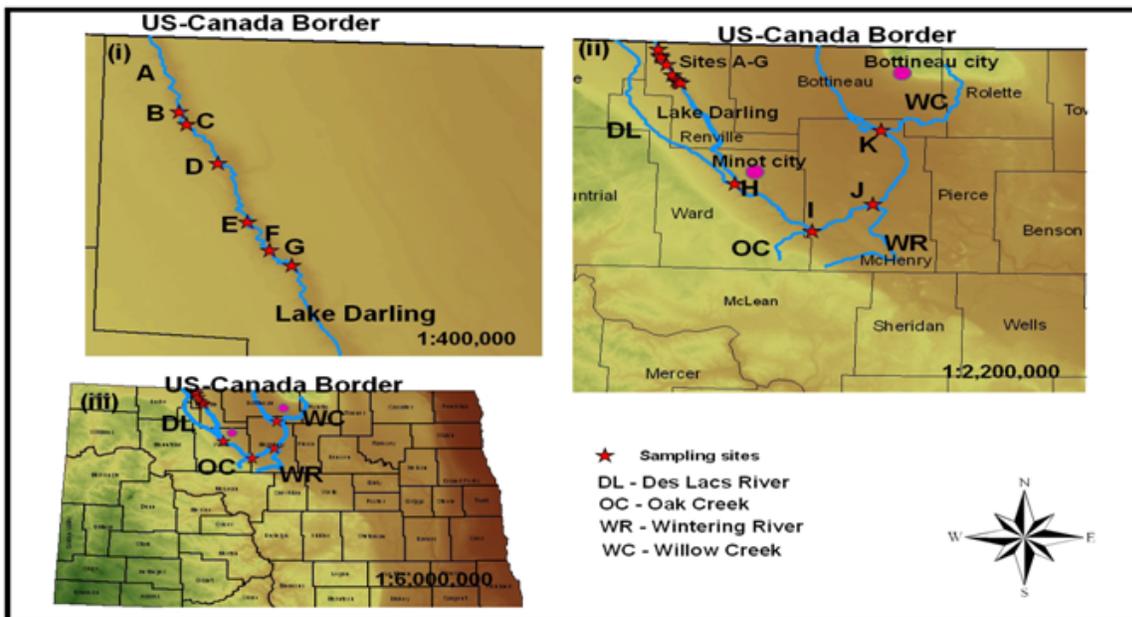


Figure 2: Souris River sampling sites. ((i) – Map showing Sampling sites in the upper Souris River area, (ii) – Map showing the four larger tributaries, (iii) – Map showing the general location of Souris River in ND, USA).

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

2.3.2. 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, samples were acid digested and analyzed in a Perkin Elmer Elan 6000 ICP mass spectrometer 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).

2.3.3. Loss-on-ignition

See 2.1.3.

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

See 2.1.4.

2.3.5. Data analysis

Minitab 15 statistical software (Minitab® 15.1.30) was used for all statistical analyses. 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 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. 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.

$$[X]_D = a_x[X]_T + b_x[X]_U$$

and $a_x + b_x = 1$

and therefore

$$a_x = \frac{[X]_D - [X]_U}{[X]_T - [X]_U}$$

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 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.

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

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

2.4. Multi element fingerprinting approach to identify arsenic, selenium and cadmium contribution from tributaries to the Turtle River sediments.

2.4.1. Study area

The Turtle River is a tributary of the Red River of the North in northeastern North Dakota (Figure 3). 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. There are three major tributaries to the Turtle River; Kellys Slough, Salt Water Coulee and Fresh Water Coulee (US EPA 2004).

