

**IT'S SEDIMENTARY, MY DEAR WATSON:  
IMPLICATIONS OF WATERSHED PROCESSES ON THE SEDIMENT  
FINGERPRINTING APPROACH**

by

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## **Abstract**

The sediment source fingerprinting approach is based on the assumption that the potential sources of sediment within a watershed can be linked to in-stream sediment by using the inherent physical or biogeochemical characteristics of the sediment (i.e., sediment properties) as fingerprints. At present, one of the main limitations of the sediment source fingerprinting approach is the ability to link sediment back to their sources due to the non-conservative nature of many sediment properties. Ideally, sediment properties do not change as the sediment (i.e., transported unconsolidated soil or rock particles) move through a watershed allowing for a direct comparison between sources and sediment. However, sediment collected downslope or downstream from its source is often found to have a finer grain-size distribution and a higher organic matter content as compared to the source material as the smaller and less dense particles are preferentially mobilized and transported. Accounting for changes in both particle size distribution and organic matter content are important as many fingerprint concentrations are correlated with both properties, but it is unclear as to what is the best approach to account for these changes. In an effort to provide a more reliable and robust link between sources and sediment, a series of experimental and observational studies were conducted to investigate the factors that control particle size and organic matter selectivity and their subsequent effect on a broad suite of geochemical fingerprints. These studies investigated particle selectivity at the landscape scale, represented by a sequence of hillslope, riparian and fluvial environments. Processes within each of these three environments were found to preferentially mobilize and transport fine-grained and organic-rich particles. Many commonly used particle size and organic matter correction

factors assume that the relation between both particle size and fingerprint concentrations are similar for all fingerprints. However, this research has demonstrated that these relations are fingerprint specific in terms of the magnitude, direction and linearity which suggests that the use of correction factors needs to be given careful consideration. In addition, a watershed-scale application of the sediment fingerprinting approach found that the scale of observation and the geomorphic connectivity of the watershed influenced the apportionment results. Overall, this research can be used to guide sampling design and protocols, fingerprint selection, data correction factors and the interpretation of apportionment results.

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## **Foreword**

This dissertation was completed and supported as part of a larger Natural Science and Engineering Research Council (NSERC) strategic project – development of fingerprinting techniques for sources of sediment and associated phosphorus within agricultural watersheds of Canada – to David A. Lobb, Philip N. Owens and Ellen L. Petticrew. The overall goals of the larger strategic project were to: 1) enhance environmental fingerprinting techniques for use in agricultural watersheds in Canada and elsewhere in the world; and 2) enhance the understanding of the sources of sediments and phosphorus, and use this understanding to improve conceptual and predictive models for improved management of watershed resources.

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## **Publications**

Each chapter in this dissertation was conducted in collaboration with others. These contributions are acknowledged here by indicating order of authorship by relative contributions to the works. Additional details of contributions to each section of this dissertation are outlined below.

### **Chapter 2:**

Koiter AJ, Owens PN, Petticrew EL, Lobb DA (2013) The behavioural characteristics of sediment properties and their implications for sediment fingerprinting as an approach for identifying sediment sources in river basins. *Earth-Science Reviews* 125:24–42.

Koiter was the principle author and researcher. All coauthors contributed conceptual ideas and provided editorial support.

### **Chapter 3:**

Koiter AJ, Owens PN, Petticrew EL, Lobb DA (In revision, 2016) The role of soil surface properties on the particle size and carbon selectivity of interrill erosion in agricultural landscapes. *Catena*.

Koiter was the principle author and researcher and was responsible for the experimental design, field work, laboratory analysis, statistical analysis and data interpretation. All coauthors contributed conceptual ideas and provided editorial support.

### **Chapter 4:**

Koiter AJ, Owens PN, Petticrew EL, Lobb DA (In preparation, 2016) Suitability of particle size and organic matter correction factors in sediment source fingerprinting investigations: the example of two contrasting watersheds in Canada.

Koiter was the principle author and researcher and was responsible for the experimental design, field work, laboratory analysis, statistical analysis and data interpretation. All coauthors contributed conceptual ideas and provided editorial support.

### **Chapter 5:**

Koiter AJ, Owens PN, Petticrew EL, Lobb DA (In preparation, 2016) Particle size and organic carbon selectivity within edge-of-field and riparian zones and its implications for sediment fingerprinting.

Koiter was the principle author and was responsible for laboratory analysis (South Tobacco Creek site only), statistical analysis and data interpretation. Experimental design, soil sampling and  $^{137}\text{Cs}$  analysis was completed by Lobb and Owens (Elma site) and Vandenbygaart et al. (*Global Change Biology* 18:1441–1452) (South Tobacco Creek site). All coauthors contributed conceptual ideas and provided editorial support.



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# 1 Introduction

It has been argued that the fictional character Sherlock Holmes, created by Arthur Conan Doyle, is one of the world's first forensic geoscientists (e.g., Ruffell and McKinley 2005; Dawson and Hillier 2010). For example, the story titled "The five orange pips" written by Conan Doyle and first published in 1891 tells of how Sherlock Holmes deduced the origin of his client, John Openshaw, when John came to 221B Baker Street to seek his help.

"You have come up from the south-west, I see." [Sherlock Holmes]

"Yes, from Horsham." [John Openshaw]

"That clay and chalk mixture which I see upon your toe caps is quite distinctive." [Sherlock Holmes]

-- AC Doyle, *The Adventures of Sherlock Holmes*, Project Gutenberg, Champaign, Ill.

In this case, Sherlock Holmes was able to identify the source of the soil/sediment particles on John Openshaw's shoe based on the unique physical characteristics of that material. While forensic geoscience was used to solve mysteries within the stories of Sherlock Holmes, similar principles can be used to identify watershed sediment sources which help improve both soil and water quality management.

## 1.1 Non-point source pollution in agricultural watersheds

According to 2009 polls, a majority of Canadians believe that fresh water is Canada's most important natural resource and that water pollution is the greatest threat to the nation's fresh water resources (Ipsos 2009; Nanos 2009). Agriculture has been identified as one of the major threats to water quality in Canada as a result of high sediment and nutrient loads in runoff as well as other agricultural products including pesticides, herbicides, bacteria and antibiotics (Vörösmarty et al. 2010). Agriculture in Canada covers approximately 7% (6.8

million ha) of the total land area, and within the last 50 years, the number of farms in Canada has decreased while the average size and productivity of farms has increased (Environment Canada 2001). This intensification has been achieved through advances in crop and animal genetics, chemical inputs, technological improvements and innovative farming practices (Burkart 2007). These trends can have unintended consequences including a high risk of erosion and a nutrient surplus in soils which then have high potential to be lost through runoff and sediment transport, which in turn can compromise environmental and human health (Berka et al. 2001).

Excessive nutrient loading, mainly nitrogen and phosphorus, in surface waters can lead to eutrophication (i.e., excessive plant and algal growth in an aquatic ecosystem) which has a wide range of effects including hypoxia, fish kill, algal blooms, toxicity, increases in turbidity and changes in the quantity and composition of aquatic plants and animals (Heisler et al. 2008; Conley et al. 2009; Nixon 2009). Nutrients are lost from agricultural land in either the dissolved or the particulate form and the dominant form of the nutrient is primarily controlled by the interactions between physical and biogeochemical properties of the nutrient and the soil. For example, the majority of the total phosphorus loss from land is in the particulate form because of the high affinity of the element towards soil particles due to reactions with clay and Fe-, Al- and Mn-oxides (Correll 1998; Owens 2008; Withers and Jarvie 2008). Due to these properties much of the phosphorus is lost through erosional processes whereas, in contrast, the majority of nitrogen is lost in the dissolved form as soluble organic nitrogen or nitrate as these compounds are not readily adsorbed by soil particles and are easily lost through leaching and surface runoff water (Correll 1998; Owens 2008).

While nutrients and other contaminants that move in association with sediment can result in water quality problems the physical presence of sediment itself can also impact aquatic ecosystems. Increasing the suspended sediment concentration results in greater turbidity which reduces the amount of energy available for photosynthesis and plant material is an important food source for many aquatic species. It has also been demonstrated that an increase in turbidity will interfere with the foraging success of visual predators. Both of these processes can result in a change the abundance and composition of aquatic plants and animals (Waters 1995). In addition, the deposition of fine-grained sediment on to a gravel channel bed can damage important aquatic habitat. For example, the siltation of gravel channel beds reduces the survival of salmonids eggs and alevins by creating a physical barrier that can prevent emergence and lower the dissolved oxygen within the redd (Chapman 1988). Furthermore, continued accelerated sediment deposition in reservoirs and harbours will result in a reduction in both capacity and overall lifespan as well as impact navigation (Vörösmarty et al 2003).

Agricultural research over the past century has produced an enormous amount of information on both sediment and nutrient dynamics within agricultural watersheds. In addition, researchers have developed and evaluated numerous soil erosion and nutrient management practices to reduce soil erosion and improve nutrient efficiency in an effort to reduce the negative environmental impacts while maintaining production. One tool that can be utilized is a nutrient management plan which is concerned with balancing nutrient inputs (i.e., fertilizer application) with nutrient outputs (i.e., crop removal though harvesting). Within this approach considerations are given to the type, rate, timing and application method of nutrients and the crop requirements. This type of approach aims to prevent the

accumulation of nutrients within the soil profile and reduces the amount of nutrient available to be lost to the aquatic environment (Beegle et al. 2000; Sharpley et al. 2004). Another approach aims to reduce the transport of sediment and nutrients off the land into the aquatic environment. This is achieved by employing practices that limit erosion and surface water flow or intercept and immobilize sediment and nutrients. Some of the more common practices include retaining or installing riparian zones (also known as buffers or vegetative filter strips), cover crops and conservation tillage (Sharpley et al. 2004; Kleinman et al. 2005; Zhang et al. 2010).

Issues of excessive sediment and nutrient pollution in agricultural watersheds often arise from diffuse, or non-point, sources. The problems of sediment and nutrient pollution are best managed at the watershed scale because the watershed is the morphological unit which controls water, sediment, chemical and energy fluxes and because management decisions need to be made within this context (Owens 2008). However, watersheds can have a large land area and encompass many different land uses and stakeholders, Furthermore, the processes and pathways in which sediment and nutrients are delivered to the aquatic environment are different and the controlling factors are both temporally and spatially variable. With no clearly defined entry points, high spatial and temporal variability, large land base and multiple stakeholders, this type of pollution is difficult to allocate, manage and mitigate (Owens et al. 2005; Smith et al. 2011).

## **1.2 Identifying sources of sediment**

Identifying the sources of sediment within a watershed is useful for both watershed management (e.g., sediment pollution abatement) and for understanding Earth surface

processes (e.g., landscape evolution). The identification of the dominant sources of sediment is an important requirement in the design of effective sediment management plans as it allows for the most effective use of financial and human resources by targeting the most problematic sediment sources (Walling 2005). Walling (2005) contrasts watershed-scale sediment source identification with soil conservation programs whereby the former is concerned with down-stream sediment issues and needs to consider a greater number of potential sources (e.g., streambanks, channel incision, in-field), while the latter only seeks to reduce on-site (i.e., within a field) soil erosion. As a result, soil conservation programs may not dramatically reduce the sediment yield of a watershed if soil surface erosion is not the dominant source of sediment and other management actions may need to be taken (e.g., streambank stabilization) to reduce the sediment yield. Sediment source identification is also an important component part of the study of Earth surface processes and dynamics. Sediment source identification has been used to help build and constrain sediment budgets (e.g., Minella et al. 2014), assess the geomorphic connectivity of a watershed (e.g., Wethered et al. 2015), interpret and model sediment yield data (e.g., Fox and Martin 2015) and understand the interactions between geomorphology and land use activities (e.g., Belmont et al. 2011).

There are several approaches to identifying and assessing the sources of sediment and quantifying the relative contributions of each source to the total sediment load. A review by Collins and Walling (2004) identified two broad categories of methods that can be used to identify the sources of sediment within a watershed. The first category is the indirect approach whereby soil erosion and sediment mobilization are measured or evaluated *in situ* and the relative contributions of each sediment source are then inferred. The indirect approach uses techniques including: mapping, surveying (e.g., erosion pins, GPS, cross-

profiling), photogrammetry, erosion plots, suspended sediment flux monitoring, remote sensing and soil erosion tracers. The second category is the direct approach where there is an attempt to directly link sediment sources to in-stream sediment. The techniques used in the direct approach include: erosion vulnerability indices, sedigraphs and hysteretic loops and sediment fingerprinting. Furthermore, Walling (2005) described three main limitations of the techniques used with the indirect approach to assessing the sources of sediment: 1) they often require *a priori* assumptions as to the likely sources of sediment, which in some cases may not be clear; 2) difficulty scaling up plot-scale estimates of erosion to watershed-scale estimates due to high spatial and temporal variability; and 3) these techniques provide information only on the mobilization of sediment and lack information concerning sediment delivery and fluvial transport. It is because of these limitations that a direct approach to identifying and assessing the sources of sediment is typically preferable. Sediment source fingerprinting shows promise as an effective tool for gathering information on the sources of sediment and sediment-associated nutrients and contaminants within a watershed (Walling et al. 2008; Davis and Fox 2009; Owens et al. 2016).

### **1.3 Sediment fingerprinting**

The sediment fingerprinting approach refers to working in an upstream direction in an inferential manner to determine the relative contributions from different sources of sediment to collected downstream sediment. The approach is based on the idea that one or more of the natural physical or biogeochemical properties of the sediment will reflect the source from where it originated and can be used to trace it back to its source(s). Walling (2013) reviewed and documented the history and evolution of the sediment fingerprinting approach. The

development of sediment fingerprinting began in the mid 1970's and its use and continued refinement has since grown exponentially due to both an increasing need for information on sediment sources (see Section 1.2) and technological advances (e.g., characterization of new sediment fingerprint properties) (Walling 2013). Early sediment fingerprinting studies were often qualitative in nature, used  $\leq 2$  fingerprints and were able to discriminate between two source types (e.g., surface and subsurface sources). Developments in analytical techniques have expanded the range of fingerprint properties (e.g., compound-specific stable isotopes; Reiffarth et al. 2016), which subsequently has also expanded the number and types of potential sediment sources that can be successfully discriminated among (e.g., forest, pasture and cultivated land; Hancock and Revill 2013). Furthermore, there have been developments in the statistical methods and models used to both select fingerprints (Section 1.3.3) and estimate the relative contributions of each sediment source (i.e., mixing models; Section 1.3.4).

Overall, the sediment fingerprinting approach consists of four main steps: 1) identification and characterization of potential sediment sources; 2) characterization of collected sediment; 3) selection of sediment fingerprints; and 4) estimating the relative contributions from each source using a statistical mixing model. These four steps are described in detail below.

### **1.3.1 Identification and characterization of potential sources**

Identifying the potential sources of sediment within a watershed is the first step in the sediment fingerprinting approach and can include either, or both, spatial- (e.g., agriculture and forest land use) or process-based (e.g., rill and gully erosion) source types. There are

many possible sources of information that can be used to help in the process of identifying the potential sources of sediment within a watershed including: land use, geology, soil and topographic maps, air photos and satellite imagery, previous research as well as visual field observations. The types of potential sources that are identified are typically driven by research or management goals and by using different groupings of sediment sources (i.e., based on land use and geology) the information provided can be used to understand the interactions between multiple factors. After potential sources of sediment within a watershed are identified, a sampling campaign is designed to collect samples that are representative of the potential sediment sources. However, the importance of the sampling campaign including the number of samples collected, sampling methods, and the sampling design used to characterize sources cannot be understated as it has been shown to influence the final sediment apportionment results (e.g., Du and Walling In press). In some studies, the classification of potential sediment sources is an iterative process whereby two or more potential sediment sources, previously identified, are grouped together as the fingerprints provide poor discrimination between them (i.e., fingerprint properties are similar between the potential sediment sources) (e.g., Barthod et al. 2015).

Sample preparation prior to measuring fingerprints is also a major consideration within the sediment fingerprinting approach and the most common method is drying followed by sieving (e.g.,  $< 63 \mu\text{m}$ ) to remove coarse-grained particles from analysis. This is done in an effort to limit differences in particle size and organic matter between the source and sediment (see Section 3.1 for additional information). However, different grain-size fractions have unique temporal and spatial patterns of erosion and transport (e.g., Haddadchi et al. 2015) and it is important that the grain-size fraction selected is both representative of

sediment being transported through the watershed and relevant to the research question being asked.

There is a wide range of soil and sediment properties that have been used as fingerprints including: geochemical, biochemical, radiochemical, isotopic, morphometric, optical and magnetic properties (for a review of fingerprint properties, see Foster and Lees 2000). In many cases, the soil and sediment properties that are measured are a function of budget, timeline, equipment, expertise or prior knowledge of the potential sources, or a combination of these factors.

### **1.3.2 Characterization of sediment**

Many different types of sediment have been used in sediment fingerprinting projects including: suspended, channel bed, floodplain, lake or reservoir sediments (for more detail regarding the different sediment types, see Haddadchi et al. 2013). Suspended and bed sediments from river channels are the most common type of sediment used as this type of sediment has the greatest environmental impact and often reflects contemporary watershed processes. Sediment deposited on floodplains and lake beds are often used to reconstruct a historical record of the changes in the sources of sediment (for a review on fingerprinting historical sediment fluxes, see D'Haen et al. 2012). Sediment is typically collected at the watershed outlet and conclusions are made based on the results from these samples at this location, which are then extended to the entire watershed. The sample preparation and fingerprint characterization methods should be consistent with those of the potential sediment sources to ensure the two data sets can be directly compared.

### **1.3.3 Fingerprint selection process**

The discrimination of sediment sources is based on identifying a fingerprint, or a suite of fingerprints, that can differentiate between the different potential sources of sediment. The fingerprinting approach typically uses a sequence of statistical tests to narrow down a large set of fingerprints to select a subset that can best discriminate between the different potential sediment sources (e.g., Collins and Walling 2002). In this process, fingerprints that provide little discrimination between potential sources or that are redundant are removed. Similar to the issue of sampling approaches, there is no standardized protocol to identify the optimum fingerprints. Typically, the first part of the fingerprint selection process is to eliminate fingerprints where the concentration in one or more samples is below the level of detection. Second, fingerprints where the concentration in collected sediment is outside the range of the sources are also commonly removed as it is assumed that these fingerprints do not behave in a conservative manner.

The first statistical step is to use a parametric or non-parametric analysis of variance to remove any fingerprints that have no discriminatory ability. Subsequently, discriminant function analysis, principle component analysis or canonical correlation analysis are used to further reduce the number of fingerprints. Ideally, the fingerprints should provide a clear distinction between the sources of sediment identified. However, recent research by Palazón et al. (2015) demonstrated that different fingerprint selection methods yielded different subsets of fingerprint properties that were able to successfully discriminate between different potential sources of sediment and that the method of fingerprint selection ultimately influenced the sediment apportionment results. Furthermore, if the fingerprints are unable to

provide good discrimination between potential sources then the sources may need to be grouped together (Section 1.3.1).

#### **1.3.4 Mixing models**

Mixing models (also known as unmixing or source apportionment models) are tools that quantitatively link sources and sediment in terms of the proportion derived from each potential source; at their core, mixing models are a mass balance equation (i.e., source contributions must equal unity). Currently there are two main groups of mixing models, frequentist-based (i.e., multivariate) (e.g., Collins et al. 1997) and Bayesian-based methods (e.g., Parnell et al. 2010), and there is little consensus as to which type of mixing models are most appropriate for sediment fingerprinting. Furthermore, recent research comparing different mixing models has demonstrated that the apportionment results are sensitive to model selection (e.g., Haddadchi et al. 2014). Some of the main assumptions of mixing models, adapted from Ward (2012), are: 1) all sediment samples come from the same set of sediment sources; 2) all sediment sources are equally available in terms of amounts of sediment being delivered to the stream; 3) no potential sources of sediment are missing; and 4) sediment sources are fully characterized in terms of their sediment fingerprints. Some models will have other assumptions and caveats (e.g., normality of data) and it is important to ensure that all of the assumptions are reasonably met, or to have an understanding of how it will affect the outcome.

It is also assumed that the properties of the sediment do not change (i.e., behave in a conservative manner) as it moves through the watershed from source to sink and a direct link between source and sediment can be made. However, this is rarely the case and these changes

in sediment properties need to be accounted for. The two main processes that result in the non-conservative behaviour of fingerprint properties are particle selectivity and biogeochemical transformations and are discussed below.

## **1.4 From source to sink**

### **1.4.1 Physical transformations: particle selectivity**

Particle selectivity as a result of erosional, delivery and fluvial processes is one of the main factors influencing the non-conservative behaviour of sediment properties and is the primary focus of this dissertation. The selectivity of these processes often results in the in-stream sediment becoming enriched in both fine-grained and organic-rich particles as compared to the source material as the smaller and less dense particles are preferential eroded and transported through the watershed (Walling 1983). Both the particle size distribution and the organic matter content of soils and sediments have been demonstrated to strongly influence the concentration of many fingerprints. For example, it has been demonstrated that the concentration of many trace metals within sediment is positively correlated to both particle size and organic matter content (Horowitz 1991).

Issues of differences in grain size between source and sediment are often minimized by limiting the analysis to the <63  $\mu\text{m}$  grain-size fraction, as it is assumed that this fraction comprises the bulk of suspended sediment (Walling et al. 2000) and is less susceptible to particle selective processes. Furthermore, an allowance is still typically made for any additional particle size differences between sources and sediment (i.e., of the <63  $\mu\text{m}$  grain-size fraction) using a particle size correction factor and sometimes an organic matter enrichment factor (e.g., Collins et al. 1997; Walling et al. 1999; Owens et al. 2000). The most

commonly used correction factors are based on the ratio of specific surface area (SSA) or organic carbon content of the sediment to the SSA or organic carbon content of each source. This value is then multiplied by the fingerprint concentration for each source (Collins et al. 1997). However, such approaches are controversial (e.g., Russell et al. 2001), thus some researchers do not always use correction factors (e.g., Martínez-Carreras et al. 2010; Koiter et al. 2013). For example, Russell et al. (2001) demonstrated that the relation between concentration and SSA was not uniform across different trace elements or watersheds. Furthermore, there is also evidence that the relative contribution of organic matter to the geochemical fingerprint varies between elements (e.g., Bakircioglu et al. 2010).

Despite this, few studies have taken these problems into account and a single correction factor is commonly used for all fingerprints. The use of a single particle size correction factor for all parameters will likely to result in incorrect adjustment of some fingerprint values, which in turn will influence the results obtained from mixing models. The question remains as to whether correction factors are needed to compensate for other properties such as Fe- and Mn-oxides or carbonates, as these have also been shown to influence the concentrations of many trace elements (Horowitz 1991); clearly further work is needed to assess this. Furthermore, abrasion and disaggregation of soil particles can also result in a downstream change in particle size and further complicate the issue of particle size (e.g., Dyer and Olley 1999).

#### **1.4.2 Biogeochemical transformations**

The other major group of processes that can prevent drawing a direct link between source and sediment are biogeochemical processes. These include: ion exchange,

adsorption/desorption, complexation, dissolution/precipitation and biologically mediated reactions. For example, Parsons and Foster (2011) discuss the many limitations of using  $^{137}\text{Cs}$  as a result of biogeochemical transformations that can occur within soils and sediment. Changes in downstream environmental conditions (e.g., pH, redox potential) are likely to be a concern for transformation of sediment properties and the distortion of the fingerprint signal. Within many sediment fingerprinting studies these types of issues are often overlooked. In some cases, the behaviour of a fingerprint under changing environmental conditions have been assessed experimentally (e.g., Poulenard et al. 2012), but the more common approach is to eliminate fingerprints which behave in a non-conservative manner based on previous studies (e.g., Smith and Blake 2014).

### **1.4.3 Radionuclide transformations**

There is a long history of using cosmogenic (e.g.,  $^7\text{Be}$ ), anthropogenic (e.g.,  $^{137}\text{Cs}$ ) and natural occurring (e.g.,  $^{210}\text{Pb}$ ) fallout radionuclides (FRN) as fingerprints to measure rates of soil erosion and to assess the sources of sediment within watersheds (Mabit et al. 2008; Guzmán et al. 2013). Many FRN's have a strong affinity to fine-grained particles and organic matter and as a result tend to accumulate near the soil surface and, therefore, provide good indicators of soil redistribution and discrimination between surface and subsurface sediment sources (Evrard et al. 2015). Radionuclides, by their very nature, are a non-conservative fingerprint property due to the loss of unstable isotopes through radioactive decay. However, the characteristics of the decay process (i.e., half-life) are well understood and quantified which allow for their use within sediment fingerprinting studies. For example, if source and sediment samples are collected and the activity of these samples are determined over several

years all of the samples can be back-corrected to the same date ensuring any observed differences in activity are not related to the sample collection times (e.g., Li et al. 2008). Furthermore, the differences in half-life between different isotopes (e.g.,  $^{210}\text{Pb}$ ; half-life of 22.2 years and  $^{10}\text{Be}$ ; half-life of 1.3 million years) can be exploited to differentiate between contemporary and legacy sediment sources (e.g., Belmont et al. 2011).

## **1.5 Dissertation goals and objectives**

The primary goal of this dissertation was the continued development and refinement of the sediment fingerprinting approach. This was accomplished through: i) a review of the literature; ii) a series of small-scale experiments; and iii) a watershed-scale application of the sediment fingerprinting approach. The dissertation focuses primarily on the particle selectivity process, and to a lesser extent the biogeochemical process, and its subsequent influences on the behaviour of sediment fingerprints as sediment moves through a watershed. The overall objectives of this dissertation were to:

- 1) assess the particle size and organic matter selectivity of soil erosion, sediment delivery and fluvial transport processes;
- 2) explore the influence of particle size and organic matter selectivity on geochemical fingerprint properties;
- 3) evaluate commonly used approaches to account for particle selectivity;
- 4) investigate the role of scale and geomorphic connectivity on the sediment fingerprinting approach; and
- 5) provide recommendations to improve the reliability and robustness of the sediment fingerprinting approach.

One of the main purposes of this dissertation is to build a set of guiding principles that can be used for the successful implementation of sediment fingerprinting studies.

The dissertation begins with a review of the literature (Chapter 2) which the stage for the remaining chapters as it discusses the relevant literature with respect to the behaviour of soil and sediment properties at a range of scales, from individual soil and sediment particles through to the watershed scale. The landscape unit, represented by a sequence of hillslope, riparian and fluvial environments provides an appropriate scale at which to investigate the processes that mobilize, transport and deposit sediment in watersheds and is the logic behind Chapters 3 – 6. Specifically, in Chapters 3 and 4, the particle selectivity of hillslope processes was assessed using a rainfall simulator to mobilize sediment. Chapter 3 investigated the role of soil surface properties on the particle selectivity process, and Chapter 4 assessed commonly used correction factors and examined the effects of both particle size and soil organic matter on the concentration of a broad suite of geochemical elements. In Chapter 5, the role of the riparian zone was investigated by examining a series of soil profiles along transects that extended from the upper landscape position into the riparian zone. This approach allowed for the patterns of erosion and deposition to be assessed, which provided context for investigating the changes in particle size and organic matter content along the transect. The geochemical composition of the soil was also evaluated both along the transect and with depth. In Chapter 6, the influence of fluvial transport on the particle selectivity (size and organic matter content) was assessed using a large recirculating flume under contrasting channel bed conditions. Chapter 7 discusses the role of scale and connectivity in a watershed-scale application of the sediment fingerprinting approach. Finally, Chapter 8 presents an overall synthesis and conclusions of this thesis, and provides protocols for improved

sediment source fingerprinting.

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## **2 The behavioural characteristics of sediment properties and their implications for sediment fingerprinting as an approach for identifying sediment sources in river basins**

### **2.1 Abstract**

Sediment fingerprinting is a technique that is increasingly being used to improve the understanding of sediment dynamics within river basins. At present, one of the main limitations of the technique is the ability to link sediment back to their sources due to the non-conservative nature of many of the sediment properties. The processes that occur between the sediment source locations and the point of collection downstream are not well understood or quantified and currently represent a black-box in the sediment fingerprinting approach. The literature on sediment fingerprinting tends to assume that there is a direct connection between sources and sinks, while much of the broader environmental sedimentology literature identifies that numerous chemical, biological and physical transformations and alterations can occur as sediment moves through the landscape. The focus of this paper is on the processes that drive particle size and organic matter selectivity and biological, geochemical and physical transformations and how understanding these processes can be used to guide sampling protocols, fingerprint selection and data interpretation. The application of statistical approaches without consideration of how unique sediment fingerprints have developed and how robust they are within the environment is a major limitation of many recent studies. This review summarizes the current information, identifies areas that need further investigation and provides recommendations for sediment

fingerprinting that should be considered for adoption in future studies if the full potential and utility of the approach are to be realized.

## **2.2 Introduction**

Sediment fluxes within river basins are natural processes and are part of global erosional, weathering and biogeochemical cycles that are important for maintaining aquatic ecosystem health, resiliency and function (Owens 2008). As a society, we are altering the landscape at an unprecedented scale for the purposes of urbanization, agriculture, resource extraction, industry and recreation (Foley et al. 2005). These changes within the landscape are affecting sediment fluxes which in turn are resulting in the degradation of both the terrestrial and aquatic environments (Allan 2004; Syvitski et al. 2005; Owens et al. 2010). Some land use practices result in unsustainable soil losses, where the rate of erosion is greater than the rate of soil production leading to a reduction in productivity. This is of particular concern within agricultural areas as there is limited new land suitable for sustained cultivation (Montgomery 2007).

Both the quantity and quality of sediments can have an impact on the aquatic environment. Increases in sediment can reduce light penetration, act as a scouring agent and result in the sedimentation of the river bed. Sediment also acts as a vector for nutrients and a variety of contaminants including pathogens, industrial chemicals and metals, and plays an important role in the downstream conveyance of this material. Changes in the amount and composition of sediment can have an impact on the ecology of the aquatic ecosystem through the alteration or elimination of habitat, shifts in community composition and abundance, changes in the food web, increased mortality and a decrease in reproductive success (Henley

et al. 2000; Palmer et al. 2000; Shaw and Richardson 2001; Rabení et al. 2005; Harrison et al. 2007). In addition, increases in sediment delivery to the aquatic environment can also result in reduced reservoir capacity, a decline in drinking water quality, impairment of navigation, and impact recreational activities (Vörösmarty et al. 2003; Vörösmarty et al. 2010).

The impacts of sediment and associated nutrients and contaminants on water and aquatic habitat quality are well documented and represent a widespread problem facing many countries (Bilotta and Brazier 2008; Horowitz 2009). As the global population continues to increase, the pressures placed on our soil and water resources will also increase, and there is a need to design new resource management systems which can meet the growing demand for water, food, fibre and fuel, while safeguarding the environment. Good management of these resources requires a solid understanding of sediment dynamics, however, the often diffuse nature of sediment pollution makes obtaining reliable information as to the dominant sources of sediment and associated nutrients and contaminants within a river basin difficult (Smith et al. 2011).

### **2.3 The sediment fingerprinting approach**

Sediment tracing and sediment fingerprinting are terms that are often used interchangeably but can have different meanings and, therefore, it is important that a clear distinction be made. Sediment tracing in many instances refers to direct tracing or tracking of sediment in a downstream direction from its origins through the landscape with the assumption that the source of sediment is known. Specifically, the sources are identified using prior knowledge and the origins and behaviour of the tracers are generally well understood. Typically, the movement of the tracer and, by inference, the sediment is followed

in a downslope or downstream direction. Sediment tracing studies often use artificially introduced tracers including foreign particles (e.g., fluorescent particles; Granger et al. 2011), rare earth elements (e.g., lanthanides; Polyakov and Nearing 2004; Spencer et al. 2011) as well as fallout radionuclides (e.g.,  $^{137}\text{Cs}$ ; Ritchie and McHenry 1990; Wilson et al. 2012) to track the movement of sediment (for a review see Guzmán et al. 2013). In contrast, sediment fingerprinting generally refers to working in an upstream direction in an inferential manner to determine the source(s) of sediment, i.e., the contribution from a given source of sediment is unknown. The approach is based on the idea that one or more of the natural physical or biogeochemical properties of the sediment will reflect its source, and therefore can be used diagnostically to identify the origin(s) of the sediment. There is a wide range of natural soil and sediment properties that can be utilized as fingerprints and are related to three fundamental properties; nuclear properties, molecular identity and orbital electron properties (for a review, see Foster and Lees (2000) and Fig. 2.1). The unique sediment properties, which comprise the fingerprint, are measured in both the source and sediment samples and a statistical un-mixing model is subsequently used to estimate the contribution of sediment from each potential source (for an overview of the methodology and application of sediment fingerprinting, see Gellis and Walling (2011)). For the purposes of this review, the focus will be sediment fingerprinting as opposed to sediment tracing.

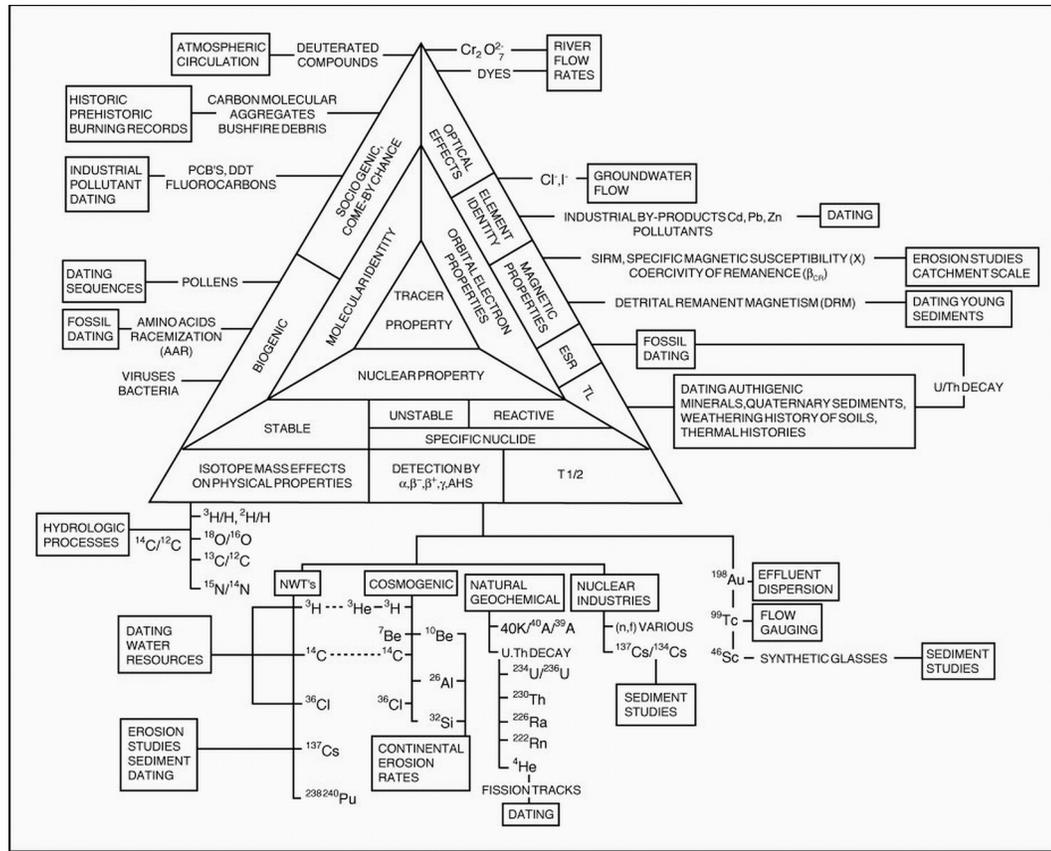


Figure 2.1: Fundamental properties of earth materials, which might be used for dating and tracing sediment sources. From Foster and Lees, 2000, reproduced with permission of John Wiley & Sons, Ltd.