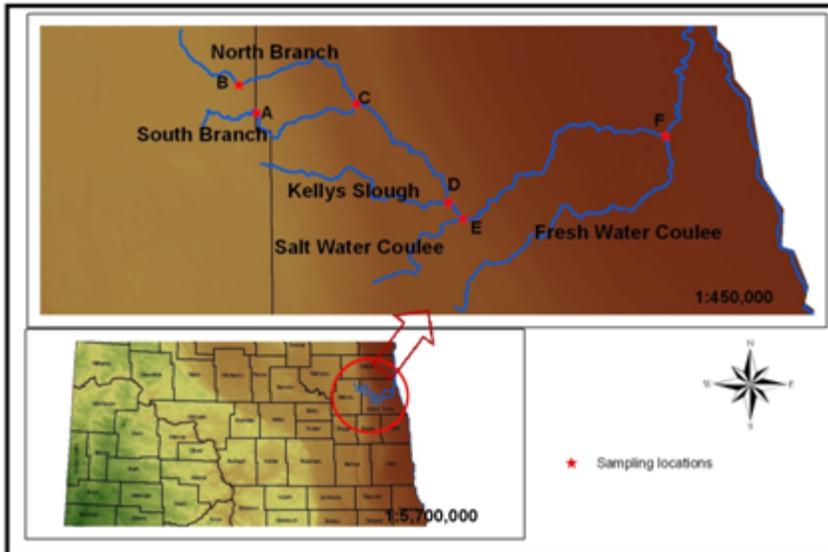


Figure 3: Turtle River sampling sites. ((i) – Map showing sampling sites in the Turtle River (ii) – Map showing the general location of Turtle River in ND, USA.

2.4.2. 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 3). 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.

2.4.3. Sample preparation and multi-element analysis

See 2.3.3

2.4.4. Loss-on-ignition

See 2.1.3.

2.4.5. Fraction of particles smaller than 63 μm ($f_{<63}$)

See 2.1.4.

2.4.6. 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 (\mathbf{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.

$$[\mathbf{X}]_D = \mathbf{a}_x[\mathbf{X}]_T + \mathbf{b}_x[\mathbf{X}]_U$$

and $\mathbf{a}_x + \mathbf{b}_x = \mathbf{1}$

and therefore

$$\mathbf{a}_x = \frac{[\mathbf{X}]_D - [\mathbf{X}]_U}{[\mathbf{X}]_T - [\mathbf{X}]_U}$$

Where,

\mathbf{a}_x -Mean contribution of tributary for element x

\mathbf{b}_x - Mean Contribution of upstream for element x

$[\mathbf{X}]_D$ - Mean Concentration of element x at the downstream location

$[\mathbf{X}]_U$ - Mean Concentration of element x at the upstream location

$[\mathbf{X}]_T$ - 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 \mathbf{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.

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

Where,

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

3. Results and discussion

3.1. Analysis of element concentrations in the sediments of the Souris River to identify the potential for using multi element fingerprinting technique for sediment tracking.

The concentrations of Ag, Cd, As, Hg, Mo, Tl, Pb, Sb, Se and Sn were below detection limits. Results of the correlation analysis showed that Be, Co, Cu and Si concentrations were not significantly correlated to any other element concentration. Several elements (Eg: Al, Fe, Mn, K, Ba, Cr, Li, and P) showed particularly strong correlations with $r^2 > 0.800$. 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 (Eg: Ba, Mg, Ca, Sr, Be, Li, K, Na, P, B, Al, Ce, Cr, V, Zn, Fe, Ni, Ti and Mn) showed strong positive correlations with $f < 63$.

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. 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 ($P \geq 0.01$).

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 3.1).

Table 1: 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	After
	Site, CS	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

For example 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.

This initial study showed that there is significant variation in element concentrations in sediments along the Souris River. The variation of element concentrations was 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 did not play a vital role in determining the trace element concentrations of the sediments of the Souris River. The results suggested 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.

3.2. Laboratory study to simulate mixing and transport of chemical elements in river systems.

The concentrations of Ag, B, Ce, Hg, Si and Zr were below detection limits.

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%. In both experiments, none of the elements showed a statistically significant correlation with LOI or $f < 63$, nor did LOI correlate significantly with $f < 63$. In the soil mixing experiment, 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 did not show a significant concentration variation either with dry/wet condition or mixing ratios. 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. 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 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.

In the river simulation experiment, 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, 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.

In this experiment the concentrations of Na, Al and K in sediments at all the levels significantly decreased over time. This observation shows that these elements are removed from the sediments by running water. Significant spatial and temporal differences in concentrations of Ca, P and Mg were identified. These element concentrations decreased with time in the top two tiers (Tiers I and II) and it increased with time in the bottom tier. 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.

3.3. Multi element fingerprinting approach to identify phosphorus contribution from tributaries to the Souris River sediments.

In this study, LOI or $f < 63$ did not show significant variations in sites or significant correlations with elements as expected. This indicates that organic matter content in this river is not an important determinant of phosphorus concentrations in 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).

The sediment contributions from tributaries of the Souris River ranged between 37.1% and 71.6% (Figure 4). 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).