Sediment fingerprinting is a technique that has been used to investigate sediment dynamics at a variety of spatial scales ranging from individual field plots (<10 m<sup>2</sup>) (e.g., Wilson et al. 2011) to large river basins (>100,000 km<sup>2</sup>) (e.g., Wang et al. 2009), at temporal scales ranging from event-based (<24 hr) (e.g., Martínez-Carreras et al. 2010b) to geological sediment records (>10,000 yr) (e.g., Yang et al. 2006), in environments ranging from forested (e.g., Smith et al. 2011) to agriculture (e.g., Russell et al. 2001) to urban (e.g., Carter et al. 2003). It has been used to determine the provenance of sediment size classes from sand (250 - 355 μm) (e.g., Maher et al. 2009) to very fine-grained (<10 μm) sediment (e.g., Wilkinson et al. 2009). A search of the Web of Knowledge citation index (April 2013), using

("sediment") AND ("tracing OR fingerprinting") as topic keywords and excluding inappropriate subject categories (e.g., health sciences), returned over 450 entries that encompassed more than 150 different journals between 1990 and 2012. The increase in the number of publications per year over the past 23 years (Fig. 2.2) reflects the increased attention that these techniques are receiving as a tool to help understand sediment dynamics. Furthermore, the rapid uptake of the technique also reflects increasing concerns over water quality and its potential as a tool for river basin managers for improved decision-making in light of increasing policy and legislation (Owens and Xu 2011). The large number and diversity of journal titles demonstrates that the technique is multidisciplinary, covering subject areas including geology, geomorphology, environmental science, soil science, oceanography, agriculture and forestry, and it is being used to answer a wide range of research questions. Table 2.1 summarizes some of the main applications of the sediment fingerprinting technique.

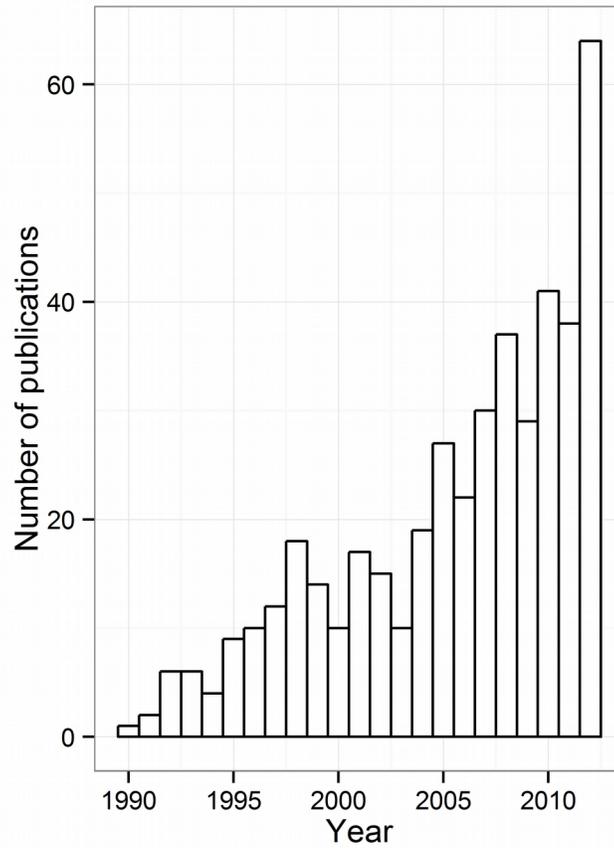


Figure 2.2: Number of publications per year between 1990 and 2013 based on a search of the Web of Knowledge citation index, using (“sediment”) and (“tracing” or “fingerprinting”) as topic keywords (April 2013).

Table 2.1: Applications of the sediment fingerprinting technique.

<b>Application</b>	<b>Example</b>
Climate change	Gingele and De Deckker, 2004
Contaminant dynamics	Bird et al., 2010
Criminal forensics	Dawson and Hillier, 2010
Environmental forensics	Saber et al., 2006
Evaluation of management practices	Collins et al., 2010a
Decision making support	Evans et al., 2006
Nutrient dynamics	Walling et al., 2008
Sediment budgets	Walling et al., 2002
Contemporary sediment fluxes	Smith et al., 2011
Sourcing organic matter	McConnachie and Petticrew, 2006
Historical reconstruction	Dearing et al., 2001

At present, one of the main limitations of the sediment fingerprinting approach is the ability to quantitatively link sediments back to their sources in a robust and reliable means due to the non-conservative behaviour of the properties of transported sediment (Davis and Fox 2009). Ideally, the composition of the sediment, including geochemical (e.g., trace metal content), biological (e.g., organic matter content) and physical (e.g., texture) properties, would not change (i.e., remain conservative) as the sediment moves through the landscape such that direct comparison between sources and sediment can be made. However, this is rarely the case and the changes in sediment properties that occur as the sediment moves through the landscape need to be taken into consideration. Davis and Fox (2009) have suggested that accounting for the fate of sediment and fingerprint properties is the least understood part of the sediment fingerprinting approach and that future research should be directed at addressing these issues as it is critical to the advancement of the technique. The processes that link the sources of sediments (e.g., cropland, channel banks) to the collected sediments (e.g., suspended sediment, channel bed sediment) are often ignored and currently represent a black-box in the sediment fingerprinting approach (Fig. 2.3).

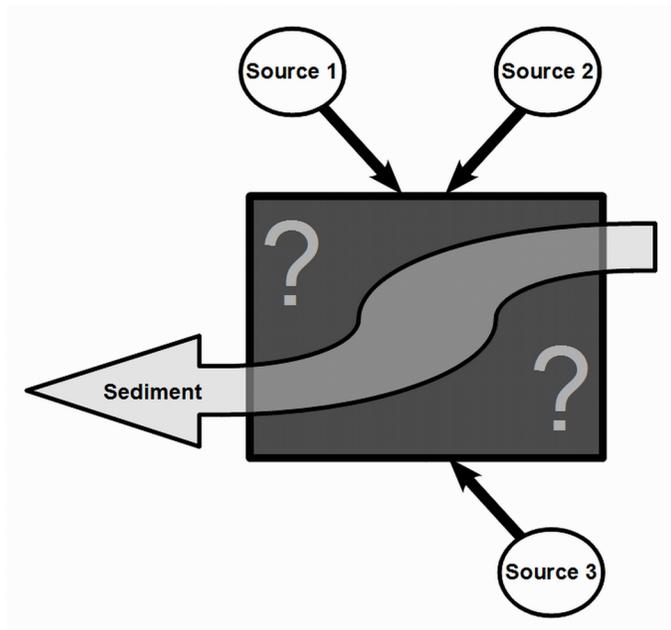


Figure 2.3: Existing blackbox approach to the sediment fingerprinting approach, whereby there is the underlying assumption of a direct link between hill slope and downstream sediment in terms of property conservativeness. Processes within the box and their influence on sediment properties are not accounted for in this approach.

The black-box approach is viewed in terms of its inputs (sediment sources) and outputs (collected sediments) with very little knowledge of how processes (e.g., erosion and transport processes) within the black-box might change the properties of the sediment during transport within the system (Fig. 2.3). The literature on sediment fingerprinting tends to assume that there is a direct connection between sediment sources and sediment samples collected downstream, while much of the broader environmental sedimentology literature identifies that there are numerous chemical, biological and physical processes that can alter sediment properties as it moves through the landscape, which can have serious implications as the sediment may no longer be representative of its source. Understanding and modelling the processes that link the sources to the sediments in terms of the non-conservative

behaviour of sediment properties is, therefore, an important aspect of improving the robustness and the utility of the sediment fingerprinting approach.

In an effort to better understand the role of sediment fingerprinting for addressing the impacts of anthropogenic activities on sediment dynamics and associated implications for water quality, this review will focus on fine-grained (<63  $\mu\text{m}$ ) contemporary (<100 yr) sediment fluxes. For reviews on tracers of coarse sediment see Sear et al. (2000) and tracers of longer-time scale sediment fluxes see D'Haen et al. (2012). The objectives of this review are twofold: (1) to identify the main processes that influence sediment properties and their implications for sediment fingerprinting; and (2) to identify concerns and recommend directions for future research. The emphasis will be on two key issues that have been demonstrated to strongly influence sediment properties. First, the issue of particle selectivity (i.e., changes in the particle size distribution and organic matter content) due to preferential mobilization, transportation and sedimentation and secondly, the physical and biogeochemical transformations that can result in the enhancement or depletion of fingerprint properties. Each issue will be discussed within the context of interpreting data based on the standard sediment fingerprinting approach and secondly how improved sampling and analytical techniques can better link sediment to sources.

Figure 2.4 demonstrates the complexity of the movement of sediment through the environment that the sediment fingerprinting approach attempts to accommodate. This conceptual framework shows the multiple spatial scales over which processes can affect the properties of soils and sediments and helps to identify the key issues to consider based on the scale of observation. Fig. 2.4 also provides the framework for the structure of this review paper, initially by looking at the nature and properties of soil and sediment particles, which

are the basis of the sediment fingerprinting technique. The scale of observation is then broadened to the landscape unit represented here by a sequence of hillslope, riparian and aquatic environments. This landscape unit provides an appropriate scale to evaluate the processes that mobilize, transport and deposit sediments and as well links the terrestrial and the aquatic environments. Finally, the river basin scale is used here as it is most often the unit of observation for sediment fingerprinting and budgeting studies (Slaymaker 2003; Owens 2005; Walling and Collins 2008); here the challenges of scaling up, linkages and the interactions of processes are discussed.

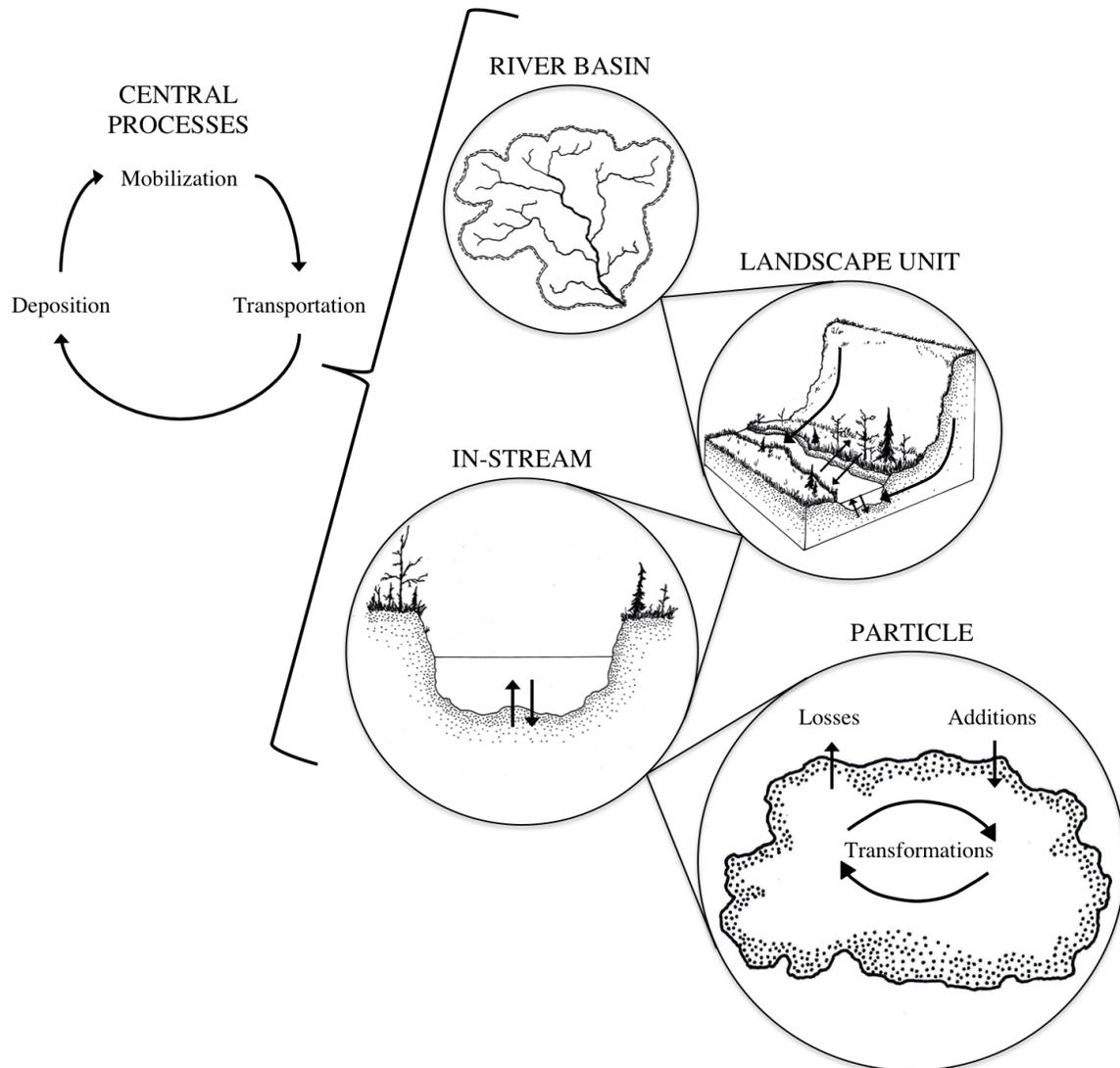


Figure 2.4: Conceptual diagram demonstrating the complexity of the sediment continuum, at multiple scales of observation, that is incorporated into the sediment fingerprinting approach.

## 2.4 Nature and properties of soil and sediment particles

Traditionally, much of the research in soil and sediment science has used the dispersed mineral fraction and gross organic matter content for the interpretation and prediction of the movement of sediment and associated nutrients, metals and other contaminants in terrestrial and aquatic systems (Horowitz 1991). However, there is increasing

recognition that soils and sediments are complex materials composed of four main components: mineral, organic matter, water and gases. The composition and physical structure of soil will reflect the interaction of parent material, climate, hydrology, amount and types of vegetation, age, weathering processes and anthropogenic activities. It is the net result of these properties and processes which makes it possible to discriminate between multiple sediment sources using natural soil properties. Potential sediment sources are commonly delineated between spatially distributed sources based on geology, soils, land use and vegetation and also vertically distributed sources including surface soils, subsurface soils and channel banks. It is the particular environmental conditions at the source that impart unique physical and biogeochemical signatures which can be utilized as fingerprints. The processes that lead to signature formation operate over longer time scales than the sediment redistribution processes involved, which in many cases is the underlying basis for their use. Knowledge of the processes that lead to signature development is key in selecting and assessing the robustness of fingerprint properties during transport through the river basin. It is also important in understanding the limitations due to the spatial and vertical distributions of fingerprint properties at the source as well as the enrichment or depletion of fingerprints during the fluvial transport of sediment. Sediment properties commonly used in sediment fingerprinting can be broadly separated into three categories; (1) geochemical, (2) biochemical and (3) physical fingerprints.

#### **2.4.1 Geochemical properties**

The geochemical properties, which include inorganic elements, radionuclides and mineral magnetism, of soils and sediments are among the most widely used fingerprints in

sediment fingerprinting studies (Walling 2005; Mabit et al. 2008). Atmospheric fallout radionuclides, such as  $^7\text{Be}$ ,  $^{10}\text{Be}$ ,  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , effectively tag surface sediments such that the concentration declines markedly with depth in the soil profile and are preferentially absorbed to clay minerals and organic matter due to their high specific surface area which renders them chemically reactive (Horowitz 1991). In recent articles, Parsons and Foster (2011) and Taylor et al. (2012) discuss the adsorption behaviour of  $^{137}\text{Cs}$  and  $^7\text{Be}$  in soils, respectively, and highlight the implications for sediment fingerprinting. Fallout radionuclides are commonly employed to discriminate between surface, subsurface and channel bank sources. In addition, these properties can also provide discrimination between cultivated and non-cultivated land, and between eroded and depositional areas as cultivation and erosional processes redistribute the fallout signal down through the soil profile and across the landscape. Fallout radionuclides, by the very nature of their radioactive decay, are non-conservative fingerprints and the characteristics of a watershed, including the magnitude of sediment storage features, are important to consider when assessing the suitability of radionuclide properties as fingerprints and interpreting the data they provide. However, most have a sufficiently long half-life and predictable decay rate to still be effective fingerprints in the study of contemporary sediment dynamics. With the exception of  $^{137}\text{Cs}$ , an anthropogenically derived radionuclide, most fallout radionuclides are naturally occurring and are continually being deposited on the surface. This can have implications for the fingerprinting technique as eroded and exposed subsurface sediments will begin to acquire a new radionuclide signature as they move through the landscape and continue to receive fallout products (Wilkinson et al. 2009). Similarly, buried sediments begin to lose the radiochemical signature due to radioactive decay. This type of non-conservative behaviour

can be advantageous as it can be used to differentiate between recently eroded (e.g.,  $^7\text{Be}$ , half-life of 53.4 days) and legacy sediments (e.g.,  $^{210}\text{Pb}$ , half-life of 22.3 years) but raises the question as to what point in time these sediments begin to represent a new source.

Mineral magnetic properties have been used as fingerprints to discriminate between various sediment sources (Yu and Oldfield 1993; e.g., Hatfield and Maher 2009) and have also been included along with other soil properties as part of a composite fingerprint (e.g., Walling et al. 1999; Gruszowski et al. 2003). Magnetic susceptibility and remnant magnetism are the two main properties used to characterize the magnetic properties of sediment and are largely related to the mineralogy of the sample (e.g., the presence of iron oxides) and the magnetic grain size. Soils have a primary magnetic signature largely related to the mineralogy of the parent material but can acquire a secondary or an enhanced signal due to minerals formed through pedogenesis, weathering, bacterial action, anthropogenic inputs and fire (Dearing et al. 1996). While these secondary processes may contribute to the ability to discriminate between sources, they may also result in post-depositional diagenesis which can obscure the linkage between the source and sediments. In addition, mineral magnetic properties have been shown to discriminate soil burned at different severities as well as unburned areas, however, recent research by Blake et al. (2006) demonstrated that there was a lack of dimensionality in the data that limits their use in sediment fingerprinting (also see Smith et al. 2013). Particle-size also exhibits a strong influence on the magnetic properties of sediment and needs to be taken into consideration in the characterization and interpretation of these properties (Oldfield and Yu 1994; Hatfield and Maher 2009). In many cases the relationship between particle size and measures of mineral magnetic properties is complex (Foster et al. 1998; Blake et al. 2006; Oldfield et al. 2009) and this complexity can make it

difficult to discriminate between sources and make comparisons between sources and sediments as a result of differences in particle size distributions.

Inorganic properties, including concentrations of heavy and trace elements and base cations, and mineral assemblages vary spatially through the landscape and vertically through the soil profile due to differences in parent material, soil forming processes and land use. Geochemical analysis of soils and sediments is commonly used in fingerprinting studies as it is a relatively quick, inexpensive and widely available technique that can yield information on 50 or more different elements depending on the analytical instrument used. As with other geochemical properties there is a strong relationship between elemental composition and particle size and organic matter content primarily due to the high specific surface area and reactivity. Secondary minerals, including clays, metal oxides (Fe, Mn, Al) carbonates and sulphates, and organic matter are important sites for chemical exchanges and reactions to occur. The dominant processes controlling the soil and sediment geochemistry include ion exchange, adsorption/desorption, precipitation/dissolution, complexation, and biologically mediated reactions. As indicated by Römken et al. (2009) and Rodrigues et al. (2010), elements can be coarsely divided into three different fractions; available, reactive and inert. The distribution of element concentrations among the different fractions and the most relevant processes are shown in Fig. 2.5. Under unchanging environmental conditions (e.g., pH, temperature, redox potential) the proportion of an element within a given fraction will remain in equilibrium. However, stable conditions rarely exist in nature, and according to Le Châtelier's principle, if a system at equilibrium experiences a change (e.g., change in pH, redox potential, etc.) then the equilibrium shifts to counteract the imposed change and a new equilibrium is established (Olmsted and Williams 2005). This can have implications for

sediment fingerprinting because as sediment moves through the river basin the proportion of a given fingerprint (element) in solution or in the particulate form may not remain static, and therefore, no longer reflect the original source of sediment. The mineralogy of soil and sediment, determined using optical or X-ray diffraction techniques, has also been used as a fingerprint in sediment fingerprinting studies (e.g., Rhoton et al. 2008). This type of characterization may provide a more robust fingerprint property as it is related to the primary mineral structure and is less affected by transformation processes (Fig. 2.5).

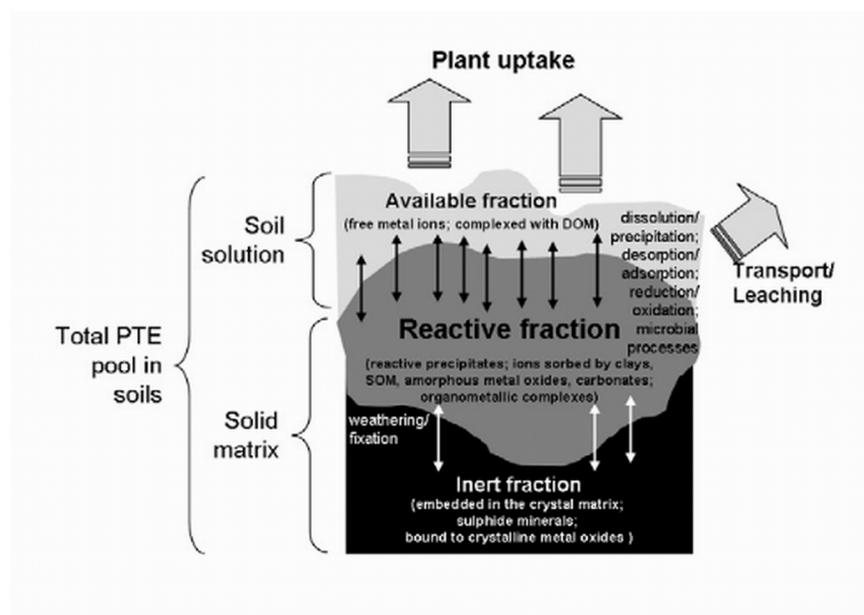


Figure 2.5: Distribution of total pools of potentially toxic elements (PTE) in soils — the size of the different fractions and the most relevant soil processes vary according to the element of interest and environmental conditions. From Rodrigues et al. 2010, reproduced with permission of Elsevier.

It can be difficult to identify if, where and to what extent transformations might be occurring within the watershed. Changes in the redox potential and pH are important watershed characteristics to consider. Therefore, identifying: (i) the location and magnitude of anaerobic (reducing) zones (e.g., wetlands and floodplains); (ii) changes in the underlying

geology (e.g., changes in pH due to the occurrence of carbonate minerals); and (iii) anthropogenic influences (e.g., sewage and industrial effluent) with respect to sediment sources and sampling locations, are important aspects to consider when assessing the conservative behaviour of sediment properties.

#### **2.4.2 Biochemical properties**

Biochemical properties, including organic elements (e.g., C, N, P), stable isotopes (e.g.,  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ ), biomarkers (e.g., lignins, sugars, fatty acids), organic chemicals (e.g., pesticides) and DNA, reflect the vegetation, microbial community and the land use practices of sediment sources. The use of biochemical properties in sediment fingerprinting studies has been receiving increasing attention as it has the potential to provide better spatial constraints for sediment sources compared to other fingerprint properties, and/or differentiate between sources that other, more conventional, properties are unable to (McConnachie and Peticrew 2006; Granger et al. 2007). Geochemical properties are generally used to differentiate between broad categories of sediment sources (e.g., forested, cultivated and pasture land), and the information generated, while providing information on sediment sources, may not be of sufficient detail for river basin managers to make effective and well informed decisions. In contrast, biochemical properties have the potential to discriminate between a greater number and different types of sediment sources (e.g., differentiate between different crop types, or tree species) and provide greater detail on sediment sources. This will allow managers to better target mitigation strategies (Gibbs 2008; Blake et al. 2012).

Biochemical processes are continually cycling carbon, nutrients and metals through the processes of immobilization and mineralization. Soil organic matter is often divided into

three fractions - active, slow and passive - which are related to their stability over time. The active fraction represents the pool of organic matter that is the most susceptible to microbial decomposition (< 2 yr), the slow fraction is moderately susceptible, and the passive fraction is the most resistant to microbial decomposition (500 - 5000 yr) (Brady and Weil 2001). This becomes important as the conveyance time of sediment through a river basin can vary widely from days to decades to centuries and some of the organic matter can be lost through decomposition. As well, organic matter is composed of many different organic compounds including carbohydrates, amino acids, lignin and polyphenols, which decompose at different rates (Brady and Weil 2001). Decompositional processes can result not only in changes in the quantity of organic matter but also in the composition (e.g., C/N ratio, organic compounds) which can be difficult to characterize. Researchers are developing compound-specific stable isotope fingerprints that target compounds that are more resistant to decay and that bind strongly to soil and sediment particles, thereby providing a more robust fingerprint (Gibbs 2008; Blake et al. 2012; Hancock and Revill 2013).

Biological activity can not only deplete an organic signal through decomposition, but sediments during their conveyance through the river basin may also acquire new and different organic properties such that they may no longer reflect their original source. Microbial activity can also transform inorganic forms to organic forms (e.g., biomethylation of mercury) which can behave differently in the environment (e.g., bio-availability) (Thayer 2002). Furthermore, there is a large difference between the density of organic particles (0.9 - 1.3 Mg m<sup>-3</sup>) and mineral particles (2.6 - 2.75 Mg m<sup>-3</sup>) (Brady and Weil 2001) which can result in the preferential transport and enrichment of organic matter of eroded material in comparison to the source material.

### **2.4.3 Physical properties**

Spectrometric methods (e.g., colour) can be used to characterize soils and sediments and can be broadly separated into two groups; reflectance/absorbance and fluorescence. There is a growing interest in using visible and near-infrared spectroscopy as an inexpensive and rapid method to characterize soils and sediments for use in sediment fingerprinting studies (Martínez-Carreras et al. 2010a; Martínez-Carreras et al. 2010b). Similarly, ultraviolet fluorescence spectroscopy has been used to characterize organic matter (Bridgeman et al. 2011), however, it has not yet been demonstrated as an effective method to characterize soils and sediments within sediment fingerprinting studies. Spectrometric characterization is sensitive to moisture content and physico-chemical alterations that can occur during transport (e.g., oxidization of iron, decomposition of organic matter, texture) (Levin et al. 2005; Summers et al. 2011). Particle shape, or morphology, is another physical property that has been used to fingerprint sediment (Krein et al. 2003; Petticrew 2005). This physical property is determined by imaging sediment particles and describing qualitatively (e.g., platy) or quantitatively (e.g., fractal dimension) the morphology of sediment particles. The shape of a particle is influenced by abrasion, disaggregation and aggregation (flocculation) that can occur as sediment moves through the landscape; such issues are discussed below.

### **2.5 Hillslope processes**

Soil erosion refers to the detachment, entrainment, transport and deposition of soil particles through the forces of wind, water and tillage, and the pattern of total soil erosion within a landscape is the sum of these three main erosional processes (Lobb et al. 2004). While the majority of research to date has primarily focused on quantifying the amount of

soil erosion and its controlling factors (e.g., Revised Universal Soil Loss Equation; Renard et al. 1991), there is a growing body of literature investigating the role of linkages and interactions between the different erosional processes (e.g., Lobb et al. 2004) and the physical and biogeochemical properties of the eroded material (e.g., Ballantine et al. 2008; Zhang et al. 2011). This is in response to the need for better characterization of the sediment and sediment-associated nutrients and contaminants moving off the land and entering surface waterways, which is in turn driven by the need to protect water quality and aquatic habitat.

### **2.5.1 Particle selectivity**

Eroded sediments are often found to have a finer grain-size distribution and a higher organic matter content compared to the source material as the smaller and less dense particles are preferentially mobilized and transported. However, some studies have found eroded sediments to be coarser (e.g., Meyer et al. 1992) or have a bimodal (e.g., Asadi et al. 2007) grain-size distribution and also to be depleted in organic matter (e.g., Nadeu et al. 2011) compared to the source material. Because of the strong relationship between particle size and organic matter content for many fingerprints (Horowitz 1991; Russell et al. 2001) it is important to have a solid understanding of the selective nature of erosion and transport processes. It is difficult to make generalizations about the influence of soil erosion on sediment properties as different erosion and transport processes and patterns will exhibit differences in particle selectivity. Therefore, it is important to consider the dominant forms of soil erosion and transport pathways for assessing the influence of particle selectivity on sediment properties as unrecognized particle selectivity can lead to false conclusions about changes in grain-size and organic matter.

An in-depth investigation of particle selectivity within the context of soil erosion warrants a closer look at what is meant by the term soil particle. In its simplest form, the term can refer to the primary mineral particles (e.g., sand, silt, clay), however, much of the soil is moved as aggregates which are a cohesive agglomeration of both inorganic and organic matter, which may have different physical and biogeochemical characteristics in comparison to the primary particles of which they comprise (Buffle and Leppard 1995a; Buffle and Leppard 1995b; Droppo et al. 1997; Droppo 2001). Therefore, making conclusions about the mobilization and transport of sediment based on absolute (i.e., physically and/or chemically dispersed) particle size distribution may result in errors as soil moves as aggregates and, therefore, the effective or aggregate particle size distribution may be more informative (Slattery and Burt 1997).

Erosional processes are selective in each step - detachment, entrainment, transport and deposition - of sediment movement (Leguédouis and Bissonnais 2004). With all forms of erosion the degree of selectivity will be a function of environmental factors including soil characteristics (e.g., texture, aggregate stability, moisture content), surface characteristics (e.g., slope, ground cover, micro-topography) and the nature of the erosive force (e.g., wind, water or tillage erosion) (Issa et al. 2006; Asadi et al. 2011). The selectivity of soil erosion is generally well correlated to the energy of the erosive process with increasing erosive force resulting in less selectivity. Armstrong et al. (2011) found that there was a greater enrichment of fine-grained sediments and organic matter under lower rainfall intensities and slopes. Similarly, Schiettecatte et al. (2008) found that interrill erosion was a selective process resulting in an enrichment of organic matter while rill erosion was found to be a non-selective process. Generally, gully erosion is not considered to be a selective process due to

concentrated flow and higher stream power. It is also important to consider interactions between different erosional processes, for example, tillage erosion may deposit sediments into a rill which will subsequently be moved by water erosion (Lobb et al. 2004). The pathways by which sediments are routed through the landscape and the degree of connectivity between hillslopes and surface waterways will also influence the particle size distribution and organic matter content. Gullies and subsurface drains provide a more direct pathway and result in less selectivity while inter-rill and rill erosion provide a more tortuous pathway and sediments undergo more cycles of mobilization, transport and deposition, which may result in a greater degree of sorting. The preferential removal of fine-grained sediment by erosional processes can lead to the armouring of the soil surface by the coarse fraction thereby limiting any additional erosion. The importance and validity of particle size correction factors can be better assessed by understanding the dominant erosional process and transport pathways.

There can also be significant spatial variations in the surface particle size distribution and organic matter content across areas as small as 35 ha (Mzuku et al. 2005). This spatial variability in soil properties adds an additional layer of complexity in the predicting of the properties of eroded sediments entering surface waterways. Studies (e.g., Sutherland 1994; Kariuki et al. 2009) have investigated the spatial variability of soil properties and provided advice on the number of samples required to obtain a statistically representative measure of soil properties (e.g., mean  $\pm$  2SD). Such information can help develop sampling strategies that improve the reliability of the fingerprint property data of the sources.

#### *2.5.1.1 Particle size and organic matter correction factors*

Issues of differences in grain size between source and sediments are often minimized

by limiting the analysis to the <63  $\mu\text{m}$  grain-size fraction, as it is assumed that this fraction comprises the bulk of suspended sediments (Walling et al. 2000) and is less susceptible to selective processes. Furthermore, an allowance is still typically made for additional particle size differences between sources and sediments (i.e., of the <63  $\mu\text{m}$  grain-size fraction) using a particle size correction factor (e.g., Collins et al. 1997; Walling et al. 1999), and sometimes an organic matter enrichment factor. These correction factors are based on the ratio of specific surface area or organic matter content of sediment and source samples and assumes a linear relationship. These corrections are commonly employed as both particle size and organic matter are known to influence biogeochemical properties. However, such approaches are controversial because little is known about the potential errors associated with the use of correction factors, such that some researchers do not use correction factors (e.g., Martínez-Carreras et al. 2010b; Martínez-Carreras et al. 2010a). Furthermore, some studies overcome the issues of differences in particle size by limiting the analysis to the <10  $\mu\text{m}$  fraction (e.g., Wilkinson et al. 2009). While this approach reduces errors due to particle size differences, it may have limitations in terms of the representativeness of transported sediment.

Russell et al. (2001) used 31 sediment properties within three catchments in the UK and found that there was a large range in specific surface areas (SSA) between the different sources and sediment and concluded that a linear particle size correction factor would be inappropriate. It was demonstrated through a particle size fractionation experiment that the relationship between particle size and the fingerprint properties was not linear or uniform across the different properties or catchments (Table 2.2). The particle size correction factor  $\nu$  was calculated as the slope/intercept of the log-linear relationship between SSA and fingerprint concentration, except in the case of  $^{137}\text{Cs}$  and unsupported  $^{210}\text{Pb}$  where  $\nu$  is equal

to the exponent as the concentration of the fingerprint is entirely particle size dependant (i.e., 0 intercept). The fingerprint properties were corrected by substituting the corresponding value of  $\nu$  in Eq. (1) for geochemical and mineral magnetic properties or Eq. (2) for fallout radionuclides.

$$(1) C_c = \{(1+\nu(\ln S_x))/(1+\nu(\ln S_s))\} C$$

$$(2) C_c = (S_x/S_s)^\nu C$$

where  $C$  is the measured property concentration,  $C_c$  the property concentration corrected for particle size,  $S_x$  is the SSA of suspended sediment collected at location  $x$ , and  $S_s$  is the SSA of the sample to be corrected. As shown in Table 2.2, Russell et al. (2001) found that the fingerprint properties had particle size correction values ( $\nu$ ) ranging between 0.12 and 4.55 and they demonstrated the wide range that could occur across catchments and within a single catchment. For example, within the Smisby catchment particle size exerts a greater influence on Na ( $\nu = 4.55$ ) than Mn ( $\nu = 0.19$ ). The property dependent correction factors are a result of differences in mineralogy and the affinity and selectivity of different ions to particle surfaces between the different size classes. This highlights the limitations and the potential errors associated with using a single correction factor for all property concentrations as it will over-correct for some elements and under-correct for others, which in turn will influence the results obtained from un-mixing models. Despite these findings, few studies have taken this into account and a single correction factor is commonly used for all properties. However, linear particle size correction factors may be useful when applied in studies where there is narrow range in particle size differences between sources and sediment and especially where relationships have previously been established between particle size and fingerprint property. For example, the relationship between  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  (e.g., He and Walling 1996; Bihari and

Dezső 2008) and phosphorus concentration (e.g., Owens and Walling 2002) and particle size has been investigated. Furthermore, there is evidence that a single organic matter correction factor may also be inadequate for the adjustment of geochemical properties. For example, Bakircioglu et al. (2010) found through sequential extractions that the proportion of metals associated with the oxidisable fraction (organic matter) in agricultural soils varied by more than 15% with the organic matter accounting for ~20 % and ~5% of the total Zn and Co content, respectively. However, property specific organic matter corrections have yet to be tested within the sediment fingerprinting technique and there is the potential to over-correct due to the correlation between grain-size and organic matter content. The question remains as to whether there needs to be correction factors to compensate for other properties such as Fe- and Mn-oxides or carbonates as these have also been shown to influence the concentrations of many trace elements (Horowitz 1991), and clearly further work is needed to assess this.

Table 2.2: The particle size correction factor,  $v$ , for the soil properties included in the sediment source models for three river basins in the UK (from Russell et al. 2001, reproduced with permission from Elsevier).

Property	Simisby	Belmont	Jubilee
Al	0.97	0.51	0.51
As	1.79	0.7	0.7
Ca	-	-	-
Cu	1.1	-	-
Fe	0.52	0.42	0.43
K	1.37	0.82	0.82
Mg	0.44	0.3	0.3
Mn	0.19	0.31	0.31
Na	4.55	1.15	1.15
Ni	3.54	-	-
Pb	0.36	0.33	0.51
Sr	1.9	0.65	0.65
Zn	0.66	0.52	0.52
Fe <sub>p</sub>	0.69	0.61	0.61
Mn <sub>p</sub>	0.45	-	-
Al <sub>p</sub>	-	0.12	0.12
Fe <sub>p</sub>	1.37	0.66	0.66
Mnd <sub>d</sub>	0.37	-	-
Al <sub>d</sub>	-	-	-
Fet	1.21	0.65	0.65
Mn <sub>t</sub>	0.41	-	-
Al <sub>t</sub>	-	0.15	0.15
TP	0.81	0.64	0.53
TN	0.84	0.76	0.76
TC	0.58	0.6	0.6
$\chi$ lf	0.73	0.25	0.25
$\chi$ fd	-	-	-
ARM	1.84	0.16	0.16
SIRM	0.85	0.41	0.41
IRM	0.58	0.36	0.36
<sup>137</sup> Cs	0.77	0.51	0.51
Unsupported <sup>210</sup> Pb	0.71	0.68	0.68

The particle size correction factor is derived from the curvilinear relationship between concentration and specific surface area. Particle size exerts a greater influence on the concentration of soil properties with increasing values of  $v$  ( $v = 0$ , no effect of particle size).

Despite research showing that eroded sediments have different physical and biogeochemical properties compared to their source, few sediment fingerprinting studies have fully taken this into account and there is currently a gap in our knowledge. Motha et al. (2002) evaluated the influence of the sediment generation process on fingerprint properties on five different sources by collecting eroded sediments generated under simulated rainfall and comparing it to source materials after accounting for differences in particle size and organic matter content. The results demonstrated that the sediment generation process, after accounting for differences in particle size and organic matter content, had an effect on some geochemical properties for some of the sources (i.e., non-conservative behaviour), had no effect on radiochemical properties and was inconclusive for the mineral magnetism properties. The results from that study were subsequently used to develop corrections for fingerprint conservativeness and were utilized in conjunction with particle size and organic matter corrections to adjust fingerprint properties in a sediment fingerprinting study (Motha et al. 2004). Particle selectivity is governed by a suite of conditions and processes that vary between river basins and it becomes difficult to make generalizations about the effects of erosional processes on particle selectivity. Therefore, it is important to consider the conditions and processes within each basin of interest before samples are collected.

While the development of more realistic correction factors may be an important research need, the misuse of untested correction factors would result in inappropriate manipulation of soil and sediment property data. Better sampling design, including the collection of more representative samples, may be a better approach. The common approach of using soil surface scrapes (approximately 0 – 2 cm) to characterize some sediment sources (e.g., topsoil) may not provide a good representation of the source. Other sampling methods,

including the collection of actively transported sediment from hillslopes during runoff events, are likely to provide a better indication of the properties of sediment coming from a given source.

### **2.5.2 Transformations**

Particle selectivity is likely the main process affecting the non-conservative behaviour of fingerprint properties on the hillslope. However, there are some transformation processes that may play an important role. There will be some losses or translocation of elements through leaching, overland flow and plant uptake. For example, in a recent review, Parsons and Foster (2011) highlighted a number of limitations in using  $^{137}\text{Cs}$  as a tracer in soil erosion studies, and one of the limitations discussed was the non-conservative behaviour of  $^{137}\text{Cs}$  as a tracer. Parsons and Foster (2011) concluded that  $^{137}\text{Cs}$  can be (i) lost through plant uptake and permanently removed by subsequent crop harvesting; (ii) released from recalcitrant sites due to weathering of minerals or the addition of  $\text{NH}_4$  or K; and (iii) leached from the soil column through the decomposition of organic matter or carried away by water soluble organic substances. Similarly, Taylor et al. (2012) characterized the adsorption behaviour of  $^7\text{Be}$  on agricultural soils and assessed its stability under changing environmental conditions. These types of investigations provide critical information on the distribution of fingerprint properties across the landscape and through the soil profile and can provide an assessment of the robustness of fingerprints within the context of the sediment fingerprinting approach (Taylor et al. 2012).

There is also evidence that sediments may become enhanced in concentrations for some properties as they move through the landscape as there will be continual additions of

some elements through atmospheric deposition (e.g., N, S,  $^{210}\text{Pb}$ ). For example, both Owens et al. (2012) and Wilkinson et al. (2009) found that eroded sediment within burnt catchments had higher  $^{210}\text{Pb}_{\text{unsupported}}$  concentrations than that of the sediment sources indicating that sediment received additional  $^{210}\text{Pb}$  fallout during transit. To recognize the importance of transformations, within the context of hillslope processes, it becomes critical to understand the processes that lead to formation of a unique signature. For example, weathering is largely responsible for the distribution of geochemical elements through the soil profile. Because weathering processes operate over longer time-scales than the sediment redistribution process involved it can provide a reliable means to discriminate between surface and subsurface sources. Changes in downstream environmental conditions (e.g., pH, redox potential) are likely to be a greater concern for transformation of sediment properties and the distortion of the fingerprint signal and this is discussed in subsequent sections.

The impact and the relative importance of these transformation processes on the sediment fingerprinting technique are not well understood or quantified and represent another gap in our knowledge (Owens and Xu 2011). In many cases, sediment sources are characterized by collecting soil samples that are 'likely' to erode in that they are from areas strongly connected to the fluvial environment. By measuring the properties of soils 'awaiting delivery' to the aquatic system an effort is made to minimize any changes in fingerprint properties that may occur during transit. However, the location of sampling points can often be subjective and the connectivity can be difficult to detect in areas where the drainage is controlled by subtle features in the landscape. This sampling approach also assumes that areas that are not well connected do not directly contribute to the sediment load. However, this may not be the case during periods of high runoff and flooding (Thompson et al. 2012).

## **2.6 Riparian and wetland processes**

The riparian zone is the interface, or transition zone, between the terrestrial and aquatic environments and is characterized by very distinct gradients in environmental conditions and processes. There are a wide range of types of riparian zones ranging from natural to engineered and intensively managed. In some cases, the movement of sediment and water through riparian zones is circumvented through surface and subsurface drains. While the characteristics of the upland areas will determine the quantity, properties and pathways of sediment being delivered, the riparian zone - through the processes of infiltration, immobilization, sedimentation and dilution - tends to attenuate, buffer, distort and intercept the flow of this material (both dissolved and particulate) to the aquatic environment (Lacas et al. 2005; Owens et al. 2007; McGuire and McDonnell 2010). Because of this, the riparian zone is of particular interest in terms of the effects it is likely to have on the conservative behaviour of sediment and associated fingerprints.

### **2.6.1 Particle selectivity**

Both laboratory and field studies have demonstrated that riparian buffer features are effective at trapping sediments (for a review, see Zhang et al. 2010). Gharabaghi et al. (2006) found that larger particles and aggregates are generally trapped within the first few meters of a buffer strip and finer material was transported further distances. Consequently, this results in the selective enrichment of fine-grained sediments and associated fingerprint properties being exported from the buffer to adjacent water-bodies (Owens et al. 2007). In addition, the efficiency of riparian areas to trap and retain sediment can vary over time. Borin et al. (2005) found that the efficiency of riparian areas varied over the first four years after planting and

Dillaha et al. (1989) demonstrated that the efficiency decreased as the vegetation became inundated with sediment. Currently, it is uncertain as to the extent of the effect that riparian zones have on particle selectivity and, therefore, the particle size distribution and organic matter content of sediments entering surface waterways.

Riparian floodplains buffer the transfer of fluvial sediment between upstream and downstream reaches of a river (Trimble 2010). Floodplains are formed by both lateral and vertical accretion of sediment. As a channel migrates across the valley floor, lateral accretion occurs as sediment is deposited on the inside of meander bend due to the decrease in velocity. Lateral accretion deposits are largely comprised of bed sediment and can account for 60 – 90 % of the total sediment accumulation in a floodplain (Fryirs and Brierley 2012). Vertical accumulation of sediment on floodplain surfaces can occur during periods of flooding when the flow is above bank-full stage and deposition of sediment is promoted by the decrease in depth and consequently the velocity and the transport capacity of the water. Walling and He (1998) found that there was significant spatial variability in sedimentation rates due to local micro-topography and flow patterns and the particle size distribution. However, it was noted that aggregated particles can complicate the relationship between sedimentation rates and particle size due to the higher settling velocities compared to individual discrete particles (Nicholas and Walling 1996; Walling and He 1998). Sediment fingerprinting studies have utilized floodplain deposits to provide information on longer-term (e.g., decadal scale) trends in sediment sources (e.g., Owens et al. 1999). The spatial variability in depositional rates and particle size distributions, and the concentrations of sediment properties (Walling et al. 1998), need to be considered in both sampling protocols and interpretation of the data.

Accumulation of fluvial sediments on floodplains can represent a significant storage

component in the overall sediment budget of a river basin. For example, Walling and Quine (1993) found that during the period between 1986 – 1989 approximately 23% of the total suspended sediment load in the main channel of the River Severn was deposited on the floodplain. Conversely, floodplains contribute sediment through the remobilization of stored sediment by lateral channel migration. While floodplains are a source of sediment in river basins, they do not necessarily represent a unique source as it is comprised of sediment previously derived from upstream sources. An evaluation of sediment collected downstream of floodplain features needs to consider that some of the sediment is being derived from floodplains, which depending on environmental conditions and storage times may be different from the fingerprint properties associated with the original sources. In addition, both the deposition of sediment onto floodplains and the subsequent remobilization through surface or lateral erosion are particle size selective processes and therefore will influence the particle size distribution of sediment being transported through reaches with such features.

Wetlands and dams/reservoirs also act as buffering features within river basins. Like riparian buffer zones, wetlands and reservoirs slow the flow of water resulting in the deposition of sediments and the trapping efficiency is largely related to the geomorphic and hydraulic conditions of these features. O'Green et al. (2010) concluded that constructed and restored wetlands receiving agricultural runoff generally exceed a sediment removal efficiency of 50%. Similarly, research by Teissen et al. (2011) found that small dams in an agricultural river basin were able to retain approximately 70% of the annual sediment load. However, there is little information about the particle size distribution and organic matter content of sediment leaving the wetlands or dams although it would be expected that coarser sediments would be retained and the fine sediment would be exported from these features.

As sediments from riparian buffers, wetlands and dams have often been used to provide information on the sources of sediment within river basins (e.g., Pittam et al. 2008), consideration needs to be given to the representativeness of the sampled sediment. For example, sediments that are deposited on floodplains during periods of high flow may have different characteristics to sediment transported during periods of lower or base flow due to differences in sediment transport capacity. In addition, as these features are likely to influence the characteristics of sediment and fingerprint properties (Walling et al. 1998), the location of these features in relationship to the sediment source and the sampling point are important considerations in interpreting the data it provides. In some cases it may be important to sample up- and downstream of these features to get a more complete picture of any changes in sediment dynamics. A large proportion of the sediment will be stored in these features and the full extent of the contribution of these upstream sources to the channel will not be fully captured at downstream sampling sites. This would result in the relative contribution of the upstream sediment source to the channel being underestimated and this can lead to poor management decision based on the incomplete assessment of sediment sources.

### **2.6.2 Transformations**

Not only are riparian zones and wetlands important features in the landscape for sediment trapping but these features are also known and used to capture and immobilize nutrients and metals; properties that are commonly employed as fingerprints. The majority of nutrient and metal retention is due to sedimentation and the absorption of elements from solution onto both the organic and inorganic sediments, resulting in an enrichment of these

constituents in the riparian/wetland features (e.g., Hoffmann et al. 2009). The anaerobic environmental conditions often found in riparian areas and wetlands can also facilitate the precipitation of minerals including Cd-, Pb- and Zn- sulphides (Du Laing et al. 2010). Plants will also cycle these elements but generally represent a temporary storage, however, under saturated conditions decomposition is retarded and there is a net accumulation of organic matter and associated elements. Some elements including N, C, S and Hg, can be lost to the atmosphere through microbially mediated processes (Vidon et al. 2010). For example, Poe et al. (2003) found that a significant amount (8 - 81 kg N month<sup>-1</sup>) of nitrogen was lost through the process of denitrification in a 5.1 ha constructed wetland receiving agricultural runoff. While the focus of the study by Poe et al. (2003) was not sediment fingerprinting it serves as a good example to highlight the transformations and subsequent loss of a commonly used fingerprint. Similarly, Taylor et al. (2012) suggested that changes in redox conditions in storage zones could result in a reduced <sup>7</sup>Be fingerprint. These transformation processes have implications for the sediment fingerprinting technique because the sediment fingerprint signal passing through buffering features can become distorted leading to errors in the source apportionment if not accounted for. This highlights the importance of assessing the behaviour of each sediment fingerprint property within the context of the environmental conditions that exist within the study river basin.

The complexity of riparian zones and wetlands presents numerous challenges in investigating the influence that landscape buffering features have on the conservative behaviour of sediment and fingerprint properties. Nevertheless, they are important features of the landscape and their effects on sediment properties warrants further investigation and consideration in assessing the behaviour of sediment properties used for sediment

fingerprinting. The extent to which these features will result in significant transformations will be river basin specific and dependent upon a number of environmental conditions.

## **2.7 Aquatic processes**

Fine-grained sediments (<63 $\mu$ m) are often thought to be transported easily and unimpeded through rivers (e.g., wash load). This assumption is one of the main reasons why this type of sediment is used in sediment fingerprinting studies as it is thought to be minimally affected by particle selectivity, making direct comparisons between sources and suspended sediment easier. However, sediment transport within the aquatic environment is episodic as sediments are continually being transported, deposited, stored and re-mobilized. Furthermore, fine-grained sediments are chemically reactive which raises concerns over the role of chemical transformations on the concentration of fingerprint properties as sediment is transported.

### **2.7.1 Sediment dynamics**

There is a shift in particle size distribution towards fine-grained and an enrichment of organic matter as particles move from the steep gradients found in headwater streams towards lower gradients found at the outlet of the river basin. The relationship between particle size and water velocity on the entrainment, transport and deposition (hydrodynamics) of sediments within river channels has been characterized as early as 1935 (e.g., Hjølström, 1935). This is, however, an oversimplification of the processes influencing the movement of sediments downstream as there are other factors that will influence particle size distribution. Aquatic plants including periphyton and macrophytes play a role in storing sediments as they trap suspended sediments by reducing the flow velocity to a point where sediments fall out of

suspension (Petticrew and Kalff 1991); they can also stabilize channel bed sediments making them more resistant to erosion (Wharton et al. 2006; Heppell et al. 2009). The stream morphology including pools, riffles and meanders will also influence the deposition and mobilization of sediments through variations in velocity. Sedimentation of coarser-grained sediment occurs at slope discontinuities along the channel (e.g., when a steep tributary meets a low-gradient trunk channel), reaches with a large decreases in slope with respect to drainage area (i.e., high concavity) and behind points of flow restriction such as culverts, bridges and weirs. These features and structures can cause considerable sedimentation to occur upstream onto floodplains (Fryirs 2013). Consideration needs to be given to the sediment sampling location with respect to these features and structures in terms of the representativeness of the sediment and the interpretation of the data they provide.

Sediments are delivered to the aquatic environment as either primary or aggregate particles but once within this environment can undergo transformations such as flocculation and disaggregation. Flocculation refers to aggregation of living and non-living biological material and mineral particles that can occur within the water column (Droppo et al. 1997). Much of the flocculation within freshwater is due to the presence of extra-cellular polymeric substances which act as a glue binding the mineral grains together (Droppo et al. 1997) and in estuarine and marine environments flocculation increases due to salts modifying the charges on fine-grained particles. For a comparison of the processes of flocculation in different aquatic environments, see Wotton (2007). These flocs have very unique physical properties including a change in the effective particle size, shape, density and porosity as compared to the primary particles from which they are made. This results in changes in the hydrodynamics of particles and an increase in the preferential settling and

storage of fine-grained sediments when hydraulic theory predicts that they should stay in suspension (Droppo 2001). For example, research by Rex and Petticrew (2008), has demonstrated the importance of the flocculation process on the in-stream retention of marine derived nutrients (i.e., salmon decay products) in British Columbia, Canada. The interaction between the organic salmon decay products and inorganic mineral sediment particles, such as silt and clay, produced larger particles, enriched in N, which were preferentially deposited into the gravel bed, thereby increasing the N content of the channel bed sediment. Similarly, research has also demonstrated the importance of flocs in the sequestration of metals in to bed sediments (Plach et al. 2011).

Disaggregation and abrasion are other processes that occur in moving water that can influence both sediment grain-size and particle shape. The literature (e.g., Lamb et al. 2008), has mainly focused on abrasion and breakage through particle collision, and tended to assume that this process is predominantly relevant over long travel distances and in systems with high stream power, suspended sediment concentrations (SSC) and bedload transport capacity; over short (<10 km) distances and low stream power, suspended sediment concentrations and bedload transport capacity, such processes are assumed to be negligible. However, Fig. 2.6, demonstrates the friable nature of sediments entering a small stream in southern Manitoba, Canada and how quickly the sediment grain-size is likely to change during fluvial transport. In situations where abrasion and disaggregation may be significant, limiting the analysis to the <63  $\mu\text{m}$  grain-size fraction and applying typical approaches for accounting for differences in particle size distribution (e.g., correction factors based on the ratio of specific surface area of sediment and source samples) may not be appropriate. For example, Belmont et al. (2007), proposed that the disaggregation of  $^{10}\text{Be}$ -deficient gravels

resulted in the dilution of  $^{10}\text{Be}$  concentration within the sand fraction in a tributary of the Clearwater River, in western Washington, USA.

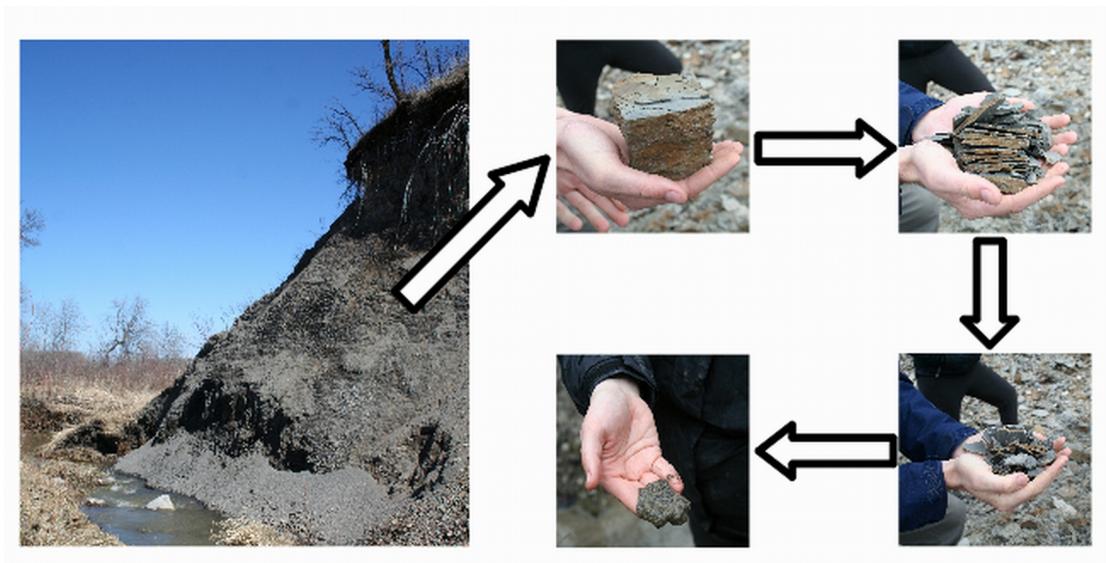


Figure 2.6: Demonstrating the friable nature of shale bedrock entering a small stream in the South Tobacco Creek watershed in southern Manitoba, Canada. Bed rock sample was easily reduced in grain size by manipulation in the hand (April 2011).

Understanding the role of transport processes on the particle size distribution of sediment is important in determining an appropriate sampling techniques and locations as well as interpreting the data they provide. Within sediment fingerprinting there are two types of sediment commonly used; suspended and bed sediments. The effective particle size of transported sediment and the local flow conditions will ultimately determine the partitioning between suspended and bed sediment and is key in understanding the relative composition of each type, in terms of the particle size distribution, of the collected sediment. A combination of sampling approaches may be necessary to get a complete assessment of the sediment dynamics within a river basin. An assessment of the strength of material entering the fluvial environment is also an important consideration as attrition of low-strength, friable material

(e.g., Fig. 2.6) can make it difficult to fingerprint the sources of sediment as the coarse fragments become a source of fine-grained sediment. Multiple sampling locations along the main stem of a channel may help in elucidating the role of attrition on the fingerprint properties of fine-grained sediments.

## **2.7.2 Transformations**

### *2.7.2.1 Transformations during transport*

Although abrasion and disaggregation of particles can influence grain-size and shape, Crockford and Olley (1998) found that they had a substantial effect on the mineral magnetic properties of several sediment sources. This was likely due to removal of iron oxide coatings from particles and their subsequent concentration in smaller grain-size classes. The magnitude of the effect was variable and differed among initial particle sizes and between the different soil sources investigated. Furthermore, Crockford and Olley (1998) concluded that these processes could influence the results from sediment tracing studies, but that it would be difficult to assess the proportion of sediments derived from breakage and abrasion. Conversely, Dyer and Olley (1999) concluded that abrasion and disaggregation (equivalent to a transport distance of 8 km) did not have a significant effect on the concentration of  $^{137}\text{Cs}$  in the fine-grained sediment fraction (<40  $\mu\text{m}$ ).

Sediment moving from the hillslope to a river channel enters into a new environment with very different conditions (e.g., pH and Eh) and it would be expected that sediment would undergo transformations as it begins to reach an equilibrium with its new environment (i.e., Le Châtelier's principle). Most biogeochemical reactions that take place within the aquatic environment occur at phase discontinuities, such as solid-liquid (sediment-water)

interfaces (Stumm and Morgan, 1996). This is one of the reasons that sediments play such a critical role in controlling water chemistry. Furthermore, colloidal, fine-grained and flocculated materials generally have higher specific surface areas and therefore are more chemically reactive (Horowitz 1991). The chemical equilibrium and rates of reaction at the sediment–water interface have been studied in detail in the laboratory and to a lesser extent in natural waters. The acidity and the redox potential are among the most important environmental variables that control the biogeochemical processes occurring at the sediment–water interface (e.g., precipitation). These variables are related to both abiotic (e.g., stream morphology) and biotic (e.g., decomposition) factors.

Biogeochemical processes within aquatic environments can result in significant changes in sediment properties. For example, phosphorus has been used as a fingerprint in sediment fingerprinting studies (Collins et al. 2010b) as it often provides good discrimination between agricultural soils and other land uses due to the higher concentrations of phosphorus as a result of fertilization. However, a review of phosphorus delivery and cycling in rivers by Withers and Jarvie (2008) identified several biogeochemical processes including sorption/desorption, precipitation/dissolution and biological cycling, that can influence the partitioning between particulate and dissolved forms of phosphorus. Owens and Walling (2002) and Withers and Jarvie (2008) also identified that point sources (e.g., sewage treatment works) can deliver significant amounts of dissolved phosphorus which can be subsequently adsorbed by sediments increasing the phosphorus concentration of sediment during transport in river channels from source to sink. The dynamic nature of phosphorus within the aquatic environment highlights the potential non-conservative behaviour of this element and would suggest that it may not be a suitable fingerprint in many situations.

However, phosphorus that is part of the primary mineral structure of the sediment offers good potential as an effective fingerprint as many phosphate minerals (e.g., apatites) have very low solubility.

The organic content of sediment transported within the riverine environments is composed of two components: (i) derived from the original source location (i.e., allochthonous component); and (ii) derived from within the river (i.e., autochthonous component). This may have implications for using organic sediment fingerprints as some of the organic composition of the fluvial sediment reflects processes within the river opposed to the original sediment source location. For example, Rex and Petticrew (2008) found that spawning salmon can contribute significant quantities of salmon-decay products (an autochthonous component) to sediment in rivers in British Columbia, Canada. Other in-channel sources of organic matter include biofilms, algae, invertebrates and periphyton. The addition of autochthonous sources of organic matter to river sediment implies that simple organic matter correction factors which are based mainly on the principle of organic matter selectivity during sediment transport along the hillslope–river continuum should not be used. Sediment fingerprints that use the biological properties of the sediment (e.g.,  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ ; McConnachie and Petticrew 2006) can, however, provide useful information on the relative contributions of allochthonous and autochthonous organic matter sources.

As sediment moves from freshwater through estuarine to marine environments it undergoes changes in pH, salinity and organic matter content which will result in changes in sediment properties as it equilibrates with its new environment (Buckley and Cranston 1991). In an investigation of the dispersal of metals in the LaHave River and Estuary system in Nova Scotia, Canada, Buckley and Cranston (1991) found changes in the distribution of

metals between bed sediment, suspended sediment and the dissolved form between the river, estuary and marine environments. A rapid decrease in dissolved Fe by >100 ppb was found between the river and the estuary environments concurrent with an increase of the same magnitude in the Fe content of the suspended sediment. There was also an increase in the Fe concentration in the bed sediments of the estuary and similar trends were found with Cu, Zn and Pb. The highest concentrations of metals were found in the sediments of the estuary compared to both the river and marine environments demonstrating that the estuary was a significant sink of these metals. The suggested mechanisms for the removal of dissolved metals within the estuary are the coprecipitation with Fe oxyhydroxides, as a result of the increase in the pH from 6.4 to 7.2, and by adsorption onto flocs, as the increase in salinity from 0.8 to 4.0 ppt promoted flocculation (Buckley and Cranston 1991). This study again highlights the non-conservative behaviour of some elements in the context of both chemical transformations and particle size effects and emphasizes the need to assess the effect of changing environmental conditions from the headwaters to the river basin outlet on the behaviour of properties selected as fingerprints.

#### *2.7.2.2 Post-depositional transformations*

Research has demonstrated that radionuclides and metals can become mobilized from stored sediments and subsequently released into the water column. Foster et al. (2006) demonstrated that  $^{137}\text{Cs}$  was mobilized from sediments deposited in a coastal lagoon in southern England. The authors suggest that the mobilization was due to differences in hydrostatic pressure between sea level and standing water levels in the lagoon which forced salt water up through the sediment column resulting in the replacement of  $^{137}\text{Cs}$  by monovalent cations on exchange sites leading to the upward migration and loss of  $^{137}\text{Cs}$  to the

water column. Similarly, Hudson-Edwards et al. (1998) presented evidence of chemical remobilization and the downward translocation of Pb, Cd, Cu and Zn from floodplain deposits in the UK. This was due to several processes including: the breakdown of metal-bearing minerals; shifts in the chemical fractions towards more soluble and reactive phases due to low pH; and accumulation of secondary Fe and Mn oxyhydroxides due to a fluctuating water-table or to the breakdown of organic matter.

Post-depositional change in sediment properties is a serious concern as it may result in sediment no longer being representative of the original source. The change in environmental conditions suggest that some sediment properties may not be suitable as fingerprints in sedimentary environments (Owens et al. 1999). Palmer and Douglas (2008) included a diagenetic component in their un-mixing model as part of an investigation of sediment sources in the North Pine Dam in Australia. As shown in Fig 2.7 the principle component analysis revealed a cluster of points not associated with one of the three sediment sources and further examinations indicated that it could be interpreted as a diagenetic component.

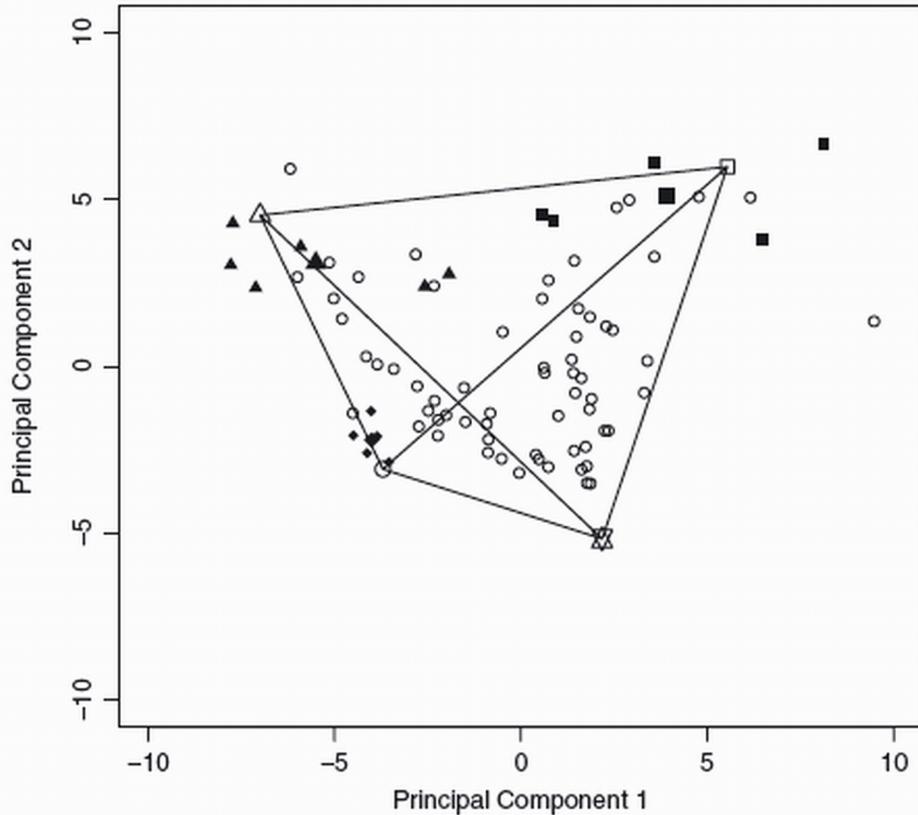


Figure 2.7: Average end members (o,  $\Delta$ ,  $\square$ ) from MCMC runs transformed into principal component space and connected to emphasize the simplex (greenstones  $\blacksquare$ , granites  $\blacktriangle$ , phyllites  $\blacklozenge$ , diagenetic component Y; the larger symbols indicate the mean scores for each group, sediment samples o). From Palmer and Douglas, 2008, reproduced with permission of the Royal Statistical Society.

There are many aquatic processes that can affect sediment properties. While the different aquatic processes and their controlling factors are generally well known there is currently a need to revisit these in terms of the influences they may have on sediment properties (e.g., post-depositional mobilization) within the context of the sediment fingerprinting approach. In particular, there is a need to evaluate each potential fingerprint and establish if it is suitable to be used in that particular river basin.

## 2.8 River basin processes

One of the biggest gaps in our understanding of the movement of sediment at the river basin scale is the ability to identify, quantify and link the different processes discussed in earlier sections. Small scale and tightly constrained experiments provide valuable insight on individual processes but there is little information as to how the different processes identified within each component of the landscape are connected to other landscape components and how they interact. For example, Stone and Walling (1997) found no clear relationship between the properties, including effective and absolute particle size, of sediment being mobilized under simulated rainfall and the properties of the sediment being transported within a stream. This may be due to the fact that the processes that connect the mobilized sediments to the sediments collected within the stream were not identified or fully accounted for. In addition, as the scale of observation increases from plot to river basin there will be new and emergent properties. For example, particle selectivity at plot scales may be dominated by slope and soil properties, at the landscape unit scale topography will exert a larger influence, and at the river basin scale the geomorphological connectivity may be the dominant property influencing particle selectivity. In many cases connectivity may be controlled by very subtle features in the landscape that are difficult to detect.