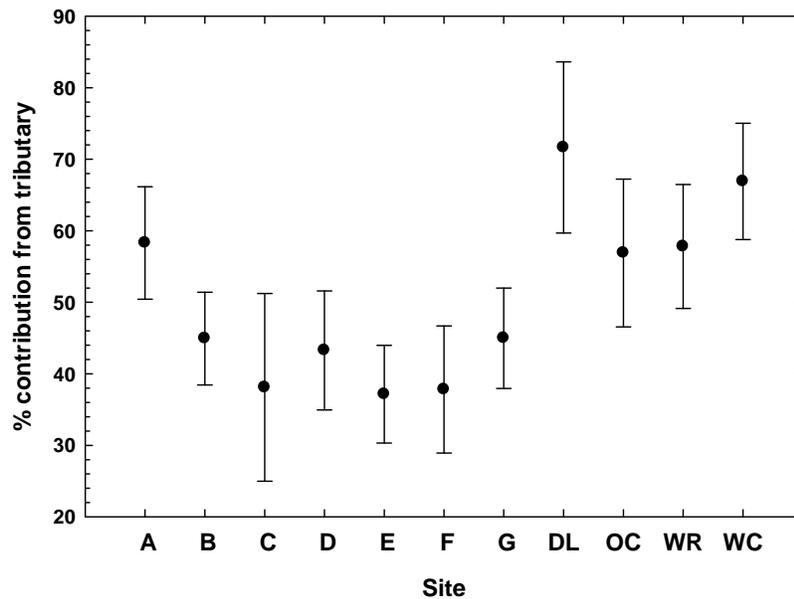


Figure 4: Average percent contribution (\pm 95% Confidence intervals) of sediments from the tributaries to the Souris River (n=40). (A-G – sites upstream of Lake Darling, DL-Des Lacs River, OC-Oak Creek, WR – Wintering River, WC- Willow Creek).

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 (Sites B to F) showed a lower phosphorus contribution compared to the phosphorus contribution from larger tributaries (Figure 5).

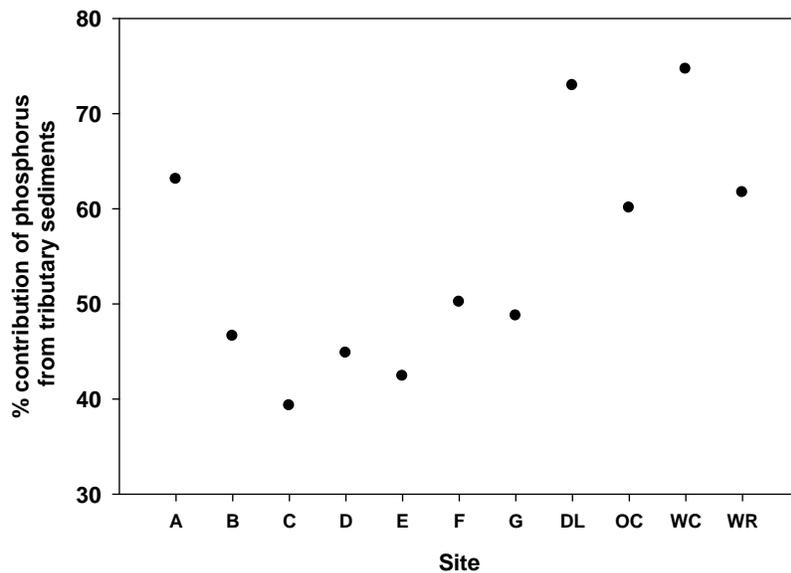


Figure 5: Percentage contribution of phosphorus from the tributaries to the Souris River. (A-G – sites upstream of Lake Darling, DL-Des Lacs River, OC-Oak Creek, WR – Wintering River, WC- Willow Creek).

The small tributary sites in the Upper Souris River area except site A (The site closest to the US-Canada Border) had relatively lower sediment contribution to the main river compared to the sediment contribution from the larger tributaries (Figure 4). The site closest to the US-Canada border had a relatively higher sediment contribution compared to the other small tributaries. The contribution of tributaries to the main river and the deposition of sediments in downstream sink areas depend on many factors, including slope, cross-sectional area, boundary resistance, flow separation, and the occurrence of obstructions to flow (Fairbridge 1978, Rosgen 1996, Leopold 2006, Charlton 2008).