Sediment does not move through watersheds in a smooth and continuous conveyor belt-like fashion but in-stream suspended sediment samples are the end result of many different intermediary processes that occur during the sediment transport continuum from the upland areas to the point of collection (Burt and Allison 2010). The discontinuities (points of storage) in sediment transport are caused by various features of the landscape, which, as

suggested by Fryirs (2013), can be broadly classified as buffers, barriers and blankets. The effective time scales for the different storage components range from event-based (e.g., fines stored in intergravel pores) to thousands of years (e.g., floodplain deposits) (Fryirs 2013). The effective storage times can have a large influence on sediment properties and have raised questions as to which point these stored sediments represent a new and unique source of sediment. For example, Belmont et al. (2011) were able to differentiate between legacy and contemporary topsoil-derived sediment stored in floodplains by utilizing the differences in the half-life of  $^{10}\text{Be}$  (half-life of  $1.36 \times 10^6$  years) and  $^{210}\text{Pb}$  (half-life of 22.3 years). Due to the long storage time (100 - 1000 years) and the relative short half-life of  $^{210}\text{Pb}$ , the legacy sediments were depleted in  $^{210}\text{Pb}$  whereas the change in  $^{10}\text{Be}$  concentration was negligible over that time scale.

In a recent article, Parsons (2012) highlighted the short-comings of use of storage terms in catchment sediment budgets suggesting that it is a poor substitute for a thorough understanding of the transit times (velocity) of sediments. The transit time of sediments through a river basin will vary depending on a number of river basin characteristics including the size of the catchment, slope and climate. Sediment transit time is an important aspect to consider when evaluating the assumption of sediment and fingerprint property conservativeness. The longer the transit time, the less likely the sediment will still be representative of its original source which may lead to erroneous results in determining the relative contribution of sediment sources. Researchers have used fallout radionuclides including  $^7\text{Be}$ ,  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$ , to determine the transit time of sediment at a variety of river basin scales and the residence times for a variety of sediment storage features. On one end of the spectrum, Wallbrink et al. (1998) estimated an average transit time of  $10 \pm 5$  years for

sediments being transported in a large (13,500 km<sup>2</sup>) catchment in New South Wales, Australia, however, there was evidence that some of the material had transit times on the order of weeks to months. On the opposite end of the spectrum, Bonniwell et al. (1999) found the transit times of sediment in a mountainous catchment (389 km<sup>2</sup>) in central Idaho to be in the range of 1.6 days in the headwaters during the rising limb of the hydrograph (snowmelt) to 130 days near the outlet during the falling limb of the hydrograph (midsummer). Even storage within the channel can have a significant influence on sediment transit times. For example, Gartner et al. (2012) found fine-grained sediment infiltrating into the bed had residence times ranging from 4 to >300 days in unregulated rivers in east-central Vermont, USA. Similarly, Skalak and Pizzuto (2010) found that the residence times of fine-grained sediments trapped behind large woody debris ranged between 1 and 60 years with an average residence time of 1.75 years. This research demonstrates there is a wide range in sediment transit times.

The approximate residence times of larger and longer-term sediment storage features in river basins can be estimated through a variety of means. Historical records can provide information as the timing of construction and decommissioning of structures including reservoirs and other flood control structures that retain sediment. Aerial photography and other survey techniques can be used to estimate changes of stored sediment over time (e.g., Brasington et al. 2003). Channel patterns and migration rates can be used to constrain floodplain residence times (e.g., Beechie et al. 2006). It is important to have good understanding of sediment transit and residence times when evaluating the assumption of sediment and fingerprint property conservativeness, as many biogeochemical transformations are slow processes (Fig. 2.5) and, therefore, changes in environmental conditions coupled

with long residence times can result in significant changes in sediment properties. This suggests that in larger river basins with numerous storage elements, and thus long sediment residence times, determining the sources of contemporary transported sediment using sediment fingerprinting may not be suitable.

## **2.9 Implications for sediment fingerprinting**

The non-conservative behaviour of sediment properties has significant implications for the sediment fingerprinting technique. Table 2.3 provides a summary of the different factors that can result in the non-conservative behaviour of sediment properties. The performance and reliability of the sediment fingerprinting can be greatly improved if the concerns surrounding the non-conservative behaviour of sediment properties are addressed. Research should be directed at lifting the lid on the black-box (Fig. 2.3) of the sediment fingerprinting technique and by incorporating the processes that link the inputs (sediment sources) to the output (collected sediment). There are three main research priorities identified that will help to address these concerns: (1) accounting for the fate of sediment and fingerprint properties; (2) fingerprint selection processes; and (3) assessment of limitations and uncertainty.

Table 2.3: Factors affecting sediment property conservativeness.

<b>Factor</b>	<b>Implication</b>
<b>Physical</b>	
Particle selectivity	Difficult to correct for differences in particle size and organic matter content between source and sediment
Aggregation/flocculation	Changes in hydrodynamic properties
Abrasion/disaggregation	Changes in particle size distribution
<b>Biochemical</b>	
Immobilization/mineralization	Temporary storage of geochemical tracers Loss or overprinting of organic tracers
<b>Geochemical</b>	
Adsorption/desorption	Changes in the sediment – water partitioning of geochemical elements
Dissolution/precipitation	Minerals have varying degrees of solubility
Oxidation/reduction	Changes in the mobility of geochemical elements
Radioactive decay/fallout	Radionuclide activity concentration can change during transport

### 2.9.1 Accounting for the fate of sediment and fingerprint properties

Accounting for changes in sediment properties that occur as it moves through the river basin is an important step in the sediment fingerprinting technique that has received insufficient attention to date. Table 2.4 shows the wide range of different approaches that have been used in dealing with the issues surrounding the non-conservative behaviour of sediment properties. The most common approaches include particle size corrections, organic matter content corrections and limiting the analysis to a particular sediment size fraction. There is no clear relationship between the approaches used and the scale of investigation, although one would expect to see a great deal more transformations as the size of river basin moves from small (<10 km<sup>2</sup>) to local (10 – 100 km<sup>2</sup>) to regional (>100 km<sup>2</sup>) scales. Furthermore, the values for these correction factors are rarely given in the literature, which makes the interpretation of the uncertainty associated with the methodology difficult to assess. There are also several cases in which there are other considerations given to the non-

conservative behaviour of sediment properties. Table 2.4 highlights how problematic it is to use the literature for deciding which approach or methodology is most appropriate to follow.

Despite our increased understanding of the various physical and biogeochemical processes that occur within landscapes, there exists a need to integrate this information and produce process- or empirical-based corrections to account for changes in sediment properties. The ratio of the specific surface area or organic matter content of sediment samples to the average values for each source (enrichment ratio) are commonly used as correction factors to account for changes in the particle size distribution, and organic matter content (Owens et al. 2000). This method of correction is a simplification of the process of particle selectivity and can result in the incorrect adjustment of fingerprint values. In addition, Russell et al. (2001) demonstrated that the particle size correction factor is not uniform across the different geochemical properties or between catchments (Table 2.2) and there is evidence that a single organic matter correction factor may also be inadequate for the adjustment of fingerprint values, especially as river sediment is composed of both allochthonous and autochthonous organic components. Further research is needed to better characterize the influence of both particle size distribution and organic matter content on sediment fingerprints.

This review has identified many different transformation processes that can change the physical and biogeochemical properties of sediment throughout the sediment transport continuum. Currently, these transformation processes are generally not included despite the potential for a distortion in the fingerprint signal. Davis and Fox (2009) have suggested that there is a need to develop and include process-based corrections, including the modelling of biodegradation of organic fingerprints and chemical modelling to account for the

equilibrating of sediment as it moves from the terrestrial to the aquatic environment. It is also essential to account for the effects of continued radionuclide fallout and decay on the radio-chemical properties of sediment as it moves through the environment.

The challenge remains to develop practical predictive models for large areas (e.g., river basin) over longer time-scales (e.g., seasonal), and not just for a particle at a given location and moment in time. The aim should be to accurately predict changes in sediment properties from the fewest, most readily and inexpensive variables. This may include identifying and ranking the relative importance and interactions of processes and environmental factors that influence the conservative behaviour of sediment fingerprints. These corrections will need to be site specific as the major factors (e.g., soils, vegetation, hydrology) regulating sediment dynamics will vary between river basins.

Table 2.4: Common approaches in dealing with issues of the conservative behaviour of sediment properties.

Particle size correction	Organic matter correction	Size analyzed ( $\mu\text{m}$ )	Other considerations	Correction values provided	Watershed size ( $\text{km}^2$ )	References
N	N	<63		NA	4.4	Martínez-Carreras et al. 2010b
N	N	<63		NA	985	Rahaman et al. 2010
N	N	<63	Conservativeness of tracer properties were assessed experimentally	NA	22	Poulenard et al. 2012
Y	N	<63		Y	1.36	Smith et al. 2011
Y	N	<63	Tracer specific particle size corrections*	Y	1.5 – 3.6	Russell et al. 2001
Y	N	<63		N	3315 – 818	Walling et al. 1999
Y	Y	<63		N	19 – 100	Collins et al. 2010b
Y	Y	<63		N	214	Collins et al. 2012
Y	N	<63	Excluded elements being discharged from point sources in solution	N	1932	Carter et al. 2003
N	N	<10	Corrected for natural decay of $^{137}\text{Cs}$ and $^{210}\text{Pb}_{\text{xs}}$	NA	17 – 629	Wilkinson et al. 2009
N	Y	<2, 2–20 20–40 40–63**	Tracer conservative correction factor (empirically-based)	N – OM corr Y – TC corr NA – PS corr	11.1	Motha et al. 2004
Y	N	<2000	Used eroded material collected on hillslope plots as source material	N	0.05	Fukuyama et al. 2010
N	N	<2000	Excluded non-conservative elements	NA	189	Mukundan et al. 2010
N	N	<2000	Excluded gypsum due its rapid dissolution	NA	907	Evrard et al. 2011
N	N	bulk***	Included a diagenetic component in the end member analysis	NA	347	Palmer and Douglas 2008

Y = yes

N = no

NA = not applicable

OM corr = organic matter correction

TC corr = tracer conservativeness correction

PS corr = particle size correction

\*See Table 2.2 for the tracer specific particle size correction factor values

\*\*Size fractionation of sediment was used in place of particle size correction factors

\*\*\*Samples contained < 5% sand

## 2.9.2 Fingerprint selection process

While it may be difficult to develop procedures to account for the biogeochemical transformations given the complexity of a river basin, focusing on selecting fingerprints that are less likely to be subject to transformations might be a more practical approach to deal with this issue. However, there are no clear guidelines in place for the selection of fingerprint properties for use in the sediment fingerprinting technique. Sediment fingerprints, especially geochemical properties, are often selected on the basis of their ability to statistically differentiate between multiple sediment sources with little discussion surrounding how the properties selected behave in the environment. An approach to determining sediment sources that is dominated by statistical tests without due regard for sediment behaviour, that is used by some researchers, may not always be the most appropriate method as some elements (e.g., Ti, Al, Li) are known to behave more conservatively (Horowitz 1991) and other elements (e.g., nutrients) tend to be more mobile and perhaps should be excluded from fingerprinting studies. Differences in geochemistry that are related to the primary mineral structure (inert fraction, see Fig. 2.5) of the sediment may provide a more robust fingerprint as it is less subject to biogeochemical transformations. There is a need to develop a framework to guide the selection of sediment properties that would be suitable to use for a given river basin. River basin variables including erosional processes, depositional environment, water chemistry, sediment transit times, size of river basin, presence of buffering features, climate and hydrology need to be taken into consideration when selecting sediment properties as fingerprints as all of these will influence the conservative behaviour of sediment properties. Selection of sediment properties best suited for the environment in which they are being used

will result in increased confidence in the sediment source apportionment results.

### **2.9.3 Assessment of limitations and uncertainty**

Multiple lines of evidence can decrease the uncertainty of source apportionment results from sediment fingerprinting. There is a wide range of techniques that can be combined with sediment fingerprinting to help constrain and support sediment source apportionment results, including field observations and survey, direct tracing, aerial photography and written historical records. For example, Collins et al. (2013) combined geochemical fingerprinting with particle tracking using the application of fluorescent-magnetic grains to assess the sources of sediment in the River Glaven basin (115 km<sup>2</sup>) in eastern England. The application of artificial tracers was to provide preliminary sub-catchment scale information on sediment loss from key components of the landscape. Similarly, Pittman et al. (2008) used the sediment fingerprint technique in conjunction with historical documentary evidence of land use to identify and evaluate the relative significance of sources of sediments collected from Aqualate Mere, a shallow lake in Staffordshire, UK. Navratil et al. (2012) used a similar approach using sediment cores from a mountainous catchment (905 km<sup>2</sup>) in the French Alps. Belmont et al. (2011) assessed the sources of sediment in the Le Sueur watershed (2880 km<sup>2</sup>), a tributary of the Minnesota River, by combining sediment fingerprinting and a suite of geomorphic change detection techniques including aerial lidar analysis, repeated terrestrial lidar scans, radiocarbon and optically stimulated luminescence dating, air photo analysis, field surveys, and water and sediment gauging with a sediment budget for the watershed.

Recent advancements in statistical un-mixing models (e.g., the use of Markov Chain

Monte Carlo algorithms) have produced results with very small margins of error (in some cases  $\pm 1\%$ ) surrounding estimates of the relative contribution of individual sediment sources. While these advancements have been important in addressing concerns over analytical errors associated with the statistical technique, caution needs to be taken in interpreting the results. The small margins of error do not include the uncertainty associated with the sampling error, or the assumptions surrounding the conservative behaviour of sediment properties. There are also issues surrounding the reporting of pertinent information including information on the environmental conditions of the river basin, data on the primary fingerprint signature of the source material and sediments, the process by which fingerprints were selected and the methodology used in source apportionment. Without this information it becomes difficult to clearly assess the research and put the results in the appropriate context. There is a need to be more forthcoming in discussing limitations of the sediment fingerprinting approach. This will allow the user of the information to better assess the uncertainty surrounding the results as it is an important part of any subsequent management or mitigation decision-making process.

## **2.10 Conclusions**

This review identifies numerous processes that drive particle size and organic matter selectivity and biological, geochemical and physical transformations from particle ( $\mu\text{m}$ ) to river basin (km) scales. Understanding and accounting for these processes is complex due to the high spatial and temporal variability and this limits the ability to reliably link sediments back to their sources. While the development of methods to account for changes in sediment properties (e.g., particle size correction factors) remains a significant research challenge, there are several ways in which these issues can be addressed including: (1) consideration of

river basin characteristics when selecting sampling locations and when interpreting the data; (2) better characterization of sediment sources through improved sampling techniques and design; (3) improved fingerprint selection including consideration of how sediment fingerprints have developed and how robust they are within the environment; (4) the inclusion of multiple lines of evidence to constrain apportionment estimates; (5) better reporting of methodology and fingerprint property data for sources and sediment; and (6) a clear assessment of the sources of error and limitations of the sediment fingerprinting study.

Sediment fingerprinting has the potential to be an effective management tool to address sediment pollution. However, Mukundan et al. (2012) stressed that in order for it to move from a research tool to a management tool there needs to be streamlining of the sediment fingerprinting technique and the establishment of standardized procedures. An important part of the process of moving the sediment fingerprinting technique from a research to management tool will be to have better accounting for changes in sediment properties, improved fingerprint selection criteria, and a clear assessment of the limitations of the techniques. These developments will improve the robustness and the utility of the sediment fingerprinting approach. However, the scientific community needs to find a balance where the sediment fingerprinting approach provides reliable information while at the same time remaining a cost- and time-effective tool for river basin management. For this, the approach also needs to be relatively simple in concept (i.e., easy to understand) and all the methodological steps need to be clear and concise (i.e., easy to understand). This will ultimately lead to better tools for determining how anthropogenic activities are affecting sediments dynamics and to the development of better management practices and improved soil and water quality.

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### **3 The role of soil surface properties on the particle size and carbon selectivity of interrill erosion in agricultural landscapes**

#### **3.1 Abstract**

The selective nature of interrill erosion – the preferential mobilization and transport of soil particles – can lead to the enrichment of fine-grained soil particles ( $< 63 \mu\text{m}$ ) and organic carbon (OC) within the mobilized soil. This study investigated the effects of slope gradient, vegetative cover, soil moisture content, texture and organic matter content, as well as their interactions on soil loss, particle size distribution and organic carbon content of soil mobilized under simulated rainfall within two contrasting agricultural regions in Canada. Overall, it was found that the eroded material was enriched in both fine-grained and carbon-rich particles relative to the source soil. It was demonstrated that dispersing and sieving both the source soil and the mobilized soil to  $< 63 \mu\text{m}$  (i.e., removal of sand and large particulate organic matter) reduced the relative enrichment of both fine-grained soil particles and OC, which would allow for a more direct comparison of physical and biogeochemical properties between the soil and mobilized soil. Furthermore, it was demonstrated that while the soil loss and the degree of enrichment were negatively correlated, there were differences in which soil surface properties had a significant effect in determining soil loss and the selectivity of both fine-grained and organic-rich soil particles and how these surface properties interacted. This suggests that while soil loss may be a good predictor of the degree of enrichment, the factors that control these two processes are different, which is important in understanding the process of selectivity. It was also shown that the OC content of both the source and mobilized soil

was positively correlated to the degree of soil aggregation in addition to the silt and clay content.

### **3.2 Introduction**

Soils are important natural resource that are depended upon for the majority of the global food and fibre production for human consumption and use. However, the growing global population has decreased the per capita arable land area and the productivity of this land is being diminished by degradation (Foley et al. 2005; Lal 2006; Pimentel 2006). One of the main causes of land degradation is soil erosion by water, wind and tillage (Lal 2006; Montanarella et al. 2016). Soil erosion reduces crop yields through the loss of organic- and nutrient-rich topsoil. Furthermore, the sediment produced by soil erosion, when delivered to surface waterways, can result in the degradation in water quality through increased turbidity and nutrient loading (Bilotta and Brazier 2008). In an effort to address these issues there has been a tremendous amount of research over the past century investigating the process of interrill erosion and its controlling factors (Dotterweich 2013).

The rate of interrill erosion is often modelled as a function of the combined effects of the inherent erodibility of the soil, slope and rainfall intensity (Elliot et al. 1987). Adjustment factors are often used to account for different site conditions, including canopy cover, ground cover, and sealing and crusting (Alberts et al. 1995). In contrast, there has been less research on the effects of these factors on the physical and biogeochemical properties of the mobilized, transported and deposited material despite the fact that soil erosion has been identified as a selective process in terms of both particle size and organic matter content (Ballantine et al. 2008; Chartier et al. 2013). For example, selectivity occurs when mobilized

soil (eroded material) has a finer grain-size distribution and a higher organic matter content as compared to the source material (soil) as the smaller and less dense particles are preferentially mobilized and transported. However, the influence of properties at the soil surface (e.g., ground cover, slope gradient and soil texture) on the preferential mobilization of soil particles has not been fully evaluated.

The preferential mobilization and transport of organic-rich soil particles are important processes as organic carbon (OC) has a large impact on soil physical (e.g., water retention), chemical (e.g., nutrient retention), biological (e.g., biodiversity) and ecological (e.g., carbon sequestration) qualities (Lal 2014). Interrill erosion and more generally, soil erosion, is an important, albeit a poorly understood, component of the global carbon (C) cycle (Van Oost et al. 2007). The erosion of OC results in the redistribution of the total OC pool within the landscape at the field-scale, both laterally and vertically, resulting in a decline in OC in eroding areas and a corresponding increase in OC in depositional areas (Van Oost et al. 2007). Fine-grained and organic-rich soil particles can act as a vector for nutrients and other contaminants (Quinton and Catt 2007; Oliver et al. 2007; Zheng et al. 2012; Yang et al. 2013). The higher concentrations of nutrients within the fine-grained and organic-rich fraction coupled with their preferential mobilization and transport results in a lateral and vertical redistribution of nutrients across the landscape increasing the environmental significance of erosion (Zhang et al. 2014). Soil erosion can also have an influence on other soil physical and chemical properties including pH, stone content, carbonate concentration and bulk density (Li et al. 2007). The net effect of soil erosion processes on the C balance and nutrient distribution depends on the scale of investigation which can range from plot- to field- to watershed-scale. Synthesizing information about the processes that regulate C and

nutrient dynamics at different spatial scales will help clarify the role soil erosion has on the global C cycle. Information on how properties of the soil surface determine the organic matter selectivity of soil erosion will also provide additional predictive capabilities regarding C and nutrient dynamics in agricultural systems.

Particle size and organic matter selectivity and the resultant enrichment within the eroded material is primarily driven by the energy regime of the raindrop impacts and overland flow, with higher energy erosional processes being less selective (Proffitt and Rose 1991; Issa et al. 2006; Schiettecatte et al. 2008; Armstrong et al. 2011). However, soil surface properties can also influence the process of selectivity. The influence of a range of soil surface properties including texture, organic matter content, vegetative cover and slope gradient on both particle size distribution and organic matter composition of eroded material have been investigated (Quinton et al. 2001; Armstrong et al. 2011; Defersha and Melesse 2012; Shi et al. 2013; Chartier et al. 2013). Information on the selectivity of interrill erosion processes is needed as input for watershed management tools including sediment budgets and the assessment of geomorphic connectivity, as fine-grained and organic-rich particles can have different patterns of erosion, transport and deposition (Stone and Walling 1997; Di Stefano and Ferro 2002). Another important watershed management tool that is influenced by particle selectivity is sediment fingerprinting (Koiter et al. 2013). The sediment fingerprinting technique uses the physical or biogeochemical properties of soils as tracers, and is employed to identify sediment sources and estimate their contributions to the total sediment load in streams (Owens et al. 2016). However, many of the properties commonly used as tracers (e.g., trace metal concentrations and fallout radionuclide activities) are sensitive to changes in particle size distribution and organic matter content. Knowledge

regarding the process of selectivity is needed to account for these changes so that a more direct comparison between source soils and sediment collected down-stream can be made (Koiter et al. 2013; Smith and Blake 2014).

The purpose of this research was to identify the significance of a range of naturally occurring soil surface properties in agricultural landscapes and their interactions on interrill erosion in terms of the enrichment of fine-grained particles and SOC. The soil surface properties examined include: vegetative cover, slope gradient, silt content, soil organic matter content and antecedent soil moisture content. The objectives of this research were: (1) to assess the enrichment of fine-grained particles ( $< 63 \mu\text{m}$ ) and SOC of mobilized soil with respect to their source soils; (2) to identify how properties of the soil surface influence soil loss and the enrichment of fine-grained particles and SOC in the mobilized soil; (3) to investigate the relation between SOC and particle size distribution (primary and aggregated) in both the source soil and the mobilized soil; and (4) to characterize the implications of the selectivity of interrill erosion for C, nutrient and geochemical fluxes.

### **3.3 Materials and methods**

#### **3.3.1 Site descriptions**

Two contrasting agricultural regions in Canada were used to investigate particle size and organic matter selectivity of soil erosion under a range of soil surface properties (e.g., vegetative cover and texture). The first region was the South Tobacco Creek (STC) watershed, which is situated in south-central Manitoba (Fig. 3.1). The STC watershed is 75 km<sup>2</sup> and is predominately agriculture with the majority of land under annual crops including wheat, canola, flax and barley. The STC watershed extends across the Manitoba Escarpment;

its upper reaches lie in undulating glacial tills and its lower reaches lie in the lacustrine sediments of glacial Lake Agassiz (Agriculture and Agri-Food Canada 2011). The soils above the escarpment are Dark Grey Chernozems with a clay-loam texture, below the escarpment the soils are Black Chernozems with a clay texture and the valley walls soils are Regosols (Hope et al. 2002). The second region was the Beaver Valley (BV) watershed which is situated in the Fraser Plateau, located in central British Columbia (Fig. 3.1). The BV watershed is predominately forested with pasture and forage land uses in the flatter valley bottom sections. This study targeted a 10 km stretch of agricultural land in the valley bottom where the soils are Dystric Brunisols and Orthic Regosols, with a sandy loam texture with 5 – 10 % coarse fragments (> 2 mm) (Lord 1984).

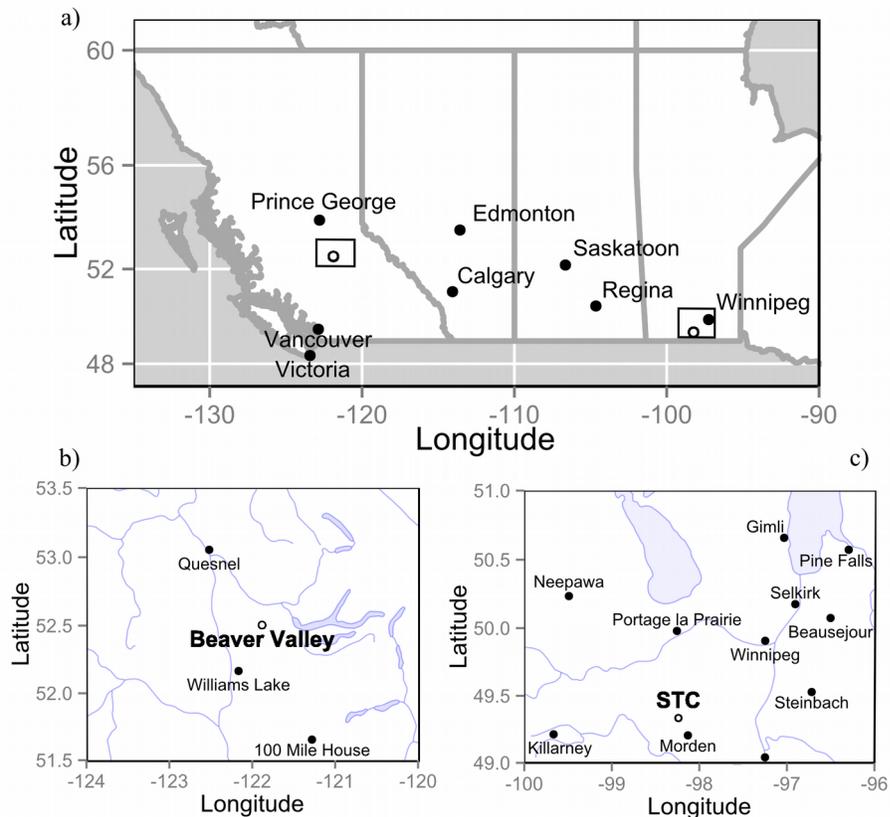


Figure 3.1: Maps showing a) the provinces of south-western Canada and the locations (inset boxes) of the two sampling sites: b) Beaver Valley (BV) watershed and c) South Tobacco Creek (STC) watershed.

In each watershed, a series of hillslopes within areas of active agricultural production were identified as being degraded and/or having a high potential for soil erosion and a moderate to high degree of connectivity to surface waterways. The assessment of soil degradation was based primarily on vegetative cover (i.e., high grazing pressures or intensive crop production) and compaction and/or soil disturbance (i.e., unmetalled farm vehicle and cattle tracks, and/or cultivation). This approach to site selection was taken as studies have shown that these areas can contribute a disproportionate amount of soil loss given their areal extent and are, therefore, of considerable interest within the context of the sediment cascade (Pietola et al. 2005; Raper 2005; Collins et al. 2010). Within the STC watershed five

hillslopes were identified that spanned the different physiographic regions of the watershed: above, within and below the Manitoba Escarpment. The hillslopes identified above and below the escarpment were cultivated fields and the hillslope within the escarpment was a forested site containing a cattle trail going down a steep valley wall towards the creek. Similarly, in the BV watershed a total of six hillslopes were identified with the disturbance ranging from winter feeding sites, areas with high grazing pressure and cattle and vehicle paths.

On each hillslope, a transect was established extending from the hilltop down to either the field or riparian edge. On each transect, rainfall simulation runoff plots were established on the upper, mid and lower slope positions. Different hillslope positions were used as this exploited the natural and contemporary patterns of soil erosion and served to expand the quantitative range of soil and surface properties investigated. Furthermore, each runoff plot was investigated on two or three occasions to obtain a broader range of soil and surface properties, particularly a broader range in antecedent soil moisture content and vegetative cover. The research sites within the BV watershed were investigated on three occasions: spring (June), summer (August) and autumn (October) of 2012 for a total of 60 rainfall simulations. However, the sites within the STC watershed were only investigated on two occasions: spring (June – prior to crop emergence) and autumn (October – post-harvest) of 2013 as the tall and dense crops created unsuitable conditions for the rainfall simulation experiment during the summer growing season for a total of 30 rainfall simulations. The runoff plots were not located in the exact same location between seasonal site visits due to soil disturbance during the rainfall simulations, but all plots for a given transect and slope position were located within 2 – 3 m of each other. By locating the runoff plots on different

hillslope positions, across different transects and in two distinctive agricultural locations, this rainfall simulator experiment reflects some of the spatial variability at the soil catena, landscape and regional scales. In addition, the measurements made during different seasons allowed for some of the temporal variability to be accounted for (e.g., vegetation cover, soil moisture, aggregate stability). For example, Stone and Walling (1997) found that the relative proportion of different grain-size fractions of sediment generated under simulated rainfall changed over the course of the year. Capturing this spatial and temporal variability allows generalizations to be developed about the significance of the various properties of the soil surface and their interactions in determining soil loss and the enrichment of fine-grained soil particles and SOC.

### **3.3.2 Rainfall simulator**

A field-portable rainfall simulator, based on the design of Clarke and Walsh (2007), was used to generate runoff at the field sites described above. Briefly, this simulator requires no power, is gravity fed and is capable of producing rainfall intensities between 50 - 200 mm hr<sup>-1</sup> with a drop size distribution and kinetic energies similar to natural rainfall (Clarke and Walsh 2007). For an intensity of 200 mm hr<sup>-1</sup> Clark and Walsh (2007) reported a median drop size of 4.15 mm and a total storm kinetic energy of 727 J m<sup>-2</sup> (over a 20-minute storm event). Due to the small footprint of the rainfall simulator used in this study, the area of the runoff plots was limited to 0.16 m<sup>2</sup>. The small runoff plot dimensions limited this study to the investigation of then selectivity of interrill or sheet erosion processes as the short slope length limited the formation of rills. The plot boundaries were constructed from stainless steel plates (40 cm long and 15 cm tall) and the plates were pushed 5 – 10 cm into the soil; care was

taken to minimize soil disturbance and to ensure a water tight seal with the soil during the installation process. On the down-slope edge a shallow triangular gutter collected the runoff into 1 L polyethylene bottles, similar to the design reported in Cao et al. (2015). Deionized water was used in the rainfall simulations to ensure consistency across all simulations. A rainfall intensity of 200 mm hr<sup>-1</sup> was used; while this intensity is high, it can provide information on the characteristics of the soil mobilized under rainfall and, importantly, within the requirements of this research, provide an adequate sample mass (> 2 g) for analyses within a reasonable time frame. The rainfall simulation was run until there was 40 min of continuous runoff and the runoff was divided into two separate samples, again to ensure adequate sample mass for analysis. Within the literature, the reported time to reach a steady-state condition using rainfall simulators ranges from < 5 min (e.g., Asadi et al. 2007) to > 20 min (e.g., Armstrong et al. 2011) and this variability is related to differences in the applied rainfall rate and soil surface properties (e.g., texture, antecedent moisture, slope) (Proffitt et al. 1991). Within this study, the first 20 min of runoff (0 – 20 min) is likely more representative of easily erodible material while the second 20 min (20 – 40 min) is more representative of erosion under steady-state conditions. This sampling design is similar to the approach of Jin et al. (2009) where rainfall rates of 65 – 105 mm hr<sup>-1</sup> were applied over a 0.27 m<sup>2</sup> plot and runoff samples were collected in 15 min segments over a 90 min period. Due to low samples masses, Jin et al. (2009) aggregated the samples into two discreet samples (0 – 60 and 60 – 90 min) to allow for nutrient, SOC and particle size analysis. Despite the runoff sample aggregation Jin et al. (2009) found an effect of sampling period on the enrichment of SOC.

Source soil samples (0 – 2 cm) were collected immediately outside the plot

boundaries prior to the start of the rainfall simulation in order to characterize the antecedent soil moisture content, SOC content and particle size distribution. The percent vegetative cover of the runoff plot was measured using digital photography and ImageJ image analysis software (Schneider et al. 2012). Photographs were taken with a Fujifilm FinePix Z33WP 10 mega pixel camera held parallel to, and approximately 1.5 m from the surface. Each digital image covered the entire plot area (0.16 m<sup>2</sup>) and was analyzed for vegetative cover by contrasting the difference in light-coloured vegetation with the dark-coloured soil (Koiter and Lobb 2008). The gradient of the soil surface was measured using a clinometer (Jordán and Martínez-Zavala 2008). A summary of the soil surface properties for both watersheds can be found in Table 3.1.

Table 3.1: Summary of soil surface (0 – 2 cm) characteristics for both the Beaver Valley and South Tobacco Creek watersheds.

	Clay* (%)	Silt* (%)	Sand (%)	> 2mm (%)	Veg. cover (%)	Soil moisture (%)	Gradient (%)	Soil org. carbon (%)	Soil org. matter (%)	Particulate org. matter (%)
Beaver Valley watershed										
Min.	4.5	22.4	17.6	2.1	4.1	3.2	1.7	2.8	6.4	3.3
1 <sup>st</sup> Quartile	6.2	33.3	44.3	4.6	38.7	13.8	5.2	5.0	10.8	5.3
Median	8.4	42.9	47.5	7.7	68.9	31.9	8.7	6.3	12.9	7.2
Mean	8.6	41.3	50.1	12.3	62.8	35.2	8.9	6.1	12.9	10.2
3 <sup>rd</sup> Quartile	10.0	46.1	60.3	16.2	86.7	50.7	10.5	6.8	14.1	12.7
Max.	17.4	67.2	72.8	40.6	100.0	110.7	21.3	9.6	19.5	33.8
South Tobacco Creek watershed										
Min.	10.9	47.0	9.3	0.0	2.0	12.7	1.7	1.2	3.6	0.7
1 <sup>st</sup> Quartile	11.9	57.8	15.8	0.1	9.5	23.0	1.7	2.8	6.4	1.2
Median	14.7	61.3	24.0	3.3	20.3	31.3	5.2	3.5	8.4	1.5
Mean	15.7	61.1	23.3	5.2	34.0	32.0	11.7	3.3	8.4	2.1
3 <sup>rd</sup> Quartile	19.7	65.0	31.1	7.9	51.0	38.2	14.5	4.2	10.7	1.9
Max.	22.6	75.4	34.9	24.4	98.0	61.8	51.0	5.1	12.8	17.4
Overall										
Min.	4.5	22.4	9.3	0.0	2.0	3.2	1.7	1.2	3.6	0.7
1 <sup>st</sup> Quartile	7.2	39.9	27.8	3.5	19.5	20.6	5.2	3.9	9.1	2.0
Median	10.0	46.2	44.2	6.1	55.8	31.7	8.7	5.1	11.3	5.4
Mean	10.9	47.9	41.2	9.9	53.2	34.1	9.8	5.2	11.4	7.5
3 <sup>rd</sup> Quartile	13.5	58.8	53.0	12.9	83.5	45.3	10.5	6.4	13.5	9.0
Max.	22.6	75.4	72.8	40.6	100.0	110.7	51.0	9.6	19.5	33.8

\* Measured using laser diffraction which tends to underestimate clay and over estimate silt proportions relative to more common sedimentation techniques

### 3.3.3 Laboratory analysis

#### 3.3.3.1 Source soil and mobilized soil

A process flow diagram describing the sample preparation, subsampling and the analysis for both the source soil and mobilized soil is found in Fig. 3.2. The collected source soils were passed through a 2-mm sieve, the coarse stone fragments and large pieces of organic matter were removed and the sample was oven-dried. Prior to drying, a subsample was removed and stored at 4 °C and was used to measure the aggregated, or effective particle size distribution (EPSD) and for determination of the gravimetric moisture content. Runoff samples were left to settle in a cool dark room for 48 hrs and then the clear supernatant was

siphoned off and the samples were oven-dried and weighed. Prior to settling, the runoff samples were gently stirred to resuspend the soil particles and a representative subsample was removed and stored at 4 °C and used for the determination of the EPSD.

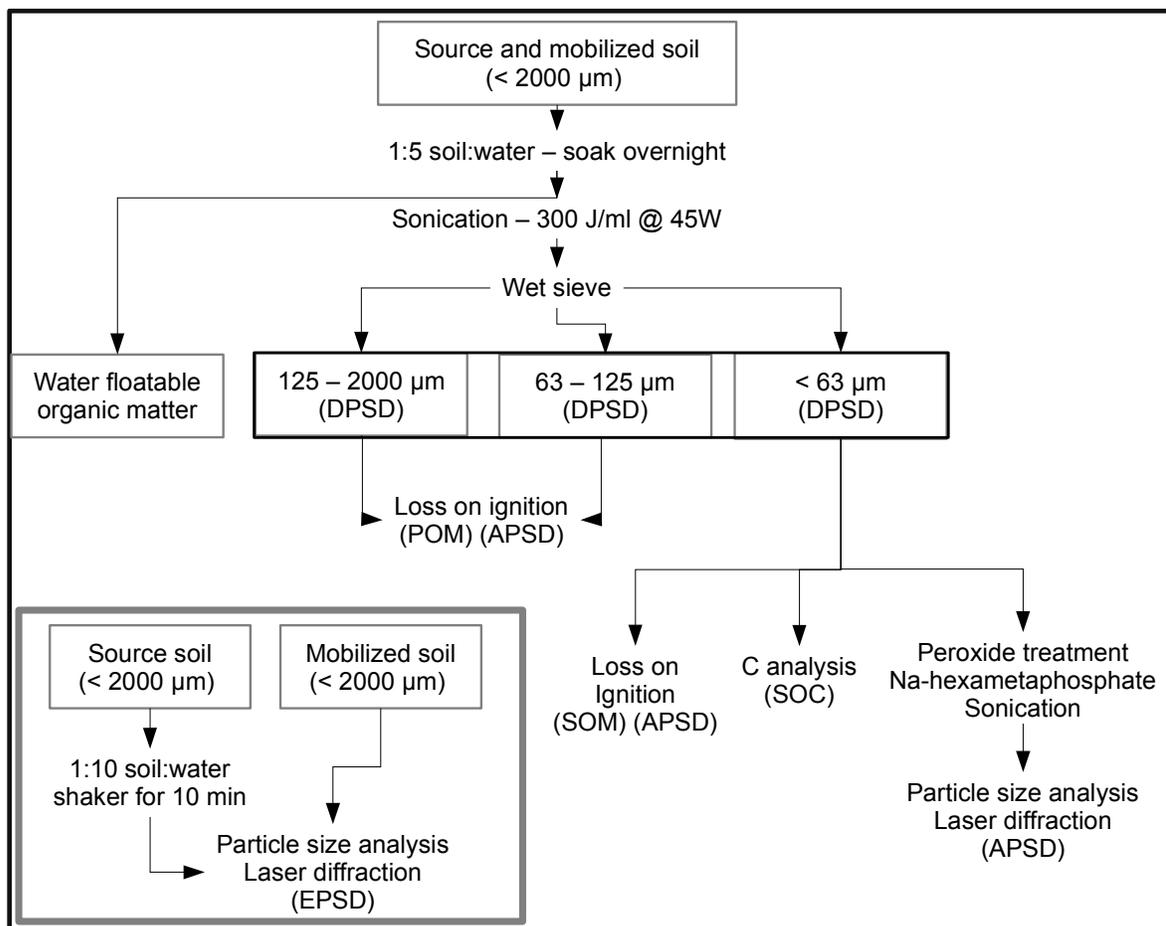


Figure 3.2: Schematic showing the sample preparation, subsampling and analysis for the effective particle size distribution (EPSD; see inset), dispersed particle size distribution (DPSD), absolute particle size distribution (APSD), particulate organic matter (POM), soil organic matter (SOM) and soil organic carbon (SOC).

### 3.3.3.2 Particle size analysis

The EPSD for the source soil samples was measured by combining field-moist soil with deionized water (1:20 ratio of soil to water) in a 25 mL centrifuge tube and placing the sample on a reciprocating shaker (25 rpm) for 10 min. The samples were then measured for

EPSD immediately by laser diffraction (Malvern Mastersizer 3000, Malvern, UK). These samples were introduced directly to the dispersion unit (600 mL) and the pumping/stirring speed was set low (1800 rpm) to limit aggregate breakdown but fast enough to prevent settling. Similarly, the EPSD for the runoff samples was measured by introducing the sample directly into the dispersion unit with no prior disaggregation or removal of organic matter.

For the dispersed particle size distribution (DPSD), the oven-dried samples (up to 15 g) were weighed and placed in 100 mL beakers and deionized water was added to make a 1:5 ratio (soil to water) slurry. The samples were vigorously stirred for 15 min and allowed to settle for 12 hrs and the coarse organic matter that was floating on the surface was removed using a scoopula and was dried and weighed. The remaining sample was disaggregated using an ultrasonic probe (Misonix S-4000, Qsonica, Newtown, CT, USA) with a power output of 45 W and the duration of sonication for each sample was adjusted so that the amount of energy delivered was  $300 \text{ J mL}^{-1}$  (based on the total sample volume) (Yang et al. 2009). The samples were sonicated while in an ice bath and the sonication energy was pulsed (2 min on, 1 min off) to prevent the over-heating of the sample and probe. The disaggregated samples were washed, using approximately 500 mL of deionized water, through nested 125- and 63- $\mu\text{m}$  sieves resulting in three size fractions: 2000 – 125, 125 – 63 and < 63  $\mu\text{m}$ . The two larger particle size fractions were back-washed into glass beakers and the < 63- $\mu\text{m}$  fraction was transferred into a 1000 mL beaker and all three size fractions were oven-dried and weighed.

For the primary, or absolute particle size distribution (APSD), both source soil and mobilized soil samples received the same particle size analysis protocol that combines both sieving and laser diffraction techniques. For the < 63- $\mu\text{m}$  fraction, a subsample of both the oven-dried source and mobilized soil were digested with hydrogen peroxide (35 %) to

remove organic matter and an aliquot of sodium hexametaphosphate and sodium carbonate was added following the procedure of Kroetsch and Cang (2007). The sample was re-sonicated following the same procedure outlined above. The particle size of the < 63- $\mu\text{m}$  fraction was then measured using laser diffraction. The sieving and laser diffraction particle size techniques were merged by multiplying the percent < 63  $\mu\text{m}$  (by mass) by the percent in each size class measured by laser diffraction (by volume). This method assumes a uniform particle density and has been used by other researchers (Nadeu et al. 2011). The mass of the organic matter in each size fraction was accounted for based on the loss-on-ignition values.

#### *3.3.3.3 Soil organic carbon and organic matter analysis*

Organic matter and SOC analyses followed the same protocol for both source and mobilized soil. Organic matter was determined for each of three particle size fractions (i.e., 2000 – 125, 125 – 63 and < 63  $\mu\text{m}$ ) using the loss-on-ignition technique (550 °C for 1 hr). The total mass of organic matter content was estimated by multiplying the total mass of each size fraction by the organic matter content (%). Particulate organic matter (POM) was estimated by summing of the organic matter content across the 2000 – 125 and 125 – 63  $\mu\text{m}$  size fractions (Yang et al. 2009). Soil organic matter (SOM) was determined as the mass of organic matter in the < 63- $\mu\text{m}$  fraction (Yang et al. 2009).

Similar to the SOM analysis, SOC was measured as the C contained within the < 63  $\mu\text{m}$  size fraction; however, due to the large number of samples the particulate (> 63  $\mu\text{m}$ ) organic carbon (POC) was not measured. No pretreatment was used to remove inorganic forms of carbon as test samples did not effervesce with the addition of 10 % hydrochloric acid and the pH (1:2 ratio of soil to water) of the soils were < 7.5 which indicate that carbonates are not present in significant quantities. Therefore, total C was used to estimate

organic C content. Total C analysis was measured using an elemental analyzer (Elemental Combustion System ECS-4010, Costech Analytical Technologies Inc, Valencia, CA, USA). The SOC mass in each sample was estimated by multiplying the mass of the <63- $\mu\text{m}$  fraction by the C content (%).

### 3.3.4 Data analysis

#### 3.3.4.1 Enrichment ratios and aggregation index

Enrichment ratios (ER) are a convenient way to compare the properties of mobilized soil to the source soil. Enrichment ratio values  $> 1$  indicate an enrichment, and values  $< 1$  indicate a depletion as compared to the source soil. For example, the enrichment ratio for SOC ( $ER_{SOC}$ ) for the mobilized soil was calculated as:

$$ER_{SOC} = [SOC]_{mobilized} / [SOC]_{source} \quad (1)$$

Where  $[SOC]_{mobilized}$  is the organic carbon content (%) in the mobilized soil and  $[SOC]_{source}$  is the organic carbon content (%) in the source soil. Enrichment ratios for the different size classes and soil organic matter fractions were calculated using the same procedure.

The aggregate silt and clay (ASC) index (Igwe 2000) was used to investigate the degree of aggregation in both the source and mobilized soil samples and was calculated as:

$$ASC = < 63 \mu\text{m}_{DPSD} - < 63 \mu\text{m}_{EPSD} \quad (2)$$

Where  $< 63 \mu\text{m}_{DPSD}$  is the sum of the clay and silt fraction (%) in the disaggregated form (DPSD) and  $< 63 \mu\text{m}_{EPSD}$  is the sum of the clay and silt fraction (%) in the aggregated (i.e., EPSD) form.

#### 3.3.4.2 Statistical analysis

All statistical analysis was undertaken using R Statistical Software v3.3.2 (R Core

Team 2016) through RStudio Integrated Development Environment v0.99.903 (RStudio 2016). Linear mixed models (R package nlme version 3.1.128 Pinheiro et al. 2016) were used for all analyses with transect and runoff plot as random factors. Runoff plot was included as a random factor to control for the fact that the two runoff samples (i.e., 0 – 20 and 20 – 40 min runoff samples) are not independent (temporal pseudoreplication). Hillslope position (i.e., upper, mid and lower) was added as a covariate to control for any inherent variability along the length of a transect. Data were centred (i.e., predictors have mean of 0) prior to analysis to improve the interpretation of main effects and interactions. Since interaction between variables can influence the interpretation of main effects, all two-way interactions were investigated and added to the model in a backward stepwise process based on the likelihood ratio test ( $p$ -value  $< 0.1$ ). Normality and homogeneity of variance were assessed visually and response variables were transformed, when necessary, to meet these assumptions. All models were checked for multiple collinearity (all variation inflation factors (VIF) were  $< 5$  and condition numbers (i.e., kappa) were  $< 20$ ) (Quinn and Keough 2002).

All graphical plots were created using the R package ggplot2 v0.9.3.1 (Wickham 2009). Differences in enrichment ratios between the two runoff periods were assessed by post-hoc pairwise comparisons with the Bonferroni  $p$ -value adjustment method when the model showed a significant main effect of runoff period or an interaction between the variable (e.g., size class) and the runoff period (R package multcomp version 1.4-0; Hothorn et al. 2008). Data were averaged across all runoff plots for each runoff period and plotted showing the standard error about the mean. For all other analyses, graphical plots were created with non-transformed data and show the model relation (regression line). Each relation was plotted while holding all other variables constant. In cases where interactions

were significant the modelled relations represent  $\pm 1$  standard deviation about the mean and data were also categorized based the mean value for a given soil surface property. Pearson correlation coefficients were calculated to assess the relation between enrichment ratios and soil loss as well as SOM and SOC content.

## **3.4 Results**

### **3.4.1 Soil loss**

There was a large range in the total mass of mobilized soil generated under the simulated rainfall. The distribution was heavily positively skewed and the soil loss was on average 37.5 (+100.1, -27.3) g m<sup>-2</sup> per 20 min runoff period ( $\pm 1$  standard deviation, log<sub>10</sub> back-transformed). There was a small difference in soil loss between the two runoff periods with the 0 – 20 min runoff period showing a higher soil loss when the antecedent soil moisture was high (Fig. 3.3; Table 3.2A). The soil loss was negatively correlated to the amount of vegetative cover (%) and showed a significant interaction with the antecedent soil moisture conditions and soil organic matter content. Low soil moisture conditions combined with low vegetative cover resulted in the higher soil loss and low soil organic matter content with low vegetative cover also resulting in higher soil loss (Fig. 3.3). Furthermore, runoff plots with a high slope gradient and a high soil moisture content tended to have the greatest amount of soil loss and the effect of slope gradient diminished under drier soil surface conditions (Fig. 3.3).

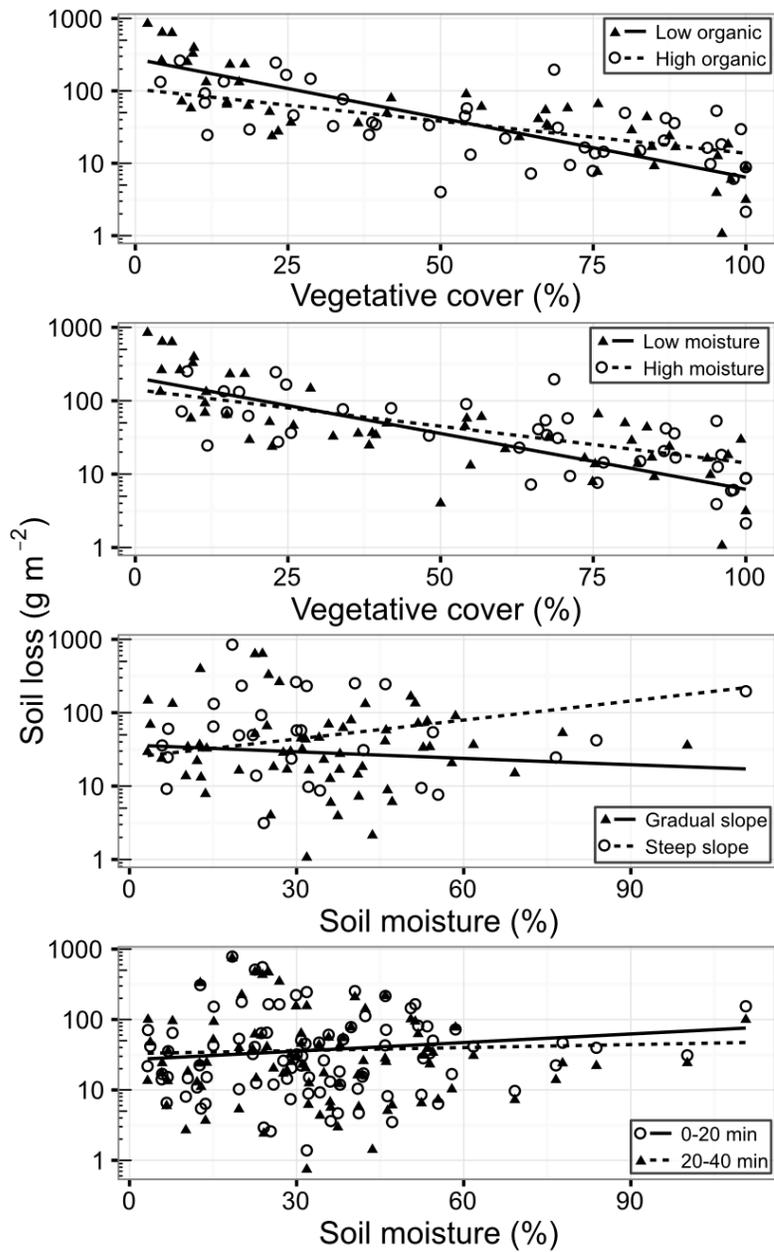


Figure 3.3: The significant ( $p$ -value < 0.05) correlations between soil surface properties and soil loss. See Table 3.2(A) for additional details.

Table 3.2: Results of linear mixed effects models looking at the correlation between soil surface properties and: (A) soil loss; (B) enrichment ratio (ER) of fine-grained sediment; and (C) enrichment ratio (ER) of soil organic carbon (SOC). Runoff period contrasts compares 0 – 20 min to 20 – 40 min.

Analysis	Parameter	Estimate	Std. Error	df	t value	P-value
<b>(A) Soil loss</b> Log <sub>10</sub> (g m <sup>-2</sup> )	(Intercept)	1.662	0.065	85	25.538	< 0.001 ***
	Vegetative cover (%)	-0.013	0.001	68	-10.295	< 0.001 ***
	Gradient (%)	0.015	0.005	68	3.049	0.003 **
	Silt (%)	0.006	0.003	68	1.763	0.082
	Soil organic matter (%)	-0.003	0.012	68	-0.247	0.806
	Soil moisture (%)	0.004	0.002	68	2.077	0.042 *
	Runoff period	-0.003	0.023	85	-0.118	0.906
	Slope position (upper vs mid)	-0.172	0.086	68	-1.994	0.051
	Slope position (lower vs mid)	-0.133	0.084	68	-1.593	0.116
	Veg. cover (%) X Soil org. (%)	0.001	< 0.001	68	2.790	0.007 **
	Veg. cover (%) X Soil moist. (%)	< 0.001	< 0.001	68	2.136	0.036 *
	Gradient (%) X Soil moisture (%)	0.001	< 0.001	68	2.254	0.027 *
	Gradient (%) X Runoff period	-0.004	0.003	85	-1.644	0.104
	Silt (%) X Soil org. (%)	0.002	0.001	68	1.981	0.052
Soil moisture (%) X Runoff period	-0.003	0.001	85	-2.412	0.018 *	
<b>(B) Fine-grained soil (&lt; 63 μm) ER</b> 1/( $63_{runoff}/63_{source}$ )	(Intercept)	0.677	0.012	86	58.538	< 0.001 ***
	Vegetative cover (%)	-0.001	< 0.001	69	-2.554	0.013 *
	Gradient (%)	0.003	0.001	69	2.893	0.005 **
	Silt (%)	0.011	0.001	69	16.487	< 0.001 ***
	Soil organic matter (%)	0.006	0.002	69	2.495	0.015 *
	Soil moisture (%)	-0.001	< 0.001	69	-3.461	0.001 **
	Runoff period	0.056	0.007	86	7.679	< 0.001 ***
	Slope position (upper vs mid)	-0.011	0.014	69	-0.793	0.431
	Slope position (lower vs mid)	0.022	0.014	69	1.582	0.118
	Veg. cover (%) X Gradient (%)	< 0.001	< 0.001	69	-2.070	0.042 *
	Silt (%) X Gradient (%)	< 0.001	< 0.001	69	-1.925	0.058
	Soil moisture (%) X Gradient (%)	< 0.001	< 0.001	69	4.556	< 0.001 ***
Silt (%) X Runoff period	-0.002	0.001	86	-4.022	< 0.001 ***	
<b>(C) Soil organic carbon ER</b> (SOC <sub>runoff</sub> /SOC <sub>source</sub> )	(Intercept)	1.690	0.084	85	20.012	< 0.001 ***
	Vegetative cover (%)	< 0.001	0.001	66	0.236	0.814
	Gradient (%)	-0.015	0.007	66	-2.071	0.042 *
	Silt (%)	-0.023	0.004	66	-5.599	< 0.001 ***
	Soil organic matter (%)	-0.050	0.013	66	-3.879	< 0.001 ***
	Soil moisture (%)	0.003	0.002	66	1.554	0.125
	Runoff period	-0.152	0.019	85	-7.927	< 0.001 ***
	Slope position (upper vs mid)	0.044	0.064	66	0.691	0.492
	Slope position (lower vs mid)	-0.058	0.059	66	-0.980	0.331
	Soil org. (%) X Gradient (%)	-0.003	0.002	66	-1.964	0.054
	Soil moist. (%) X Gradient (%)	< 0.001	< 0.001	66	-2.027	0.047 *
	Silt (%) X Soil moisture (%)	< 0.001	< 0.001	66	-1.766	0.082
	Silt (%) X Soil org. (%)	0.002	0.001	66	2.110	0.039 *
Silt (%) X Runoff period	0.007	0.001	85	4.954	< 0.001 ***	

\* significant at p < 0.05; \*\* significant at p < 0.01; \*\*\* significant at p < 0.001

### 3.4.2 Particle size selectivity

The runoff plots (i.e., source soil) investigated had average surface (0 – 2 cm) clay (< 2  $\mu\text{m}$ ), silt (2 – 63  $\mu\text{m}$ ) and sand (63 – 2000  $\mu\text{m}$ ) contents of  $10.9 \pm 4.7\%$ ,  $47.9 \pm 13.3\%$  and  $41.2 \pm 17.3\%$ , respectively ( $\pm 1$  standard deviation). Overall, the mobilized soil generated under simulated rainfall were enriched in very fine-grained particles (all size fractions < 20  $\mu\text{m}$ ) and depleted in coarse-grained particles (all size fractions > 63  $\mu\text{m}$ ) as compared to the source soil for the APSD (Fig. 3.4a). The two smallest APSD fractions (< 2 and 2 - 20  $\mu\text{m}$ ) had significantly lower ERs during the second runoff period as compared to the first runoff period. In contrast, the largest fractions (125 – 2000  $\mu\text{m}$ ) showed a significant increase during the second runoff period. Considering only the < 63- $\mu\text{m}$  fraction (Fig. 3.4b), there was still an enrichment of the very fine-grained particles (all size fractions < 20  $\mu\text{m}$ ), but the values are closer to 1, and the difference between the two runoff periods is no longer significant. For the coarser silt fractions (20 – 40  $\mu\text{m}$  and 40 – 63  $\mu\text{m}$ ), there was a depletion compared to the source soil and the ER values are significantly closer to 1 during the second runoff period.

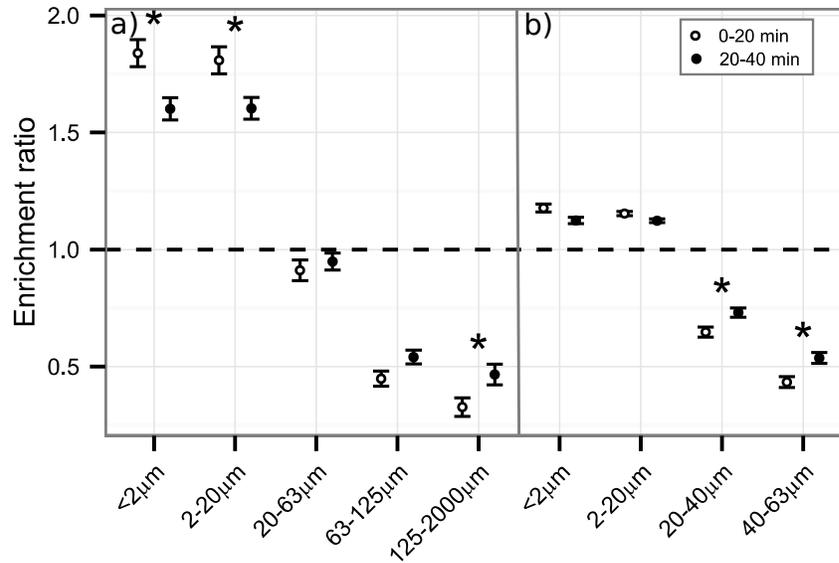


Figure 3.4: Enrichment ratios for the eroded sediment with respect to the source soil for the different absolute particle size classes (mineral component only). Investigating the: a) total sediment (< 2000 μm) and b) silt and clay only (< 63 μm). Error bars indicate ± 1 standard error and \* denotes a significant difference (p-value < 0.05) between the 0 – 20 and 20 – 40 min runoff periods.

The particle size enrichment ratios for the EPSD measurements (i.e., aggregate soil particles) show an enrichment in the three smallest particle size classes (< 63 μm), a depletion in the largest size class (> 125 μm) and the 63 – 125 μm fraction had values close to 1 (Fig 3.5). In comparison with the APSD measurements (Fig. 3.4), the EPSD had ERs twice as high for the two finest fractions as well as enrichment ratios > 1 for the size fractions between 20 and 125 μm whereas the APSD showed a depletion. Furthermore, there was higher variability in the ERs and there were no significant differences between the two runoff periods.

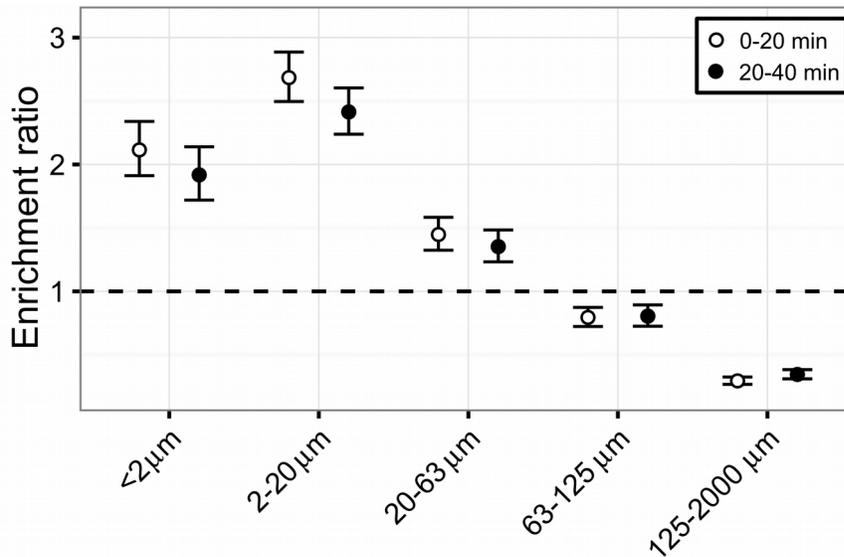


Figure 3.5: Enrichment ratios for the eroded sediment with respect to the source soil for the different effective particle size classes (mineral and organic components;  $< 2000 \mu\text{m}$ ) Values have been  $\log_{10}$  back-transformed. Error bars indicate  $\pm 1$  standard error and \* denotes a significant difference (p-value  $< 0.05$ ) between the 0 – 20 and 20 – 40 min runoff periods.

Similar to soil loss, the distribution of  $ER_{<63}$  was heavily positively skewed and the ER was on average 1.41 (+0.38, -0.25) across both runoff periods ( $\pm 1$  standard deviation, inverse back-transformed). There was a small difference in  $ER_{<63}$  (APSD) between the two runoff periods with the 0 – 20 min runoff period showing higher  $ER_{<63}$  when the source soil had a low silt (%) content and this difference diminished as the silt content of the source soil increased (Fig 3.6; Table 3.2B). Overall the  $ER_{<63}$  was negatively correlated with the silt content (%) of the source soil. The effect of the gradient of the runoff plot on the  $ER_{<63}$  showed an interaction with both the amount of vegetative cover and antecedent soil moisture content. The degree of enrichment was greater when the runoff plots had a gradual slope coupled with a higher moisture content and the effect of gradient diminished under dryer surface soil conditions (Fig. 3.6; Table 3.2B). Similarly, the degree of enrichment was smaller

when the gradient of the runoff plot was higher and this effect diminished with increasing vegetative cover. Finally, the soil organic matter content of the surface soil had a small effect on the with runoff plots with low soil organic matter resulting in a greater amount of enrichment. Overall, there was a negative correlation between  $ER_{<63}$  and soil loss with a Pearson correlation coefficient of -0.34 (p-value < 0.001).

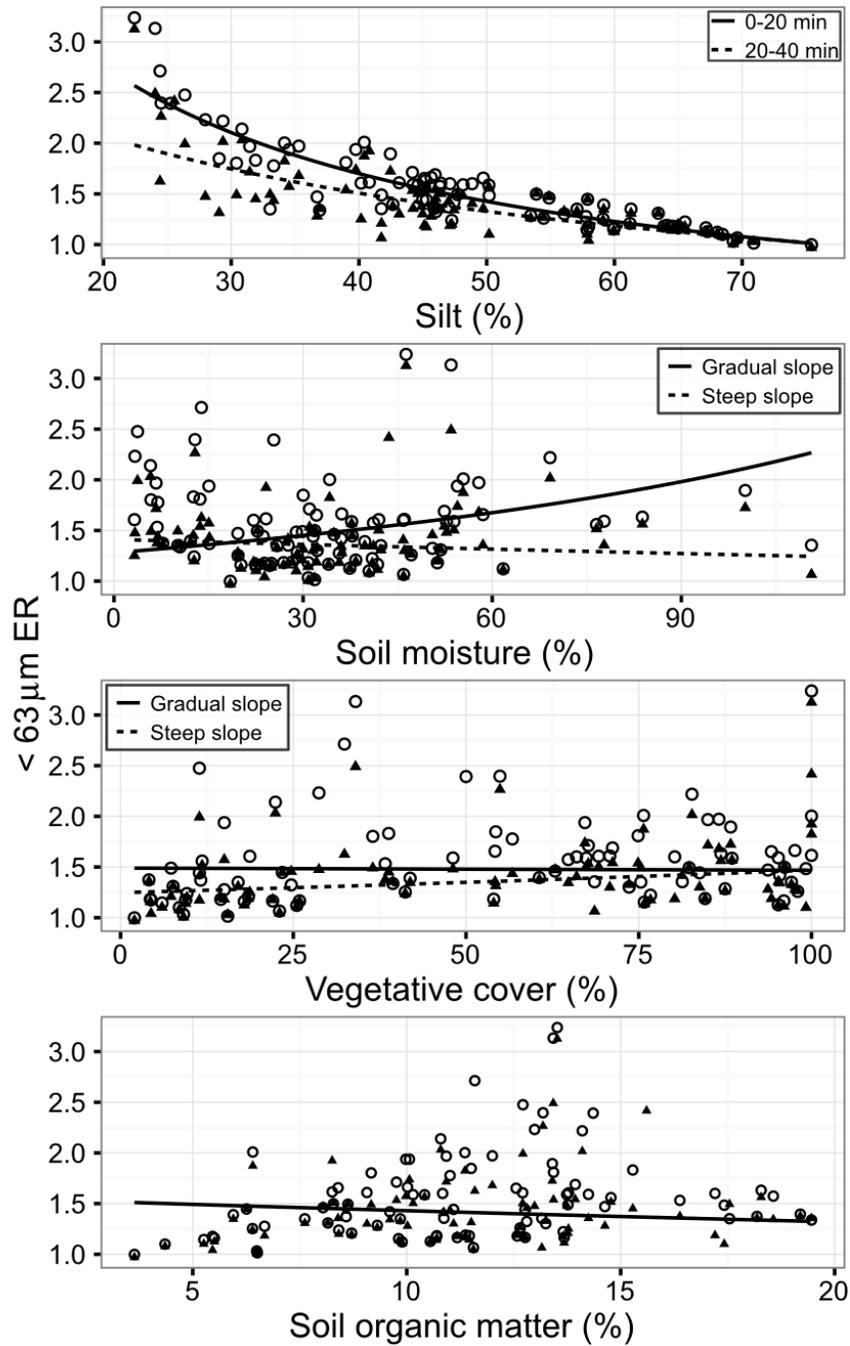


Figure 3.6: The significant ( $p$ -value  $< 0.05$ ) correlations between soil surface properties and the amount silt and clay ( $< 63 \mu\text{m}$ ; mineral component only) enrichment ratio of eroded sediment with respect to the source soils. See Table 3.2(B) for additional details.

### 3.4.3 Organic matter selectivity

The source soils investigated had an average surface (0 – 2 cm) SOC, POM and SOM contents of  $5.2 \pm 1.9$  %,  $7.8 \pm 7.3$  % and  $11.4 \pm 3.5$  %, respectively. Overall the mobilized soil generated under simulated rainfall were enriched in SOC, POM and SOM as compared to the source soil (Fig. 3.7a). Both the SOC and SOM enrichment ratios were significantly lower during the second runoff period (20- 40 min). Considering only the < 63- $\mu\text{m}$  fraction (Fig. 3.7b) there is still an enrichment of the SOC and SOM, however, the values are closer to 1 and the difference between the two runoff periods are no longer significant. The enrichment of SOC ( $ER_{\text{SOC}}$ ) was negatively correlated to the slope gradient (%), SOM (%) and < 63- $\mu\text{m}$  fraction (%) and positively correlated to soil moisture content (%) (Fig. 3.8; Table 3.2C). The SOM content of the source soil was the variable that has the largest effect on the  $ER_{\text{SOC}}$ .

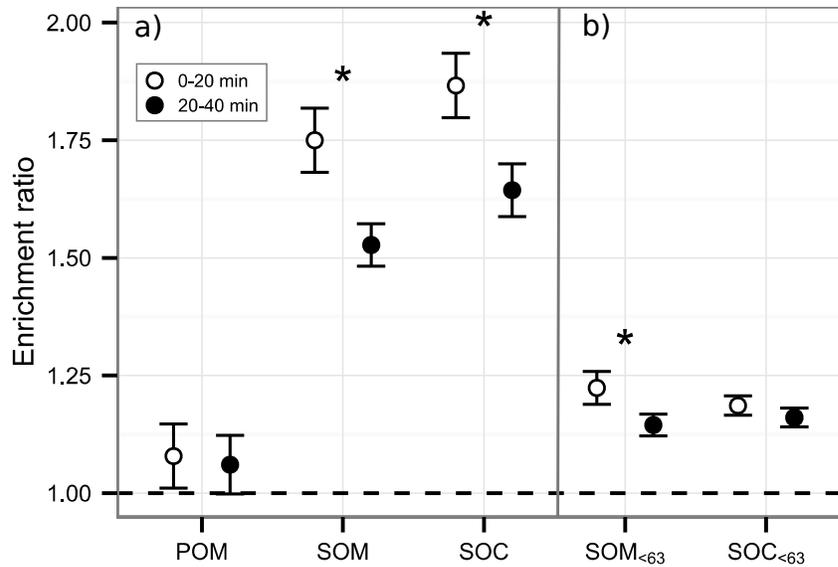


Figure 3.7: Enrichment ratios for the eroded sediment with respect to the source soil for particulate organic matter (POM), soil organic matter (SOM) and soil organic carbon (SOC) fractions. Investigating the: a) total sediment (< 2000  $\mu\text{m}$ ) and b) silt and clay only (< 63  $\mu\text{m}$ ). Error bars indicate  $\pm 1$  standard error and \* denotes a significant difference (p-value < 0.05) between the 0 – 20 and 20 – 40 min runoff periods.