The land use associated with the two areas of the field study, the upstream small tributary sites or the downstream large tributary sites, may explain the differences in P concentrations and contributions in the Souris River. The smaller tributaries that were draining land in US showed a lower phosphorus contribution compared to the larger tributaries in the lower Souris River area. But the site closest to the US-Canada border showed a relatively higher contribution of phosphorus compared to the other smaller tributaries in the upper Souris River area. This site drains land in the Canadian portion of the river and the land use around the drainage basin is unknown. The other smaller tributaries (Sites B-F) of the upper Souris River drain land within the Upper Souris River Wildlife Refuge, thus much of the land is not intensively used by humans. The land-use in the watersheds of the larger tributaries (Des Lacs River, Oak Creek, Willow Creek, and Wintering River) is dominated by agriculture; more than 99% of the land in the lower Souris River watershed is used for agricultural activities (USEPA 2004, NRCS 2007). Approximately 80% of the land used for agricultural activities is used for growing crops. Other potential nonpoint-sources of phosphorus in the lower Souris River area are chemical, fertilizer, and manure applications, or livestock grazing.

3.4. Multi element fingerprinting approach to identify arsenic, selenium and cadmium contribution from tributaries to the Turtle River sediments.

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 Whiskey 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 Whiskey 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 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 (Figure 6). 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.

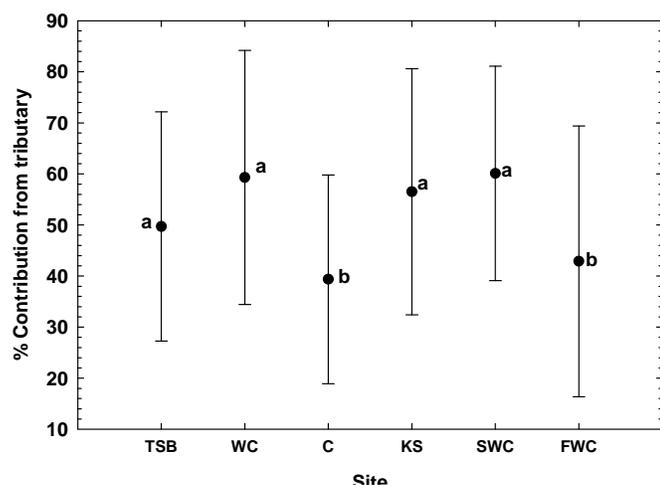


Figure 6: Percentage contribution of sediments \pm 95% Confidence interval from the tributaries to the Turtle River. (Different lowercase letters indicate significant differences in contribution). TSB – Tributary to the south branch of the Turtle River, WC – Whiskey Creek, C – Confluence of North and South Branch, KS – Kellys Slough, SWC – Salt Water Coulee, FWC – Fresh Water Coulee).

The highest contributions of As, Se and Cd were recorded in Whiskey Creek (Figure 7). 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. This indicates that Whiskey Creek was a major contributor of trace elements and sediments to the main river.

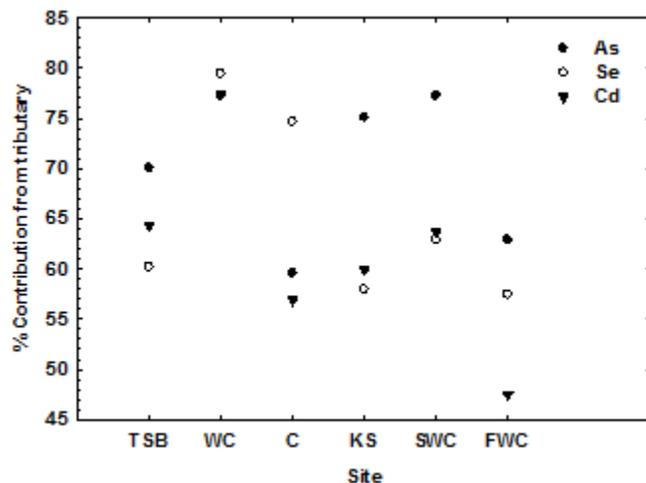


Figure 7: Percentage contribution of As, Se and Cd from the tributaries to the Turtle River (TSB – Tributary to the south branch of the Turtle River, WC – Whiskey Creek, C – Confluence of North and South Branch, KS – Kellys Slough, SWC – Salt Water Coulee, FWC – Fresh Water Coulee).

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, 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, 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.

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. 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).

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