There was a small difference in  $ER_{SOC}$  between the two runoff periods with the 0 – 20 min runoff period showing higher  $ER_{SOC}$  when the source soil had a low silt content and this difference diminished as the silt content of the source soil increased (Fig. 3.8; Table 3.2C). Overall the  $ER_{SOC}$  was negatively correlated with silt content of the source soil but showed an interaction with the soil organic matter content of the surface soil. Runoff plots with a lower soil organic matter content tended to result in the greatest amount of enrichment, but this effect diminished with increasing silt content. The antecedent soil moisture content was positively correlated with the  $ER_{SOC}$  when the slope gradient was gradual, however, under steeper slope gradients the antecedent moisture content had little effect on the  $ER_{SOC}$ . Similar to the  $ER_{<63}$ , there was a negative correlation between  $ER_{SOC}$  and soil loss with a Pearson

correlation coefficient of -0.34 (p-value < 0.001).

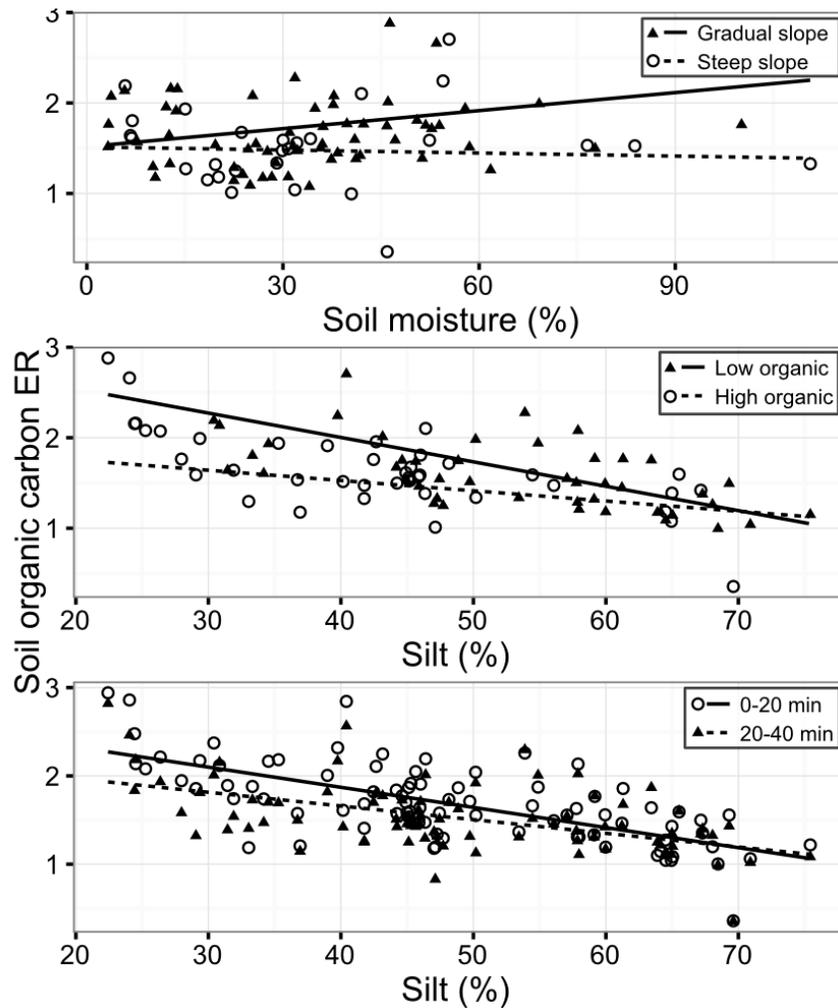


Figure 3.8: The significant (p-value < 0.05) correlations between soil surface properties and the soil organic carbon enrichment ratio of eroded sediment with respect to the source soils. See Table 3.2(C) for additional details.

### 3.4.4 The relation between SOC and particle size

The SOC content of both the source and mobilized soil was positively correlated with the ASC index (Fig. 3.9; Table 3.2A). There was not a significant interaction between the source and mobilized soil and the ASC index indicating that the relation was similar between the source and mobilized soil. Overall, there was a significant positive correlation of the SOC

content and the amount of fine-grained particles ( $< 63 \mu\text{m}$ ) as well as a significant interaction between the amount of clay and silt and the source soil (Fig. 3.9; Table 3.2B). The relation between SOC and the amount of fine-grained material for the source soil had a higher correlation compared to the mobilized soil and there was no difference between the two runoff periods. However, much of variation in the data, for both the ASC index and the clay and silt content, was explained by the random factor of transect and accounts for much of the spread of the raw data around the modelled relation.

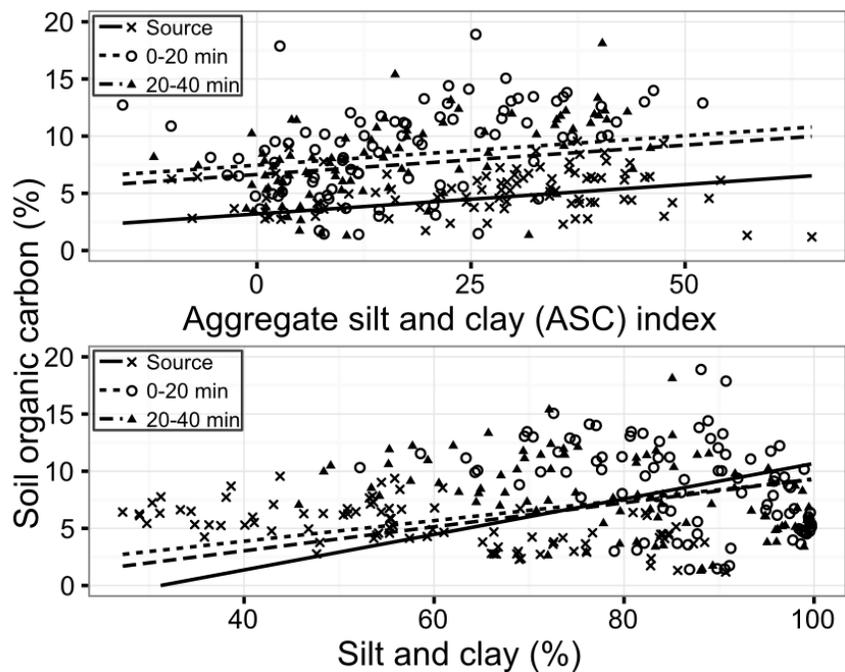


Figure 3.9: The correlations between aggregated (ASC index) and absolute particle size (clay + silt) and the soil organic carbon content for the source soils and the eroded sediment. See Table 3.3 for additional details.

Table 3.3: Results of linear mixed effects models looking at the the correlation in soil organic carbon with soil aggregation (A), and soil organic carbon with the amount of clay and silt (B). Sample type contrasts compares Source vs 0 – 20 min (1) and 20 – 40 vs 0 – 20 min (2).

Analysis	Parameter	Estimate	Std. Error	df	t value	P-value
<b>(A) Soil organic carbon (%)</b>	(Intercept)	8.224	0.814	172	10.102	< 0.001 ***
	ASC index	0.051	0.007	172	7.516	< 0.001 ***
	Source vs 0 – 20 min (1)	-4.264	0.204	172	-20.885	< 0.001 ***
	20 – 40 vs 0 – 20 min (2)	-0.819	0.191	172	-4.289	< 0.001 ***
	Slope position (upper vs mid)	0.120	0.308	77	0.391	0.697
	Slope position (lower vs mid)	0.717	0.314	77	2.287	0.025 *
<b>(B) Soil organic carbon (%)</b>	(Intercept)	6.720	1.268	170	5.302	< 0.001 ***
	Clay + silt (%)	0.090	0.012	170	7.473	< 0.001 ***
	Source vs 0 – 20 min (1)	-0.247	0.255	170	-0.970	0.333
	20 – 40 vs 0 – 20 min (2)	-0.321	0.166	170	-1.929	0.055
	Slope position (upper vs mid)	-0.291	0.312	77	-0.932	0.354
	Slope position (lower vs mid)	1.137	0.319	77	3.561	< 0.001 ***
	Clay + silt (%) X Sample type (1)	0.065	0.010	170	6.524	< 0.001 ***
	Clay + silt (%) X Sample type (2)	0.015	0.010	170	1.504	0.135

\* significant at  $p < 0.05$ ; \*\* significant at  $p < 0.01$ ; \*\*\* significant at  $p < 0.001$

## 3.5 Discussion

### 3.5.1 Soil loss

The amount of soil loss as it relates to soil surface properties is generally consistent with the literature on interrill erosion. The inherent erodibility of the soil is primarily controlled by soil texture, SOM, soil structure, and permeability (Renard et al. 1991). Soil with a high silt and very fine sand content are typically the most erodible because this size class of soil particles does not form stable aggregates and as a result are easily mobilized and transported by overland flow (Shabani et al. 2014). Furthermore, silty soil tends to have lower infiltration rates as compared to soil with a higher percentage of sand which results in larger amounts of overland flow (Rawls et al. 1993). The results from this study are in agreement with this as there was a trend ( $p$ -value  $< 0.1$ ) with an increase in the amount of soil loss with increasing silt content of the source soil (Table 2A).

Soil with a low SOM content also tended to be more erodible because SOM binds smaller soil particles together making them more resistant to mobilization and SOM improves infiltration and can reduce overland flow (Le Bissonnais and Arrouays 1997; Franzluebbers 2002). In this study, the effect of SOM on reducing soil loss was greatest when vegetative cover was low, and had a smaller effect under high vegetative cover conditions. The role of vegetative cover in this study is consistent with the literature on interrill erosion where the amount of vegetative cover is one of the most important factors influencing soil loss. For example, the STC watershed had an overall lower vegetative cover ( $34.0 \% \pm 31.9$ ) as compared to the BV watershed ( $62.5 \% \pm 29.0$ ) with a corresponding soil loss of more than 100 % higher than the BV watershed. The amount of vegetative cover can change over time, and, as a consequence the potential for erosion is not constant throughout the year (Fig. 3.10). Therefore, during periods of low vegetative cover, SOM content has a greater contribution in reducing soil loss.

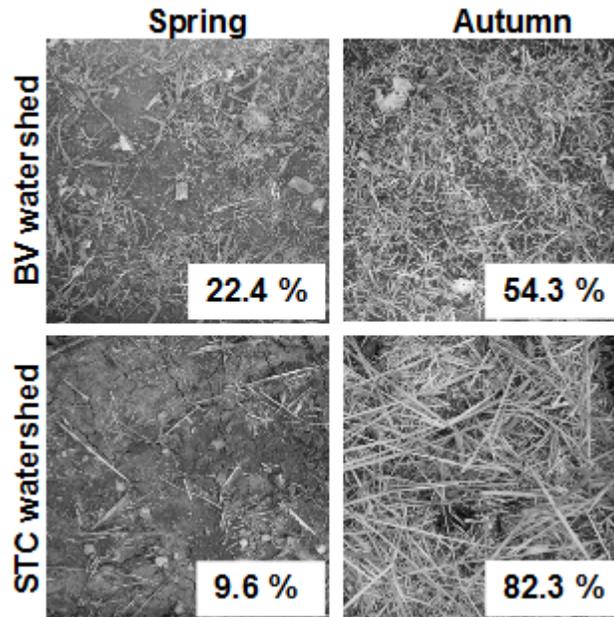


Figure 3.10: An example of two sampling sites demonstrating the change in the percent vegetative cover between the spring and autumn seasons for the Beaver valley (BV) and South Tobacco Creek (STC) watersheds with the percent cover in brackets.

Dryer soil with low amounts of vegetative cover resulted in greater soil loss and this may be due to the breakdown of aggregates by rapid wetting (slaking and differential swelling) and through the impact of raindrops. The aggregate breakdown products result in smaller soil particles, which more easily transported by erosional processes (Vermang et al. 2009). In contrast, low moisture soil with higher vegetative cover resulted in lower soil losses. The interception of raindrops by the vegetative cover reduces the amount of energy being transferred to the soil surface and the dry soil have a larger capacity to absorb water reducing the amount of overland flow. This is in contrast to the results of Li et al. (2015) where the antecedent moisture had a larger effect on soil loss as compared to vegetative cover

with higher moisture soil generating higher soil losses. This contrast may reflect a difference in the relative contributions of both splash and interrill erosion. Splash erosion is more sensitive to changes in vegetative cover while interrill erosion is more affected by antecedent soil moisture content.

Antecedent soil moisture content can also impact soil erodibility through its influence on both infiltration and the stability of soil aggregates, as the rapid wetting of dry soil aggregates can result in disaggregation (i.e., slaking) (Warrington et al. 2009) which can then result in surface sealing reducing the infiltration rate and promoting overland flow (Sajjadi and Mahmoodabadi 2015). For example, both Vermang (2009) and Defersha and Melesse (2012) found that soil loss under simulated rainfall was greater for low moisture soil as compared to high moisture soil. The effect of soil moisture content prior to the rainfall simulation in this study was difficult to generalize, as there were significant interactions with the percent vegetative cover, slope gradient, and runoff period. There were negative Pearson correlation coefficients of -0.29 (p-value < 0.001) and -0.16 (p-value = 0.025) between the time since the beginning of the rainfall simulation and the initiation of runoff and both soil moisture and slope gradient, respectively. This suggests that, within this study, soil moisture may have a larger effect on the rate of runoff and this provides some evidence to explain the smaller effect of slope under lower soil moisture conditions.

The larger effect of slope gradient under wetter conditions may occur as a result of increase runoff due to saturation-excess overland flow. In general, wetter soil, when rained upon, will become saturated more quickly, causing more rapid initiation of overland flow as compared to dryer soil. However, the soil moisture content throughout the soil profile needs to have been considered to fully assess the implications of saturation-excess overland flow to

both the rate of runoff and soil loss. Interrill erosion is generally greater under steeper slope conditions as the gradient is proportional to the runoff velocity which increases the transport capacity of the runoff (Fox and Bryan 1999). The overall effect of slope in this study was consistent with other research; steeper slope gradients had higher soil losses (e.g., Shi et al. 2012). Overall, the vegetative cover and the gradient of the runoff plot had the largest effect on soil loss, but the interactions with other soil surface properties demonstrate that soil loss due to interrill erosion is a complex process.

### **3.5.2 Particle size selectivity**

It was expected that the larger particle size fractions ( $> 63 \mu\text{m}$ ; APSD) of the mobilized soil would be depleted with respect to the source soil as larger particles have a higher threshold shear stress and are less likely to be eroded (Fig. 3.4) (Shields 1936). The response, in terms of the enrichment of the fine-grained fraction ( $< 63 \mu\text{m}$ ; APSD), was less predictable as this fraction has more potential to aggregate into larger particles that are more resistant to detachment and require greater amounts of energy to be transported as compared to the individual non-aggregated particles that comprise the aggregate soil particle. The factors that determine the differences in the particle size enrichment ratios between the EPSD and APSD (Figs 3.4 and 3.5) are the disaggregation of aggregates during the simulated rainfall event and the removal of organic matter (POM and SOM) prior to the APSD measurement. It is difficult to separate the contribution of either component when comparing the two particle size measurement types. However, what is clear is that smaller particles were preferentially mobilized and transported as the higher enrichment ratios for the smaller particle size classes suggest that not enough energy, from raindrop splash or overland flow,

was available to mobilize and transport the larger aggregates.

There are some interesting parallels in the results between the soil loss and the  $ER_{<63}$  analysis (Figs 3.3 and 3.6, respectively). Increases in either the slope gradient or the silt content of the source soil generally resulted in lower enrichment ratios and these same factors also resulted in higher soil losses. These properties, as discussed above, can result in an increased velocity and higher amounts of runoff, thus increasing the competence of the overland flow. These results are consistent with other research that has also shown that there is a significant correlation between soil loss or discharge and particle size selectivity (Armstrong et al. 2011; Yang et al. 2013). For source soil with a lower silt content, the 0 – 20 min runoff period had higher enrichment ratios compared to the 20 – 40 min runoff period and this may be due to the flush of small, loose and readily available soil particles at the soil surface. These results suggests that supply of the most easily eroded size fraction is limited. This finding is consistent with Asadi et al. (2007) where the median particle size of the mobilized soil, generated under simulated rainfall, increased over time becoming closer in size to the source soil.

The interaction between soil moisture and the slope of the runoff plot on the  $ER_{<63}$  is similar to soil loss where higher soil moisture and gradual slope gradient result in both lower soil loss and higher enrichment and this may be related to the lower transport capacity of the overland flow and reduced aggregate disintegration under these conditions. Overall, the amount of vegetative cover had a relatively small effect on the  $ER_{<63}$  suggesting that raindrop impact on the soil surface had a small effect on the disintegration of soil aggregates and the resultant enrichment of fine-grained material. Both Shi et al. (2012) and Wang et al. (2014) found that soil mobilized under simulated rainfall had a higher enrichment of fine-grained

particles with increasing mulching rates or lower kinetic energy.

The SOM content of a soil is generally positively correlated to the soil aggregate stability and size (Le Bissonnais 2016). The increased stability of soil aggregates prevents the disintegration into smaller and more easily erodible particles and, therefore, limiting the loss of fine-grained soil particles (Legu dois and Bissonnais 2004). Soil with a low degree of aggregation would experience less selectivity as a result of interrill erosion and have  $ER_{<63}$  values closer to 1.0. It was unexpected that the SOM content of the runoff plot would have an overall negative correlation with the  $ER_{<63}$ . However, the variability between transects was very high and transects with higher SOM content had an overall higher  $ER_{<63}$ , but within a transect, plots with a higher SOM content had a lower  $ER_{<63}$ . This suggests that the role of SOM on the particle size selectivity is more site specific.

While the same soil surface properties that were significant factors in determining soil loss were also significant factors in the particle size selectivity, there were differences in their interactions. This indicates that there are some differences in the determining factors between soil loss and the particle size selectivity of interrill erosion processes.

The fact that soil erosion results in the preferential mobilization and transport of fine-grained soil particles is the one of the main reason that many sediment fingerprinting studies have sieved samples to  $< 63 \mu\text{m}$  in an effort to limit the differences in particles size between source soil and sediment collected downstream. This allows for a more direct comparison in terms of biogeochemical properties (e.g., trace metal concentration, colour and cation exchange capacity) (e.g., Walling et al. 1999). The results from this study show that the sieving approach does reduce the differences in particle size between source and mobilized soil, however, it does not eliminate it all together. There is still an enrichment of the very

fine-grained particles and a subsequent depletion of the coarse silt-size fraction after sieving. Furthermore, this study has also shown that the degree of selectivity is not static and can vary based on antecedent soil surface conditions and that there was a significant amount of spatial variability (i.e., the random factor transect was an important component of the overall variance). It is also important to put the relative significance of the selectivity of interrill erosion processes in perspective with other watershed processes (e.g., fluvial transport) in terms of determining the extent of downstream fining of sediment. For example, Koiter et al. (2015) found a reduction of ~ 55 % in the median grain-size in less than one hour of fluvial transport in an artificial channel using a recirculating flume.

The small enrichment of the very fine-grained particles after sieving still may present issues in the direct comparisons between mobilized and source soil as the smaller particles tend to have a higher SSA and are more chemically reactive (Horowitz 1991) and, therefore, geochemical and radiochemical elements of interest may be concentrated in these finer fractions. Researchers will sometimes use correction factors in addition to sieving procedures to account for the differences in particle size. A commonly used approach is to use the ratio of SSA between the sediment and source material and multiply it by the geochemical concentration of a given element (e.g., Collins et al. 1997). However, these correction factors can be problematic as it assumes that the relation between SSA and concentration is the same for all elements in terms of linearity, magnitude and direction, which is often not the case (Smith and Blake 2014; Koiter et al. 2015).

### **3.5.3 Organic matter selectivity**

The smaller enrichment ratio for the POM fraction as compared to the enrichment of

SOM is likely due to the larger particle sizes (i.e.,  $> 63 \mu\text{m}$ ) of this material which, as described earlier, requires more energy to mobilize and transport compared to smaller particles. However, for the mineral component of the mobilized soil there was a depletion in these particle size classes and the difference between the organic and mineral components in terms of enrichment is likely due to difference in particle density and shape. There is a large difference between the density of organic particles ( $0.9 - 1.3 \text{ Mg m}^{-3}$ ) and mineral particles ( $2.6 - 2.75 \text{ Mg m}^{-3}$ ) (Brady and Weil 2001). Visual observations of the POM showed that most of the POM was either crop residues left after harvest (STC soil) or dead grasses (BV soil) and the particle shapes were typically blade shaped (long and flat) (Zingg shape classification; Zingg 1935). Both the shape and density of the POM require less energy to mobilize compared to the mineral component of equivalent size (Le Roux 2005). Both the SOM and SOC showed similar trends, as the two characteristics are highly correlated. The results show a higher degree of enrichment with the SOM as compared to the POM which is likely due to the smaller particle size of the SOM relative to the POM. Similar to the mineral fraction, sieving to  $< 63 \mu\text{m}$  reduced, but did not eliminate, the difference between the source soil and the mobilized soil.

There are similarities between the  $ER_{<63}$  and  $ER_{\text{SOC}}$  analysis in terms of some of the effects of the main factors and their interactions (Figs 3.6 and 3.8). These similarities may, in part, be due to the SOC and the  $< 63\text{-}\mu\text{m}$  size fraction aggregating together and being mobilized as aggregated soil particles. For example, the silt content and its interaction with the runoff period, as well as the interactions between the slope and antecedent soil moisture, have very similar effects on both the  $ER_{<63}$  and  $ER_{\text{SOC}}$ . Furthermore, similar to the  $ER_{<63}$  analysis, there was a significant negative correlation between soil loss and the  $ER_{\text{SOC}}$ , which

is consistent with other research (e.g., Schiettecatte et al. 2008). Interestingly, the soil with the lower SOM, which also corresponds to soil with low SOC, had higher SOC enrichment ratios. This may be due to the lower aggregation potential of low SOM content soil and small non-aggregated and low density SOC-rich aggregate particles being more easily mobilized (Fig. 3.8). It is difficult to generalize this relation at a larger scale as the BV watershed soil had an average higher SOM content ( $12.9 \% \pm 2.9$ ) as compared to the STC watershed soil ( $8.4 \% \pm 2.5$ ) with a corresponding average  $ER_{SOC}$  of more than 20 % higher than the STC watershed.

The enrichment of SOC or SOM can have similar effects as the enrichment of fine-grained soil particles in terms of the influence on geochemical composition of the material as organic matter also has a high SSA and is chemically reactive (Horowitz 1991). There are also methods available to correct for differences in organic matter content and these are often applied in addition to particle size corrections. A commonly used approach is to use the ratio of SOM or SOC of the sediment to the source and multiply it by the geochemical concentration of a given element (e.g., Collins et al. 1997). However, these correction factors can be problematic as they assume that the relations between SOM or SOC and concentration are the same for all elements in terms of linearity, magnitude and direction. Furthermore, the use of a particle size correction factor in addition to an organic matter correction factor also assumes that the effects of organic matter and particles size are additive, but the amount of fine-grained particles and organic matter are often positively correlated (Ma et al. 2015). Further research is clearly needed to assess these correction factors. Consequently, several researchers have identified that correcting for both particle size and organic matter selectivity should be treated with caution and potentially avoided (Smith and Blake 2014). Furthermore,

the organic matter selectivity of the water erosion process has implications for the redistribution of C within the landscape and its loss to surface waterways. When assessing the role of soil erosion in C dynamics this research shows that there is a disproportional amount of C being mobilized and transported relative to the source soil (i.e.,  $ER_{SOC}$  is typically  $> 1$ ) and that total soil loss is insufficient in characterizing C redistribution and loss.

#### **3.5.4 The relation between APSD, EPSD and SOC**

The results for this study show that SOC is positively related to the degree of aggregation in soil, which is consistent with the concept of SOC and its associated microorganisms acting as a binding agents. The mobilized soil had an overall higher SOC content, but a similar relation with the aggregation index, suggests that SOC-rich aggregates are being preferentially mobilized and transported and are stable (i.e., do not breakdown due to the simulated rainfall). This phenomenon may be related to the differences in densities between SOM and the mineral component. In addition, Williams and Petticrew (2009) found that the SOC content was an important factor influencing aggregate stability. The amount of fine-grained soil particles was positively correlated to the ASC index (data not shown) in source soil as clay, similar to SOC, can act to bind particle together and these results are consistent with other studies (e.g., Ma et al. 2014).

The amount of fine-grained soil particles mobilized was positively correlated to SOC content in both the source and mobilized soil, which is consistent with other research (Feller and Beare 1997). This correlation may be due to the long-term higher nutrient and moisture content often associated with fine-textured soil which promotes vegetation growth. Increasing amounts of clay and silt can promote aggregation and the formation of organo-

mineral complexes which can protect SOC from decomposition. The steeper regression line for the source soil, as compared with the mobilized soil, is likely due to the preferential mobilization and transport of fine-grained soil particles as the presence of sand in the source soil acts to dilute the SOC measurements (e.g., mass and density differences). The effect of sand-sized soil particles on SOC can also be seen by comparing Figs 3.7a and 3.7b whereby the removal of sand size particles reduces the difference (i.e., ER closer to 1) between source and mobilized soil. The high variance component associated with the random factor transect suggests that the exact relation between SOC and measures of particle size (i.e., APSD and EPSD) is site-specific.

### **3.6 Conclusions**

Soil mobilized under simulated rainfall resulted in an enrichment of both fine-grained soil particles and SOC relative to the source soil. There was an enrichment of both aggregated and dispersed soil particles  $< 20 \mu\text{m}$  with the aggregated particles having a greater amount of enrichment. This demonstrates that the EPSD was more affected by interrill erosion processes than the APSD. Furthermore, the ERs of SOM, SOC and particle sizes  $< 20 \mu\text{m}$  (APSD) were greater for the 0 – 20 min as compared to the 20 – 40 min runoff period providing evidence that there is a flush of easily erodible small and organic-rich soil particles. This may also provide an indication that there is a change in the erosional process (splash vs. overland flow) between the two sampling periods. Furthermore, the mobilized soil had an overall higher SOC content, but a similar relation with the aggregate silt and clay index, providing evidence that the SOC-rich aggregates being preferentially mobilized have a high degree of stability. Sieving to  $< 63 \mu\text{m}$ , a common approach to limit the differences in

particle size and SOC between source and eroded soil, did reduce the enrichment ratio but did not eliminate it. This demonstrates that further procedural steps, including sieving to a smaller particle size or the use of correction factors may be needed to account for these differences which will allow a more direct comparison of biogeochemical properties between source and mobilized soil.

There were similarities in terms of soil surface properties and their interactions and the subsequent effects on soil loss and the selectivity of small and organic-rich particles. The soil surface moisture content and its interaction with the gradient of the runoff plot were common across all three analysis where high soil moisture coupled with gradual slope resulted in lower rates of soil loss and greater enrichment of fine-grained material and SOC. There were also some differences in the main factors determining the soil loss including the amount of vegetative cover (%); while this had a large effect on soil loss it had a relatively small effect on the  $ER_{<63}$  and no effect on the  $ER_{soc}$ . The enrichment of both fine-grained soil particles and SOC were negatively correlated with soil loss providing evidence that the rate of soil loss can be used to estimate the degree of selectivity. However, the differences between the factors and their interactions that determine soil loss and selectivity demonstrate that predictions of particle size and SOC enrichment based on the rate soil loss alone may not adequately describe the process of selectivity. Overall, it was difficult to rank the relative importance of the individual soil surface properties that influence particle size and organic matter selectivity as there were significant interactions between some of the soil surface properties.

This study investigated the selectivity of interrill erosional processes on the fine-grained soil particles and SOC under simulated rainfall conditions. However, this research

has also only considered interrill erosion by raindrop splash and overland flow over a short distance and the assessment of other erosional processes (e.g., rill, gully, wind and tillage erosion) and their interactions on selectivity are an important research objective. Soil erosion is just the first step in the sediment cascade and there will be additional selectivity in each step including the delivery through riparian zones (Syversen and Borch 2005) and fluvial transport down-stream (Koiter et al. 2015). There is an important research need to link each of these steps in terms of the magnitude and the determining factors of the particle size and SOC enrichment (Koiter et al. 2013). This will allow for the improvement of processed-based watershed models and management tools.

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## **4 Suitability of particle size and organic matter correction factors in sediment source fingerprinting investigations: the example of two contrasting watersheds in Canada**

### **4.1 Abstract**

This study investigated the conservative behaviour of geochemical fingerprints through the soil mobilization process. This was accomplished by comparing the concentrations of a broad suite of geochemical elements of sediment eroded from small plots, in two contrasting agricultural regions in Canada, by simulated rainfall. All samples were sieved to isolate the fine-grained fraction ( $< 63 \mu\text{m}$ ) prior to analysis in an effort to limit the differences in both particle size and organic matter content. Despite sieving the samples, there were still particle size and organic carbon content differences between the source soil and the eroded sediment which has been shown to influence the concentrations of many geochemical elements. To account for these differences, particle size and sometimes an additional organic matter correction factors are often applied to the source soil concentrations in an attempt to make the two sample types more directly comparable. The particle size and organic matter correction factors are typically based on the ratio of specific surface area (SSA), or soil organic carbon (SOC) content, between the eroded material and source material and the same correction factors are applied to all elements. The effectiveness of these commonly used correction factors was evaluated. It was demonstrated that for most elements the particle size correction factor resulted in an over-correction of the source soil relative to the eroded sediment and that using the organic matter correction factor in addition exacerbated this over-correction. For

most elements, the uncorrected source soil concentrations showed a smaller difference in concentrations relative to the eroded sediment as compared to the corrected source soil. Linear mixed effects models were used to further investigate the relation between elemental concentrations and SSA and SOC. It was found that the magnitude, direction and interactions of the relation was generally both element and watershed specific. This study highlights some of the potential issues with applying the same correction factors to account for difference in particle size and organic matter content to a broad suite of elements.

## **4.2 Introduction**

Information on the relative contribution from different sources of sediment within a watershed is an important part of understanding sediment dynamics and is used for the development of sediment management plans. In particular, fine-grained sediment ( $< 63 \mu\text{m}$ ) is one of the greatest environmental concerns as a significant amount of nutrients, heavy and trace metals, radionuclides, pharmaceuticals, pesticides and other industrial contaminants are transported in association with this fraction (Owens et al. 2001; Oliver et al. 2007; Maskaoui and Zhou 2010; Zheng et al. 2012). This is primarily due to the higher specific surface area (SSA) and chemical reactivity of this material as compared to coarse-grained sediment (e.g., sand and gravel) (Horowitz 1991). However, the high spatial and temporal variability of sediment delivery to surface waterways can make the identification of the dominant sources of sediment at the watershed scale difficult (Smith et al. 2011).

Sediment fingerprinting is a technique that is based on the concept that one or more of the natural physical or biogeochemical properties of the sediment (i.e., fingerprints) will reflect its source, and therefore can be used diagnostically to identify the origin(s) of the

sediment (see Davis and Fox 2009 for a review of the sediment fingerprinting approach). The sediment fingerprinting approach has been used for a variety of different applications including agricultural (e.g., Koiter et al. 2013a), forest harvesting (e.g., Motha et al. 2003), wildfires (e.g., Owens et al. 2012) and urbanization (e.g., Carter et al. 2003). The potential sources of sediment that are most often identified within sediment fingerprinting studies include topsoil and channel bank or other subsoil sources. However, sediment management plans often require more detailed information on the spatial extent of the sources of sediment to make appropriate and cost effective land use or remediation decisions. As a result there is interest in expanding the range of potential tracers (e.g., biomarkers) to better differentiate between land use types (i.e., different crop types within an agricultural region) (Blake et al. 2012; Reiffarth et al. 2016).

There is a wide variety of soil and sediment properties that have been utilized as fingerprints including fallout radionuclides, geochemistry, colour, mineral magnetic and stable isotopes (Haddadchi et al. 2013). The sediment properties selected as fingerprints need to: (1) provide good discrimination between potential sources of sediment; and (2) behave conservatively (i.e. fingerprints should not be affected by the sediment generation, delivery and transport processes in a way that cannot be quantified). There are many statistical approaches that have been used to select the best suite of fingerprints that maximize the discriminatory power between the sources of sediment (e.g., discriminant function analysis, canonical analysis) (Collins and Walling 2002). However, it is more difficult to assess the suitability of fingerprints in terms of the conservative behaviour of sediment as it is transported through a watershed.

Ideally, the physical and biogeochemical properties of the sediment do not change as

sediment moves through a watershed and thus a direct comparison of source and sediment can be made. However, the particle size and organic matter selectivity of the soil erosion, sediment delivery and fluvial transport processes generally results in eroded sediments having a finer texture and higher organic matter content due to the preferential mobilization and transport of the small and less dense soil particles (Slattery and Burt 1997; Di Stefano and Ferro 2002; Asadi et al. 2011). There are also other processes that can alter the physical and biogeochemical properties of sediment during transport from source to sink including abrasion/breakage, adsorption/desorption and organic matter decomposition (see Koiter et al. 2013b for a review of these processes). The latter processes have not received much attention in the literature as it can be difficult to predict the behaviour of fingerprints in the environment. However, changes in particle size and organic matter content are often accounted for by first limiting the analysis to the fine-grained fraction (i.e.,  $< 63 \mu\text{m}$ ) as the larger grain sizes are preferentially deposited upstream. Secondly, particle size, and sometimes an organic matter, correction factors are then applied to the fingerprint data set to further correct for any remaining differences in particle size and organic matter. The commonly used correction factors are based on the ratio of specific surface area (SSA) and soil organic carbon (SOC) between the collected sediment and the source material (e.g., Collins et al. 1997). The correction factor value(s) are then multiplied by the concentration in the source material for each fingerprint so as to make the resultant values more comparable to those of the collected sediment.

There has been an increase in the number of sediment fingerprinting studies that use the geochemical composition of the sediment as potential fingerprints as a single standard laboratory procedure (i.e., ICP-MS following a digestion with acid) can yield information on

a broad suite of elements (> 50) that can each be used as a potential tracer. The basis of using particle size and organic matter correction factors in conjunction with geochemical fingerprints is that the concentration of many geochemical elements are dependent on the particle size and organic matter content (Horowitz 1991). The commonly used correction factors assumes a linear and positive relation between both SSA and SOC and the geochemical concentration. In addition, applying both a particle size and an organic matter correction factors assumes that the effects of SSA and SOC on the geochemical concentration are additive. However, some researchers do not use both, citing that SSA and SOC are often correlated which can result in the over-correction of fingerprint values (e.g., Dutton et al. 2013). The use of correction factors also assumes that the relations are the same for each element; however, there is a growing amount of evidence to suggest that the direction and magnitude of these relations is element specific and varies between watersheds (Russell et al. 2001; Smith and Blake 2014).

The use of correction factors have been shown to affect both the fingerprint selection process and ultimately the apportionment results. For example, Smith and Blake (2014) found that through the combination of both particle size and organic matter correction factors the relative differences in the values of excess  $^{210}\text{Pb}$  between sources were altered with the corrected channel bank source having higher values as compared to cultivated and pasture surface soils. This is inconsistent with the atmospheric deposition of  $^{210}\text{Pb}$  which has been shown to effectively label topsoil and the fact that channel banks are primary composed of subsoil and should exhibit the lowest values (Mabit et al. 2014). Furthermore, Smith and Blake (2014) demonstrated that the use of the combined correction factors for Tamar Gunnislake watershed, UK, resulted in a change to the source apportionment results by 45 %,

as compared to uncorrected values, and subsequently came to a different conclusion as to the dominate source of sediment. Therefore, without an adequate assessment of the relations between SSA and SOC with geochemical concentrations prior to using correction factors there is an unknown amount of uncertainty and error being incorporated into the sediment fingerprinting approach.

In this study, the particle size and organic matter selectivity and its subsequent effect on the geochemical composition of eroded sediment was investigated in two contrasting agricultural watersheds in Canada, using a rainfall simulator to generate eroded sediment. The objectives of this research were to investigate: (1) the physical and biogeochemical properties of source soils and eroded sediment; (2) the relations between SSA and SOC and their interactions on the geochemical concentration for a broad suite of elements; and (3) the suitability of commonly used correction factors to account for differences in particle size and organic carbon content between source soil and eroded sediment.

## **4.3 Methods**

### **4.3.1 Watershed descriptions**

The South Tobacco Creek (STC) watershed is located in south-central Manitoba (see Koiter et al. 2013a for a detailed watershed map). The STC watershed is 75 km<sup>2</sup> and is predominately agriculture with the majority of land under annual crops. The STC watershed extends across the Manitoba Escarpment; its upper reaches lay in undulating glacial tills and its lower reaches lay in the lacustrine sediments of glacial Lake Agassiz (Agriculture and Agri-Food Canada 2011). The soils above the escarpment are Dark Grey Chernozems with a clay-loam texture, while below the escarpment the soils are Black Chernozems with a clay

texture and the valley walls soils are described as a Regosol (Hope et al. 2002). The second region was located in the Beaver Valley (BV) located in central British Columbia (BC). This region is predominately forested (including both grazing and forest harvest land uses) with pasture and forage land uses in the flatter valley bottom sections. This study targeted a 10 km stretch of agricultural land. The soils in this study site are Eutric and Sombric Brunisols, with a sandy loam texture with 5 – 10 % coarse fragments (> 2 mm).

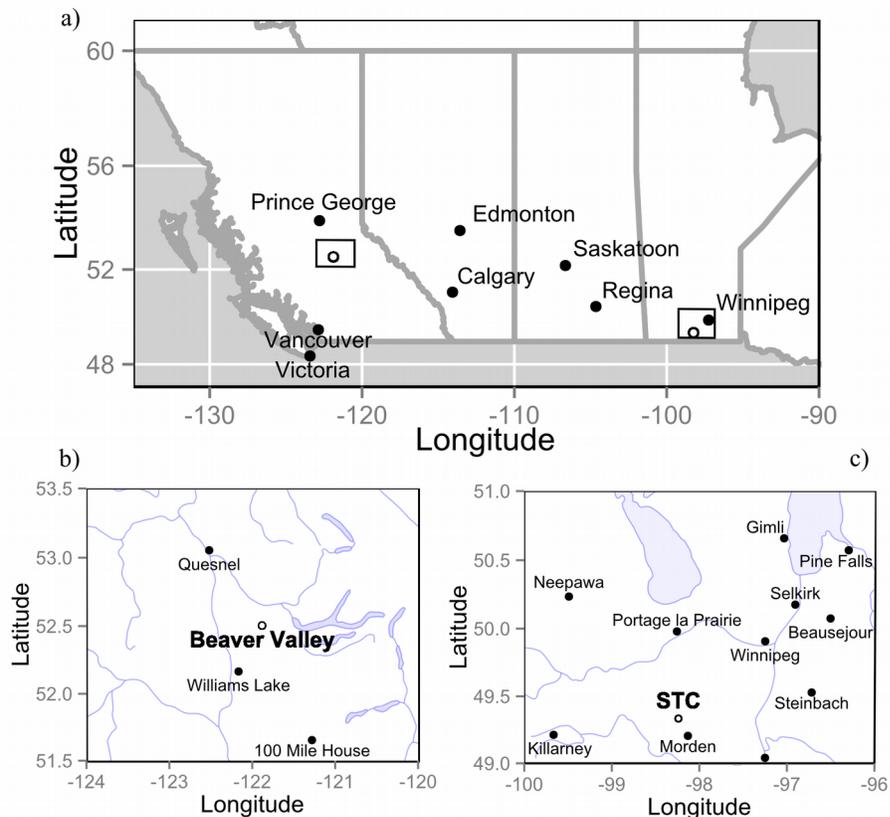


Figure 4.1: Maps showing a) the provinces of south-western Canada and the locations (inset boxes) of the two sampling sites: b) Beaver Valley (BV) watershed and c) South Tobacco Creek (STC) watershed.

Within each of the watersheds, five (STC watershed) and six (BV watershed) hillslopes were identified as being degraded and/or having a high potential for soil erosion and some degree of connectivity to surface waterways. This approach was taken as studies

have shown that these areas can contribute a disproportionate amount of sediment given their areal extent (Pietola et al. 2005; Raper 2005; Collins et al. 2010). On each hillslope a transect was established and plots were setup on the upper, mid and lower slope positions. Each watershed was investigated on two to three occasions in order to get a broader range of surface properties, particularly a broader range in antecedent moisture conditions and vegetative cover. The research sites within the BV watershed were investigated on three occasions: spring (June), summer (August) and autumn (October) of 2012 for a total of 54 rainfall simulations. However, the sites within the STC watershed were only investigated on two occasions: spring (June – pre-emergence) and autumn (October – post-harvest) of 2013 as the tall and dense crops created unsuitable conditions for the rainfall simulation experiment during the summer growing season, thereby resulting in a total of 30 rainfall simulations.

#### **4.3.2 Soil and sediment sample collection**

A gravity-fed rainfall simulator (Clarke and Walsh 2007) was used to generate sediment under a high rainfall intensity ( $200 \text{ mm hr}^{-1}$ ); while this intensity is high, it can provide information on the characteristics of the sediment generated under rainfall and, importantly, within the requirements of this research, provide an adequate sample mass (i.e.,  $> 1 \text{ g}$ ) for analysis within a reasonable time frame. The runoff plot was  $0.16 \text{ m}^2$  ( $40 \times 40 \text{ cm}$ ) with stainless steel plot boundaries and a triangular-shaped collection funnel at the downward plot edge. The generated runoff was gravity fed to 1 L polyethylene bottles. A total of 40 min of continuous runoff were collected and the samples were split into two runoff periods, 0 – 20 min and 20 – 40 min. Source soil samples (0 – 2 cm) were collected outside the plot

boundaries and sampling tools were cleaned between samples to reduce contamination.

### **4.3.3 Data analysis**

#### *4.3.3.1 Laboratory analysis*

The source soil samples were air-dried and passed through a 2 mm stainless steel sieve to remove coarse fragments and vegetation. The sediment in the runoff samples were allowed to settle at room temperature ( $\sim 20$  °C) for 48 hours and the clear supernatant was siphoned off and the eroded sediment allowed to air-dry. Both the the air-dried soil and eroded sediment samples (up to 15 g) were weighed and placed in 100 mL beakers and deionized water was added to make a 1:5 (soil:water, by volume) slurry. The samples were disaggregated using an ultrasonic probe (Misonix S-4000, Qsonica, Newtown, CT, USA) with a power output of 45 W and the duration of sonication for each sample was adjusted so that the amount of energy delivered was  $300 \text{ J mL}^{-1}$  (based on the total sample volume) (Yang et al. 2009). The samples were sonicated while in an ice bath and the sonication energy was pulsed (2 min on, 1 min off) to prevent the over heating of the sample and probe. Previous work has shown that sieving to  $< 63 \mu\text{m}$  is an effective way to reduce the differences in both particle size and organic carbon between source and eroded sediment (Section 3). Therefore, each sample was washed through a  $63 \mu\text{m}$  sieve and transferred into a 1000 mL beaker and oven-dried. All analyses were confined to the  $< 63 \mu\text{m}$  fraction.

Each source soil and eroded sediment sample was subsampled for particle size, organic carbon and geochemical analyses. For the absolute particles size analysis, samples were digested with hydrogen peroxide (35 %) to remove organic matter and an aliquot of a solution of sodium hexametaphosphate and sodium carbonate was added following the

procedure of Kroetsch and Cang (2007). The sample was sonicated following the same procedure outlined above. The specific surface area (SSA) of the source soil and eroded sediment samples were measured using a laser diffraction system (Malvern Mastersizer 3000, Malvern, UK) (0.01 – 3500  $\mu\text{m}$  diameter measurement range) assuming a constant particle density of  $2.65 \text{ g cm}^{-3}$ .

No pretreatment was used to remove inorganic forms of carbon (C) as test samples did not effervesce with the addition of 10 % hydrochloric acid and the pH of the soils (1:2; soil:water mixture) were typically  $< 7.5$  which indicates that carbonates are not present in discernible quantities. Therefore, total C is used to estimate organic C content. Total C analysis was measured on samples using an elemental analyzer (Elemental Combustion System ECS-4010, Costech Analytical Technologies Inc, Valencia, CA, USA).

Samples were analyzed for a broad suite of geochemical elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn and Zr) using inductively coupled plasma mass spectrometry (ICP-MS) following a microwave-assisted digestion with aqua-regia (ALS Mineral Division, North Vancouver, BC, Canada). Of the 51 elements investigated seven (Au, Ta, Re, Ge, Hg, W and Te) were below the detection limit in one or more of the samples and were removed from subsequent analysis.

#### *4.3.3.2 Correction factors*

In addition to comparing the geochemical concentrations of the eroded sediment directly to the source soil (uncorrected), two sets of corrected source soil concentrations were also assessed. The two correction factors used are based on the differences in SSA and SOC between the eroded sediment and the source soil and are commonly used in sediment

fingerprinting research (e.g., Collins et al. 1997). The particle size correction factor ( $SSA_{corr}$ ) was calculated as:

$$SSA_{corr} = SSA_{sediment} / SSA_{soil} \quad (1)$$

Where  $SSA_{sediment}$  is the SSA ( $m^2 g^{-1}$ ) of the eroded sediment and  $SSA_{soil}$  is the SSA ( $m^2 g^{-1}$ ) of the source soil. Similarly, the organic matter correction factor ( $SOC_{corr}$ ) was calculated as:

$$SOC_{corr} = SOC_{sediment} / SOC_{soil} \quad (2)$$

Where  $SOC_{sediment}$  is the organic carbon content (%) in the sediment and  $SOC_{soil}$  is the organic carbon content (%) in the source soil.

The particle size corrected geochemical concentration for the source soil was calculated as:

$$Me_{SSA_{corr}} = Me_{soil} \times SSA_{corr} \quad (3)$$

Where  $Me_{SSA_{corr}}$  is the particle size corrected concentration of a given element (ppm),  $Me_{soil}$  is the concentration of a given element (ppm) in the source soil and  $SSA_{corr}$  is the particle size correction factor as calculated in Equation 1.

The combined particle size and organic matter ( $SSA_{corr} + SOC_{corr}$ ) corrected geochemical concentration of the source soil is calculated as:

$$Me_{SSA+SOC_{corr}} = Me_{soil} \times SSA_{corr} \times SOC_{corr} \quad (4)$$

Where  $Me_{SSA+SOC_{corr}}$  is the is the combined particle size and organic matter corrected concentration of a given element (ppm),  $Me_{soil}$  is the is the concentration of a given element (ppm) in the source soil,  $SSA_{corr}$  is the particle size correction factor as calculated in Equation 1 and  $SOC_{corr}$  is the organic matter correction factor as calculated in Equation 2.

The source soil was corrected based on sediment generated in both the 0 – 20 and 20 – 40 min runoff periods.

#### 4.3.3.3 *Statistical analysis*

All statistical analysis was undertaken using R Statistical Software v3.2 (R Core Team 2015) through RStudio Integrated Development Environment v0.98.1103 (RStudio 2015). Linear mixed models (R package nlme version 3.1-120; Pinheiro et al. 2015) were used for all analysis with transect and runoff plot as random factors. Runoff plot was included as a random factor to control for the fact that the two runoff samples (i.e., 0 – 20 and 20 – 40 min runoff samples) are not independent (temporal pseudoreplication). Hillslope position (i.e., upper, mid and lower) was added as a covariate to control for any inherent variability along the length of a transect. The two watersheds were analyzed separately as much of the differences in soil geochemistry would be due to differences in the underlying geologies. Differences in the geochemical concentration between the corrected source and the eroded sediment for the two runoff periods were assessed by post-hoc pairwise comparisons with the Benjamini-Hochberg p-value adjustment method when the model showed a significant main effect of runoff period, correction factor or an interaction between the two variables (R package multcomp version 1.4-0; Hothorn et al. 2008).

To investigate the relation between the geochemical concentration of all 44 elements and SSA and sample type (i.e., source soil, 0 – 20 min and 20 – 40 min runoff) and their interactions all concentrations were standardized between 0 and 1 to allow for a direct comparison between elements. For the investigation between concentrations of As and Mn (as examples of geochemical elements), and SSA, SOC and sample type the data were centred (i.e., predictors have mean of 0) prior to analysis to improve the interpretation of main effects and interactions. Since interaction between variables can influence the interpretation of main effects, all two-way interactions were investigated and added to the

model in a backward stepwise process based on the likelihood ratio test ( $p$ -value  $< 0.1$ ). Normality and homogeneity of variance were assessed visually and response variables were transformed, when necessary, to meet these assumptions. All models were checked for multiple collinearity (all variation inflation factors (VIF) were  $< 10$  and condition numbers (i.e., kappa) were  $< 20$ ) (Quinn and Keough 2002).

All plots were created using the R package ggplot2 v0.9.3.1 (Wickham 2009). Data were averaged across all plots for each runoff period and plotted showing the standard error about the mean. For all other analysis plots were created with untransformed data and show the model relationship (regression line). Each relationship was plotted while holding all other variables constant and in cases where interactions were significant the modelled relationships represent  $\pm 1$  standard deviation about the mean.

## **4.4 Results**

### **4.4.1 Particle size and organic carbon enrichment**

Despite limiting the analysis to the  $< 63 \mu\text{m}$  fraction, the eroded sediment in both watersheds was enriched in both fine-grained and organic-rich material as compared to the source soil. The  $\text{SSA}_{\text{corr}}$  averaged across both runoff periods was 1.12 and 1.17, the  $\text{SOC}_{\text{corr}}$  was 1.20 and 1.12 and the combined correction factor ( $\text{SSA}_{\text{corr}} + \text{SOC}_{\text{corr}}$ ) was 1.35 and 1.33 for the BV and STC watersheds, respectively (Fig. 4.2). These correction factors are within the range reported in other sediment fingerprinting studies (e.g., Collins et al. 1997; Smith and Blake 2014). The correction factors were significantly lower for the 20 – 40 min runoff period as compared to the 0 – 20 min runoff period for the BV watershed. This indicates that the erosional processes were less selective in terms of particle size and organic matter content

for the latter runoff period. In contrast, there were no significant differences between the two runoff periods for the correction factors in the STC watershed. There was also an overall greater amount of variability in the correction factors within the STC as compared to the BV (Fig. 4.2).

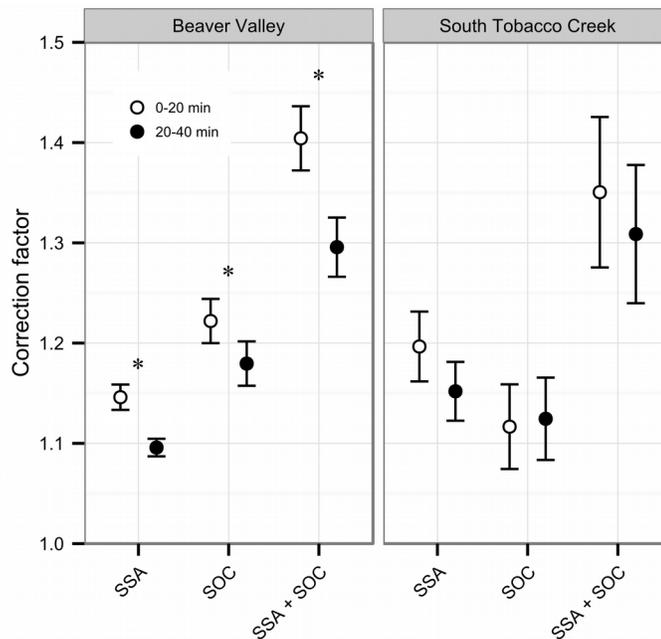


Figure 4.2: Particle size (SSA), organic matter (SOC) and combined (SSA + SOC) correction factors based on the 0 – 20 and 20 – 40 min runoff periods for the Beaver Valley, BC, and South Tobacco Creek, MB, watersheds. Values are mean  $\pm$  the standard error and \* denotes significant difference between runoff periods (p-value < 0.05).

#### 4.4.2 Geochemical composition of source soil and eroded sediment

In comparing the geochemistry of the source soil to the eroded sediment there was a lot of variability between both watersheds and elements (see Table 4.1 for a summary). Overall the geochemical concentrations for the uncorrected source soil were the most similar to that of the eroded sediment for both watersheds. However, for the uncorrected source soil there are more elements showing a significant difference between source soil and eroded

sediment for the BV watershed as compared to the STC watershed. For the uncorrected source concentrations within the BV watershed the 0 – 20 min runoff period had more elements (34) that showed a significant difference (p-value < 0.05) in concentration between the source and eroded sediment as compared to the 20 – 40 min runoff period (27 elements). These differences between the two runoff periods may be related to the changes in the particle size and organic matter selectivity as it was shown that there was less enrichment in both SSA and SOC in latter runoff periods. In contrast, for the uncorrected source soil within the STC watershed there were fewer elements overall with a significant difference between the source soil and eroded sediment.

Table 4.1: Summary of the uncorrected, particle size (SSA) corrected and combined particle size and organic matter (SSA + SOC) corrected geochemical concentrations that are significantly higher or lower (p-value < 0.05) relative to the runoff generated sediment for 44 different geochemical elements. Overall summary statistics across all elements showing the % difference relative to the generated sediment.

	<b>Beaver Valley</b>					
	0 – 20 min			20 – 40 min		
	Uncorrected	SSA	SSA + SOC	Uncorrected	SSA	SSA + SOC
No. elements – higher	4	31	43	5	24	43
No. elements – lower	23	2	0	15	2	0
No. elements – no difference	17	11	1	24	18	1
Average % difference	-2.48	11.23	36.88	-0.08	9.94	29.85
Max. % difference	71.08	94.08	136.82	68.03	84.25	116.16
Min. % difference	-20.18	-9.45	11.51	-15.97	-7.45	9.40
SD % difference	13.91	15.80	19.05	13.66	14.90	17.34

	<b>South Tobacco Creek</b>					
	0 – 20 min			20 – 40 min		
	Uncorrected	SSA	SSA + SOC	Uncorrected	SSA	SSA + SOC
No. elements – higher	3	34	40	3	33	40
No. elements – lower	3	0	0	3	1	1
No. elements – no difference	38	10	4	38	10	3
Average % difference	6.96	25.83	37.56	6.68	21.39	37.45
Max. % difference	57.70	84.77	104.99	54.18	78.38	102.07
Min. % difference	-24.10	-12.55	-4.61	-30.43	-22.07	-14.20
SD % difference	13.40	16.20	18.19	12.91	15.45	17.91

For many of the geochemical elements investigated, the use of the particle size

correction factor tended to increase the difference between the geochemical concentration of the source soil and the eroded sediment (i.e., resulted in an over-correction) as compared to the difference in concentrations between uncorrected source soil and eroded sediment (Table 4.1). The STC watershed had an overall (averaged across both runoff periods) greater increase with an average difference of 23.6 % in the  $SSA_{\text{corr}}$  corrected source soil geochemical concentrations relative to the eroded sediment as compared to an average difference of 10.6 % for the BV watershed. The combined  $SSA_{\text{corr}}$  and  $SOC_{\text{corr}}$  resulted in a considerable over-correction for almost all the elements investigated. The two watersheds were similar in terms of the overall average difference relative to the eroded sediment of 33.4 and 37.5 % for the BV and STC watersheds, respectively.

To further illustrate the influence of correction factors, the concentrations are shown for two elements, As and Mn, for both watersheds and runoff periods (Fig. 4.2). The uncorrected soil As concentrations for the BV watershed showed a significantly lower concentration than the eroded sediment for the 0 – 20 min runoff period but no difference for the 20 – 40 min period (Fig. 4.2a). However, the uncorrected Mn concentration was significantly lower than the eroded sediment for both runoff periods (Fig. 4.2b). For the STC watershed, the uncorrected source soil As concentrations showed no significant differences; however, the uncorrected source soil Mn concentrations did have significantly higher concentrations as compared to the eroded sediment for both runoff periods (Figs. 4.2c and 4.2d).

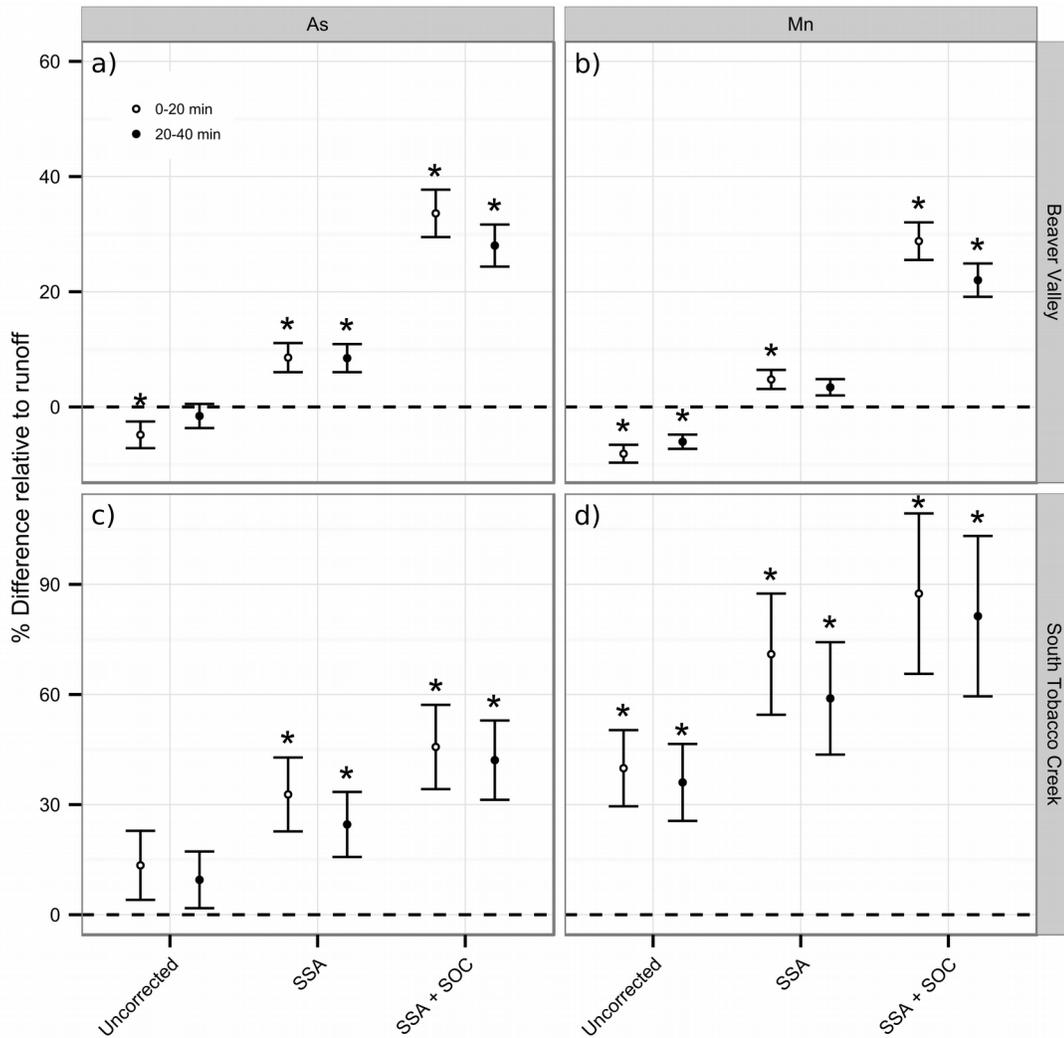


Figure 4.3: The percent difference in As and Mn concentrations for uncorrected, particle size corrected (SSA), and the combined particle size and organic matter corrected (SSA + SOC) source soils relative to the eroded sediment for the Beaver Valley, BC, and South Tobacco Creek, MB watersheds. Values are mean  $\pm$  the standard error and \* denotes significantly different than 0 (p-value < 0.05).

In addition to sieving to remove the coarse-grained sediment, particle size correction factors are the most widely used method within sediment fingerprinting studies to account for differences in particle size between source and eroded sediment. The application of the particle correction factor resulted in an over-correction for both elements, watersheds and runoff periods with the exception of the Mn concentration in the BV watershed for the 20 –

40 min runoff period (Fig. 4.2b). The  $SSA_{corr}$  resulted in a greater overestimation for As as compared to Mn within the BV watershed and the opposite trend is seen in the STC watershed where the overestimation is greater for Mn as compared to As. Overall, the over-correction was higher in the STC with an average overestimation of 28.7 and 65.0 % relative to the eroded sediment for As and Mn, respectively. The lack of consistent trends between elements and watersheds after correcting for differences in particle size, highlights the potential issue whereby the elements selected as fingerprints may be more dependent on the correction factor rather than any inherent differences in geochemical composition between sediment sources. This uncertainty in particle size correction factors has lead some studies to not use correction factors (e.g., Martínez-Carreras et al. 2010).

Both a particle size and an organic matter content correction factor are often used to account for differences in both properties between source soils and eroded sediment (e.g., Collins et al. 2012). However, the combined use of both particle size and organic matter correction factors resulted in an over-correction in both the As and Mn concentrations for the source soil relative to the eroded sediment for both watersheds and runoff periods. This is in agreement with researchers that do not use both particle size and organic matter correction factors citing the risk of over-correction of the data (e.g., Dutton et al. 2013). The relation between particle size, organic matter and their interaction on the concentration of many geochemical concentration in soils and sediment is not well quantified and it may be difficult to generalize. Other methods to account for differences in organic matter include expressing geochemical concentration on a mineral basis or ashing samples prior to analysis (e.g., Wilkinson et al. 2013).

#### **4.4.3 The relation between geochemistry and source soil and eroded sediment properties**

A summary of the relation between the geochemical concentrations and SSA for the BV watershed are presented in Fig. 4.3. For three elements (B, Na and Sn) the relation between concentration and SSA were non significant due to the low resolution of the elemental analysis for the observed range in concentration. For example, the range in B concentration ranged from 10 to 40 ppm and the resolution was 10 ppm. Furthermore, the relation between concentration and SSA for six other elements (Cd, Cu, Pb, Sb, Se, Zn) required a transformation to meet the assumptions of linear regression. Of the remaining 35 elements, 24 demonstrated a significant positive relation between concentration and SSA; however, 18 of those elements had a significant interaction between SSA and sample type (i.e., source soil, 0 – 20 min and 20 – 40 min runoff). Similarly, of the 11 elements that do not demonstrate a significant relation, 10 also had a significant interaction between SSA and sample type.

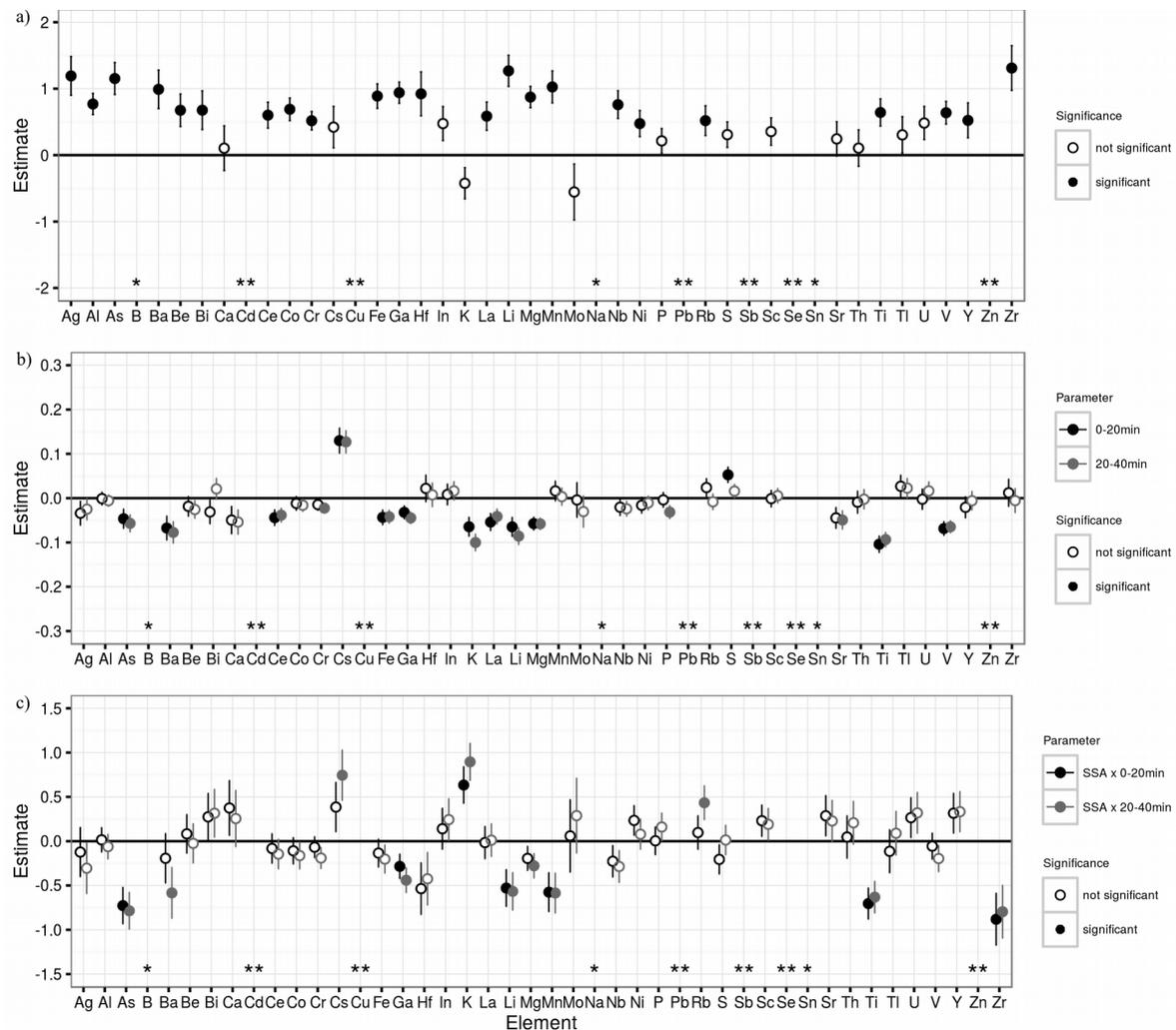


Figure 4.4: Summary of the model parameter estimates (mean  $\pm$  1 standard error) for the relation between geochemical concentration and SSA for the Beaver Valley, BC, watershed. Model parameters: (a) SSA; b) sample type (source soil as the reference level); and c) interaction between SSA and sample type (source soil as the reference level). \* low analytical resolution \*\* data transformation needed to meet model assumptions.

A summary of the relation between the geochemical concentrations and SSA for the STC watershed are found in Fig. 4.4. The relation between concentration and SSA were non significant due to the low resolution of the elemental analysis for the observed range in concentration for B, Na, Sn and Ti. Furthermore, the relation between concentration and SSA for 11 other elements (Ca, Co, Li, Mg, S, Sb, Sc, Sr, Th, U, V) required a transformation to

meet the assumptions of linear regression. Of the remaining 29 elements, 23 demonstrate a significant positive relation between concentration and SSA; however, 16 of those elements have a significant interaction between SSA and sample type. Similarly, of the six elements that do not demonstrate a significant relation all have a significant interaction between SSA and sample type.

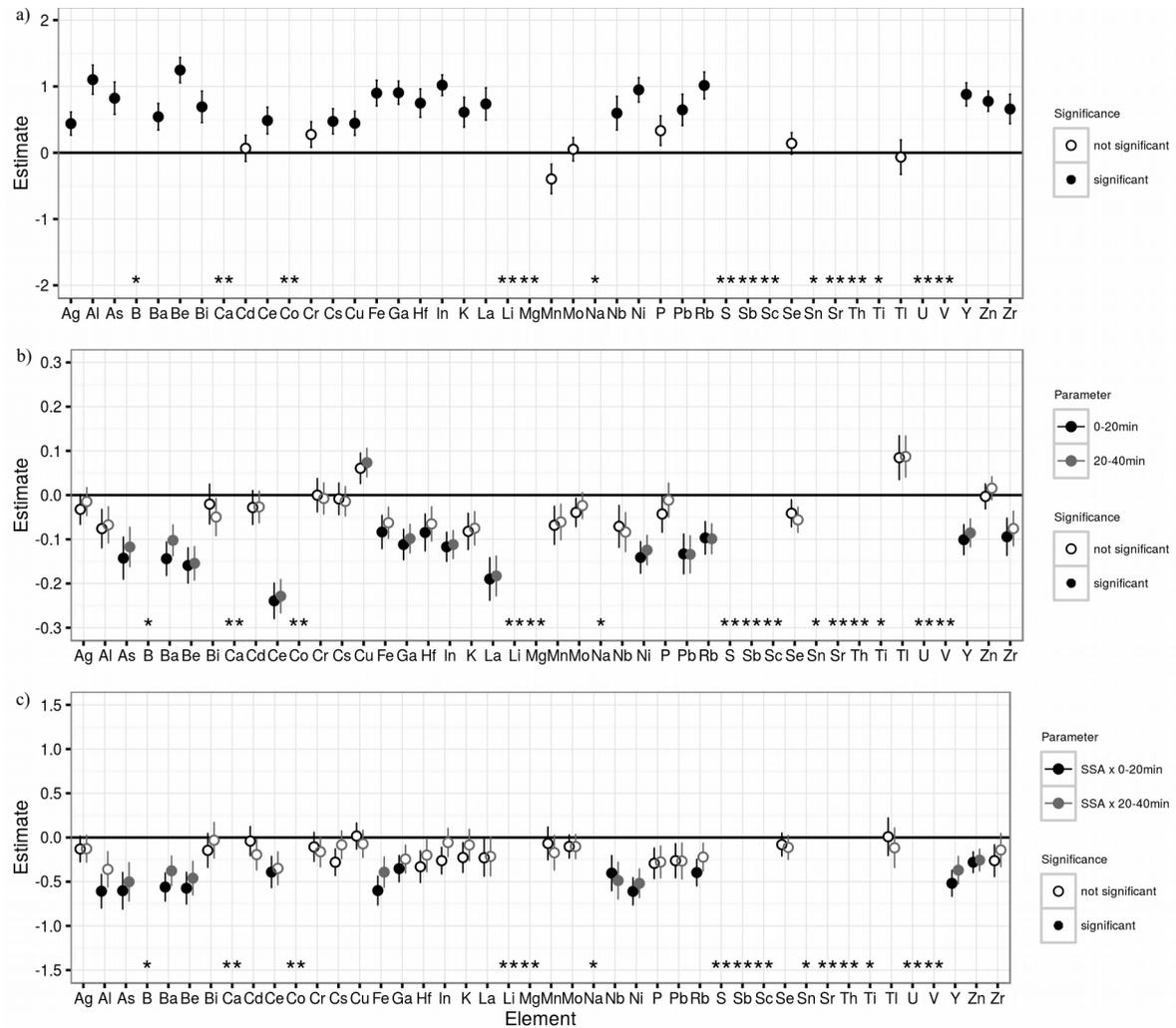


Figure 4.5: Summary of the model parameter estimates (mean  $\pm$  1 standard error) for the relation between geochemical concentration and SSA for the Beaver Valley, BC, watershed. Model parameters: (a) SSA; b) sample type (source soil as the reference level); and c) interaction between SSA and sample type (source soil as the reference level). \* low analytical resolution \*\* data transformation needed to meet model assumptions.

There are few similarities between elements and the two watersheds investigated which implies that the use of a single particle size correction factor for a broad suite of elements may be problematic. Furthermore, for a subset of elements investigated a significant interaction between SSA and sample type was present. This interaction provides that the relation between the geochemical concentration and SSA is not the same between the source soil and eroded sediment. This result indicates that developing a relation between geochemical SSA based on the size fractionation of source soils may still not be adequate. The interaction may in part be explained by the process of particle selectivity whereby changes in organic matter content confound the effect of SSA. In addition, there are a number of elements where the concentration data needed to be transformed to meet the model assumptions suggesting that the assumption of a straightforward linear relation between concentration and SSA may not be appropriate for all elements. The role of both SSA and organic matter content and their interactions on the geochemistry of both source soils and eroded sediment are explored in more detail below.

The relation between the concentration of a geochemical element and SSA and SOC was different between elements and also between watersheds and it was difficult to generalize the relations due to differences in the direction and magnitude of the slope and interactions between the SSA, SOC and sample type (i.e., source soil and eroded sediment). To highlight the variety in the relations, two elements, As and Mn were selected as examples (Table 4.2 and Figs. 4.6 and 4.7). There was an overall positive relation between the concentration of As and SSA within the BV watershed (Fig. 4.6a). However, there was also a significant interaction between the SSA and the sample type (i.e., source soil and eroded sediment) as illustrated by the different slopes for the regression lines. This indicates that the

relation between the As concentration and SSA was not the same for the source soil and the eroded sediment as the source soil had a steeper slope as compared to the eroded sediment.

The relation between the As concentration and the SOC content was different than that of the SSA as there was an overall negative relation between concentration and SOC (Fig. 4.6b).

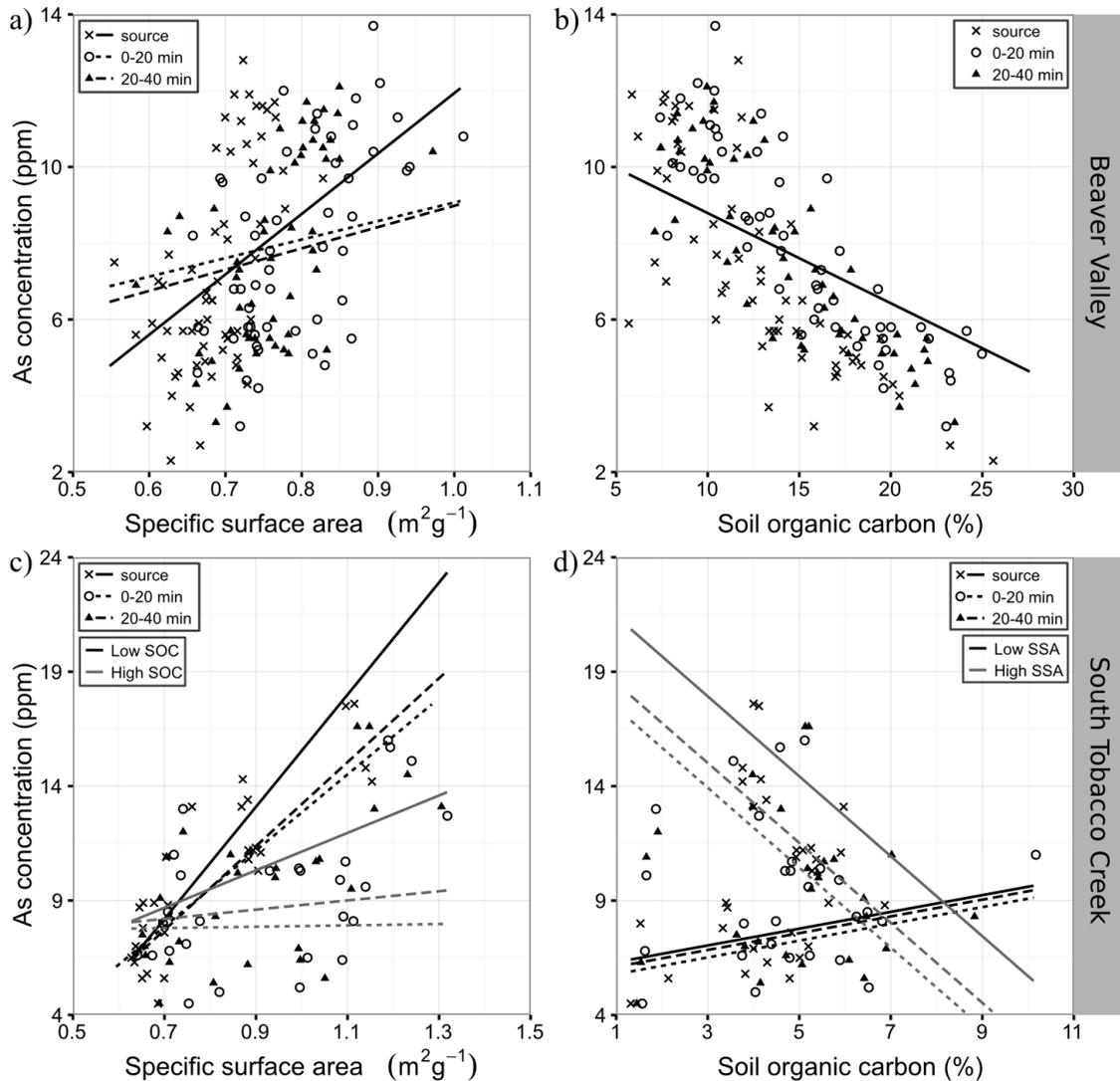


Figure 4.6: The relations between As concentration and SSA and SOC in the source soils and eroded sediment for the Beaver Valley, BC, and South Tobacco Creek, MB, watersheds. See Table 4.2 for additional details.

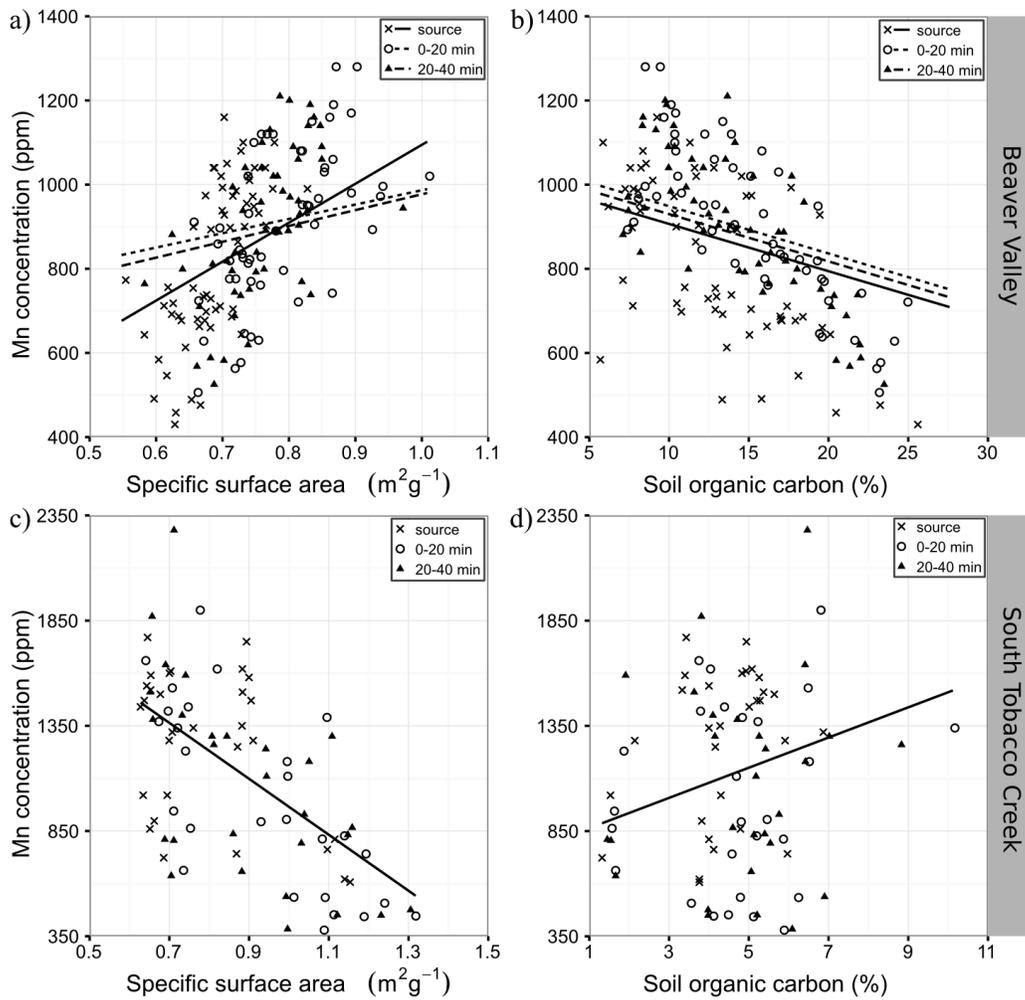


Figure 4.7: The relations between Mn concentration and SSA and SOC in the source soils and eroded sediment for the Beaver Valley, BC, and South Tobacco Creek, MB, watersheds. See Table 4.2 for additional details.

Table 4.2: Results of linear mixed effects models assessing the the correlation in the concentrations of Mn and As with SSA and SOC in the Beaver Valley and South Tobacco Creek watersheds.

Analysis	Parameter	Estimate	Std. Error	DF	t value	P(> t )	
<b>Beaver Valley Mn concentration (ppm)</b>	(Intercept)	865.99	49.06	99	17.65	< 0.001	***
	SSA	925.65	200.33	99	4.62	< 0.001	***
	SOC	-11.23	2.82	99	-3.98	< 0.001	***
	Source vs 0-20 min	42.08	19.57	99	2.15	0.03	*
	Source vs 20-40 min	23.32	17.02	99	1.37	0.17	
	Slope position (upper vs mid)	-29.27	19.68	52	-1.49	0.14	
	Slope position (lower vs mid)	2.72	21.20	52	0.13	0.90	
	SSA X Source vs 0-20 min	-584.98	185.63	99	-3.15	< 0.001	***
	SSA X Source vs 20-40 min	-549.15	189.10	99	-2.90	< 0.001	***
<b>South Tobacco Creek Mn concentration (ppm)</b>	(Intercept)	1198.79	117.46	50	10.21	< 0.001	***
	SSA	-1330.08	306.66	50	-4.34	< 0.001	***
	SOC	71.71	35.74	50	2.01	0.05	*
	Slope position (upper vs mid)	-120.38	69.89	50	-1.72	0.09	
	Slope position (lower vs mid)	-101.60	65.15	50	-1.56	0.13	
	Source vs 0-20 min	-31.75	94.49	23	-0.34	0.74	
	Source vs 20-40 min	56.50	93.68	23	0.60	0.55	
	SSA X SOC	-322.48	199.35	50	-1.62	0.11	
<b>Beaver Valley As concentration (ppm)</b>	(Intercept)	8.10	0.49	99	16.66	< 0.001	***
	SSA	15.84	2.70	99	5.87	< 0.001	***
	SOC	-0.24	0.04	99	-5.95	< 0.001	***
	Source vs 0-20 min	-0.05	0.26	99	-0.20	0.85	
	Source vs 20-40 min	-0.32	0.23	99	-1.42	0.16	
	Slope position (upper vs mid)	-0.01	0.36	52	-0.04	0.97	
	Slope position (lower vs mid)	-0.67	0.38	52	-1.77	0.08	
	SSA X Source vs 0-20 min	-10.98	2.39	99	-4.59	< 0.001	***
	SSA X Source vs 20-40 min	-10.27	2.41	99	-4.25	< 0.001	***
<b>South Tobacco Creek As concentration (ppm)</b>	(Intercept)	10.39	0.61	48	17.14	< 0.001	***
	SSA	16.34	2.43	48	6.72	< 0.001	***
	SOC	-0.69	0.23	48	-3.05	< 0.001	**
	Source vs 0-20 min	-2.26	0.54	48	-4.15	< 0.001	***
	Source vs 20-40 min	-1.55	0.54	48	-2.86	0.01	**
	Slope position (upper vs mid)	2.16	0.71	23	3.04	0.01	**
	Slope position (lower vs mid)	0.49	0.72	23	0.68	0.50	
	SSA X Source vs 0-20 min	-7.88	2.79	48	-2.82	0.01	**
	SSA X Source vs 20-40 min	-6.17	2.80	48	-2.21	0.03	*
	SSA X SOC	-4.80	1.41	48	-3.41	< 0.001	***

\* significant at  $p > 0.05$ ; \*\* significant at  $p > 0.01$ ; \*\*\* significant at  $p > 0.001$

Similar to the BV watershed, for the STC watershed there was an overall positive relation between the As concentration and SSA as well as an interaction showing that the relation is different between source soil and eroded sediment (Fig. 4.5c). However, there is

also a significant interaction between the SSA and SOC indicating that within the STC watershed the relation between As and SSA is dependent on the SOC content with soils and eroded sediment with a lower SOC having a more positive relation with SSA as compared to soils and eroded sediments with a high SOC content. The relation between the As concentration and SOC is dependent on the SSA of the source soil and eroded sediment, as samples with a lower SSA (i.e., coarser) have a positive relation and in contrast samples with a higher SSA (i.e., finer) showed a negative relation between concentration and SOC (Fig. 4.5d). Furthermore, similar to the BV watershed the relation between elemental concentration and SOC were similar between source soil and eroded sediment.

The relation between the concentration of Mn and SSA as well as SOC followed a similar pattern to the As concentration within the BV watershed. There was an overall positive relation between concentration and SSA with a significant difference in the relation between the source soil and the eroded sediment (Fig. 4.6a). As well, there was also an overall negative relation between the concentration of Mn and SOC (Fig. 4.6b). Within the STC watershed, the relation between the concentration of Mn and SSA had had an overall negative correlation (Fig. 4.6c) which is in contrast to the positive trend found within the BV watershed. In addition, there was an overall positive relation between the concentration of Mn and SOC (Fig. 4.6d), however, the opposite trend is observed within the BV watershed. Another interesting difference between the two elements, As and Mn, within the STC watershed is that there is a significant interaction between SSA and SOC for As but not for Mn.

For some of the elements investigated, a considerable component of the variation within the models was due to the random factor of transect. For example, the transect

accounted for 69 and 34 % of the total variance for Mn for BV and STC watersheds, respectively. In contrast, the transect accounted for less of the total variance for As with transect accounting for only 25 and < 1 % for the BV and STC watersheds, respectively.

## **4.5 Discussion**

### **4.5.1 Accounting for particle selectivity**

It is typically assumed that the source soil would have lower geochemical concentration as compared to eroded sediments due to the presence of coarser-grained and less reactive particles in the source soil. This material does not often get eroded due to the particle size selectivity of soil erosion processes and this phenomenon results in differences in both particle size and organic matter between source soil and eroded sediment. There are two basic approaches that can be used individually or in combination for accounting for the difference in both particle size and organic matter: 1) sample preparation; and 2) correction factors. These two approaches are discussed below.

Limiting the analysis to the fine-grained fraction (< 63  $\mu\text{m}$ ) by sieving was shown to effectively reduce differences in particle size and SOC between source soil and eroded sediment in the two study watersheds (Chapter 3). Some studies sieve to a smaller grain-size to further reduce the differences between source and eroded soil (e.g., < 10  $\mu\text{m}$ ; Wilkinson et al. 2013) but this may reduce the representativeness of the mobilized or transported sediment. Fractionating soils and sediment into different fractions (e.g., 40 – 63, 20 – 40, 2 – 20 and < 2  $\mu\text{m}$ ) and comparing similar sediment sizes can be an effective method (e.g., Motha et al. 2004; Haddadchi et al. 2015) but the fractionation process is time consuming and adds additional laboratory costs. In order to isolate the influence of organic matter on geochemical

properties, Motha et al. (2002) separated the organic matter from the mineral component by flotation in water and the organic matter was analyzed for geochemistry, however, this technique has not been well described or tested. The method of sample processing prior to geochemical analysis is an important consideration and needs to balance the benefits of reducing the differences in particle size and organic matter content between source and sediment while still remaining representative of transported sediment.

One of the main objectives of this study was to investigate the commonly used correction factors, based on the ratio of SSA and SOC between collected sediment and source soils. The data presented in this study demonstrated that these correction factors are not very effective in accounting for the observed differences in the geochemical composition between source soil and eroded sediment. Generally, the uncorrected source material had a more similar geochemical composition to the eroded sediment as compared to the corrected source. Furthermore, the influence of the correction factors varied between the two watersheds as well as between different elements. The tendency of the correction factors to over-correct geochemical concentration and the large range in the observed differences suggests that the use of correction factors, within the sediment fingerprinting approach, can change the geochemical elements selected as fingerprints and ultimately the apportionment results (Smith and Blake 2014). There is currently a need for researchers to be more forthcoming about the potential errors and uncertainty associated with the use of untested correction factors (Smith et al. 2015).

#### **4.5.2 Influence of particle size and organic matter on the geochemical composition of soil and sediment**

The relation between geochemical concentrations and both SSA and SOC was found to vary between elements and watersheds. This suggests that it is difficult to generalize the relations and that a detailed study may be needed to fully quantify the effects of particle size and SOC on geochemical concentrations. For example, Russell et al. (2001) investigated the relations between geochemical, radionuclide and mineral magnetic concentrations and SSA of source samples. To accomplish this, source samples were separated into progressively smaller grain size fractions and the fingerprint concentrations were measured for each size fraction. This information can then be used to develop watershed- and element-specific correction factors (e.g., Motha et al. 2002; Gellis and Noe 2013). In addition, this study demonstrated that the relations were different between source soil and eroded sediments which suggests that collecting actively eroding sediments may provide a better characterization of sediment sources in some watersheds as opposed to the more common approach of using soil surface scrapes and then correcting for differences in SSA and SOC.

Some of the variability observed in terms of the relation between geochemical concentrations and SSA or SOC may be a result of differences in mineralogy and the affinity and selectivity of different ions to particle surfaces between the different size classes. For example, among three different watersheds, Russell et al. (2001) found that the relation between different fingerprint concentrations and SSA was not uniform. In addition, Bakircioglu et al. (2010) demonstrated, through sequential extractions, that the partitioning of the total concentration of trace elements between the water and weak-acid (soluble and

exchangeable), reducible (bound to Fe- and Mn-oxides), and oxidizable (bound to organic matter and sulphides) fractions varied between elements. As a consequence, the large variability observed in this study does not support the application of the same particle size and organic matter content correction factors for all elements.

The transect variable accounted for much of the scatter of data points about the regression line (Figs. 4.6 and 4.7) and may be attributed to overall differences in either SSA or SOC between different transects. This indicates that, for some elements, there was considerable variation across the landscape and that the sampling design used to characterize the geochemical composition of potential sediment sources needs to consider this spatial variability. However, the impact of sampling design (i.e., spatial extent and number of samples) on the sediment fingerprinting approach has not been well explored

The resolution of the geochemical analysis for some of the elements was not sufficient to have a clear indication as to the influence of particle size or organic matter. Furthermore, seven elements were not considered as part of this study as one or more samples had concentration below the detection limit, making comparisons between source soil and eroded sediment or assessing the relation with both SSA and SOC less straightforward. The majority of sediment fingerprinting studies remove fingerprints that contain values below the detection limit or replace these values with an arbitrary value such as 1/2 the detection limit. This can result in either the removal of elements that may provide good discrimination between potential sediment sources or bias the values. There are both parametric and non parametric statistical methods available that can accommodate left censored data and provide a more robust method of dealing with such data (e.g., Helsel 2012). However, such methods have not been widely explored within the sediment

fingerprinting.

## **4.6 Conclusions**

Sediment fingerprinting is increasingly being used as a tool to assess the sources of sediment at the watershed scale. However, one of the limitations of the technique is the ability to link the sources to sediment in a reliable and robust manner. This research begins to bridge this research gap by investigating the particle size and organic matter selectivity of the soil erosional processes under simulated rainfall and its subsequent effect on the geochemical composition of eroded sediment. Despite limiting the analysis to the < 63  $\mu\text{m}$  fraction, there was still an enrichment of small and organic-rich particles in the eroded sediment and consequently a change in the geochemical composition. The use of correction factors was found not be very effective at adjusting for the differences in the geochemical composition between source soil and eroded sediment. This raises concerns about the use of correction factors and the subsequent effect on the fingerprint selection process and the potential error grounding the final apportionment results. It is generally advisable to investigate the relation between SSA, SOC and geochemical concentrations prior to correcting fingerprint data as the relations are both watershed- and element-specific.

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## **5 Particle size and organic carbon selectivity within edge-of-field and riparian zones and its implications for sediment fingerprinting**

### **5.1 Abstract**

The unique sedimentological and hydrological processes within riparian zones will buffer and intercept the delivery of sediment, nutrients and geochemical elements from up-slope. Because of this, the riparian zone is of particular interest in terms of the effects it is likely to have on the conservative behaviour of sediment and associated fingerprinting properties. This study investigated the effects of the riparian zone, within an agricultural landscape, on the accumulation of soil, and its subsequent particle size distribution, soil organic carbon (SOC) concentration and geochemical composition. This was accomplished by investigating a series of soil profiles along a transect that extended from the upper landscape position to the riparian zone. The greatest amount of soil deposition occurred within the lower landscape position, but there was also significant accumulation in the riparian zone. Overall, the soil in the riparian zone was finer-grained and had a greater SOC concentration as compared to the other landscape positions which suggests that particle size selectivity occurred as material entered into the riparian zone. It was not clear whether the difference in SOC concentration between the riparian and other landscape positions was resulting from the preferential deposition of SOC-rich particles or due to the loss or dilution of SOC due to soil disturbance (i.e., tillage). Furthermore, the riparian area had a distinct geochemical composition. While particle size and SOC concentration could explain some of the observed trends it is likely that

biogeochemical processes within the riparian zone contributed significantly to the observed geochemical composition. This research helps to explain how the riparian zone may influence sediment fingerprint properties and provides guidance on how to characterize potential sediment sources.

## **5.2 Introduction**

Agricultural land use and intensification has been associated with accelerated soil erosion and a subsequent increase in suspended sediment and nutrient loads in surface waterways (Vörösmarty et al. 2010). This has a negative impact on the aquatic ecosystem in terms of changes in the composition and abundance of aquatic plants and animals (Shaw and Richardson 2001; Rabení et al. 2005; Harrison et al. 2007) and it also impacts the quality of water used for drinking, irrigation, power generation and recreation (Vörösmarty et al. 2003; Vörösmarty et al. 2010). This type of pollution can be difficult to manage as it is typically low-dose and has high spatial and temporal variability (i.e., non-point source pollution). As a result, identifying and targeting management decisions that will maximize both soil conservation and water quality while still being cost effective can be difficult (Owens 2008). Reliable and robust information on the contributions of different sources of sediment within a watershed is required to guide the decision-making process (Smith et al. 2011).

Sediment fingerprinting is a technique that has been used since the 1970's to identify the sources of sediment within a watershed and over the past decade its use has risen dramatically (Mukundan et al. 2012; Walling et al. 2013; Koiter et al. 2013b). This technique is based on two main concepts: 1) that sediment collected down stream will reflect the physical, biological, geochemical and radiochemical properties of the original source

materials; and 2) different sources of sediment can often be differentiated based on differences within these properties (i.e. each source has a unique fingerprint) (Walling et al. 1999; Mukundan et al. 2012). A statistical mixing model is then used to estimate the relative contributions of each source to the collected sediment (for an overview of the technique, see Davis and Fox 2009). At the core of this concept is the assumption that the properties of the source material remain unaltered as the material is transported from source to sink. However, this is rarely the case, because through the processes of soil erosion, sediment delivery and fluvial transport there are typically changes in the particle size distribution and organic matter content of the sediment (e.g., Walling 1983). This is a result of particle size and organic matter selectivity, as the smaller and less dense particles are preferentially mobilized and transported (e.g., Koiter et al. 2015). To make a direct link between source material and sediment these changes in particle size and organic matter content need to be accounted for within the sediment fingerprinting approach as both particle size and organic matter have been shown to influence the concentration of some fingerprint properties (e.g, trace metal concentrations) through the high specific surface area and chemical reactivity of this material (Horowitz 1991). In addition, there are other biogeochemical processes that can also change the properties of sediment during transport through a watershed, which include adsorption/desorption, precipitation/dissolution and microbial mediated transformations (Rodrigues et al. 2010).

How to best account for these changes in sediment properties has been identified as a major limitation of the fingerprinting approach (Davis and Fox 2009). Typically both source and collected sediment are sieved (e.g., < 63  $\mu\text{m}$  or < 10  $\mu\text{m}$ ) prior to characterization in an effort to limit the differences in the particle size distribution and organic matter content (e.g.,

Wilkinson et al. 2015). However, after sieving there is often still a difference, thus a particle size correction factor, and sometimes an additional organic matter correction factor, are used to adjust the tracer values of the source samples. These correction factors are based on the ratio of specific surface area (SSA) or soil organic carbon (SOC) content of the collected sediment to the source material (e.g., Collins et al. 1997). This correction assumes that the relation between the tracer properties and both SSA and SOC are linear and of the same magnitude and direction, which may not always be correct. Research by Smith and Blake (2014) demonstrated that the conclusions drawn from sediment fingerprinting were dependent on whether or not correction factors were used. Furthermore, biogeochemical changes are more difficult to assess and account for and, therefore, these processes are often not considered. However, tracers that have been shown to be susceptible to these types of changes (e.g., P) are typically excluded from analyses (Owens et al. 1999; e.g., Smith and Blake 2014).

The riparian zone is the linkage between the terrestrial and aquatic environments and as a result is characterized by very distinct gradients in environmental conditions and processes. The riparian zone has a number of processes, including infiltration, immobilization, sedimentation and dilution, that act to buffer and intercept the flow of both dissolved and particulate material to the aquatic environment (Lacas et al. 2005; Owens et al. 2007; McGuire and McDonnell 2010). Because of these properties, the retention or installation of riparian zones (also referred to as buffers, vegetated buffer strips or vegetative filter strips) along streams is a common best management practice used in agricultural regions to moderate stream temperatures, stabilize stream banks and reduce the amount of sediment- and nutrient-rich agricultural runoff entering surface waterways (Dillaha et al.

1989; Borin et al. 2005; Dorioz et al. 2006). However, the location, design characteristics and maintenance of riparian zones are important factors to consider when assessing their efficacy in achieving water quality goals (Deeks et al. 2012). In addition, the temporal variability of material entering the riparian zone (e.g., during intense precipitation and snowmelt events), coupled with the spatial heterogeneity of physical and biogeochemical processes (e.g., due to topography and vegetation composition) are important considerations when assessing the overall buffering capacity of riparian zones (McClain et al. 2003; Vidon et al. 2010). Furthermore, the importance of riparian zones in linking sediment sources to in-stream sediment, in terms of particle selectivity and biogeochemical transformations is not well understood and is rarely, if at all, considered within the sediment fingerprinting approach.

$^{137}\text{Cs}$  has been successfully used to both estimate the rate and describe the pattern of soil erosion in agricultural landscapes (e.g., Li et al. 2008).  $^{137}\text{Cs}$  (half-life of 30.2 years) was mostly produced and released into the atmosphere through above ground nuclear weapons testing during the 1950s and 1960s. The subsequent deposition (fallout) of this radionuclide was regionally uniform and  $^{137}\text{Cs}$  is rapidly and strongly absorbed by fine-grained soil particles at the soil surface such that its concentration declines rapidly with depth. The redistribution of  $^{137}\text{Cs}$  across the landscape (i.e., inventory values) reflect the movement of soil particles and, therefore, provide information on the pattern and rates of soil erosion and deposition within the landscape over the last ~60 years. For an overview of the application of  $^{137}\text{Cs}$  to measure soil erosion rates and patterns see Ritchie and McHenry (1990).

Soil erosion processes on the hillslope determine both the quantity and quality of material being transported to the riparian zone. Riparian processes can then modify these properties through particle selectivity and biogeochemical processes as material moves

through to surface waterways. Both laboratory and field studies have demonstrated that riparian zones are generally effective at trapping sediments (reviewed in Zhang et al. 2010) and particle size selectivity within the riparian zone occurs through the selective deposition of delivered material. For example, Gharabaghi et al. (2006) found that larger soil particles and aggregates were generally trapped within the first few meters of a buffer and that fine-grained particles were transported further distances thereby resulting in the selective enrichment of fine-grained sediments and associated tracer properties being exported from the buffer to adjacent surface waterways. However, convergent topography within the landscape can concentrate runoff which can inundate riparian zones resulting in a decrease in the efficiency of riparian zones to trap of sediment (Daniels and Gilliam 1996; Dosskey et al. 2002; Helmers et al. 2005). A reduction in trapping efficiency can result in a decrease in particle size selectivity due to greater flow depth and velocity of the runoff (Bu et al. 2016).

The majority of nutrient and metal retention and accumulation within the riparian zone is due to sedimentation, absorption of elements onto soil particles and the uptake by vegetation (Hoffmann et al. 2009). The hydrologic regime of the riparian zone is different than up-slope positions due to its proximity to the channel environment and is characterized by an overall higher moisture status and a fluctuating water table. The anaerobic environmental conditions often found in riparian areas can facilitate the precipitation of sulphide minerals (e.g., ZnS) and slow down the decomposition of organic matter (Du Laing et al. 2010). Furthermore, Rinklebe et al. (2016) found that the concentration of As, Fe and Mn in soil pore water increased under reducing conditions while the release of Ba, Cd, Cu, and Sr to soil solution increased under oxidizing conditions. These changes in redox conditions can have implications for the sediment fingerprinting approach because the

fingerprint of material passing through the riparian zone may be altered (Taylor et al. 2012).

There is little advice in the literature on how best to include riparian zones within the sediment fingerprinting approach. Samples taken within the riparian zone may be considered representative of: 1) the contributing area up-slope; 2) a unique source separate from up-slope sources; or 3) a section of the stream bank (i.e., uppermost portion of the stream bank). The objectives of this research were: (1) to examine patterns of soil erosion and accumulation along the transect; (2) to characterize the changes in particle size, soil organic carbon content and geochemical composition along the transects; and (3) to discuss the implications of riparian processes for sediment fingerprinting.

### **5.3 Materials and methods**

Soil samples were collected from soil profiles that were setup along transects that extended from the upper landscape position through to the riparian zone in two agricultural fields in southern Manitoba, Canada. These samples were used to determine how erosional and riparian processes affect the particle size distribution, organic carbon content and the concentration of a variety of geochemical elements.

#### **5.3.1 Site 1**

Site 1 was originally sampled and investigated by Vandenbygaart et al. (2012) as part of a larger study assessing soil organic carbon (SOC) erosion and burial in Canadian cropland. This site is situated in south-central Manitoba (MB), Canada, near the town of Miami (Fig. 5.1) the soils in the region are calcareous Black Chernozems with a loam/silt loam texture (Vandenbygaart et al. 2012). A soil profile was excavated at upper, mid, lower and riparian landscape positions and soil samples were collected in 5 cm intervals throughout

the entire depth of the A horizon. The upper, mid and lower landscape positions were within an oil seed and cereal cropping system and the riparian zone was predominately comprised of deciduous woodland vegetation.  $^{137}\text{Cs}$  radioactivity was measured on air-dried and sieved (<2 mm) soil samples at 662 keV using broad-energy germanium gamma spectrometers with a counting time ranging from 12 to 24 h. Total  $^{137}\text{Cs}$  inventories ( $\text{Bq m}^{-2}$ ) for each soil profile were calculated utilizing bulk density measurements and are reported in Vandenbygaart et al. (2012). The samples collected by Vandenbygaart et al. (2012) were further analyzed using the methods described below.

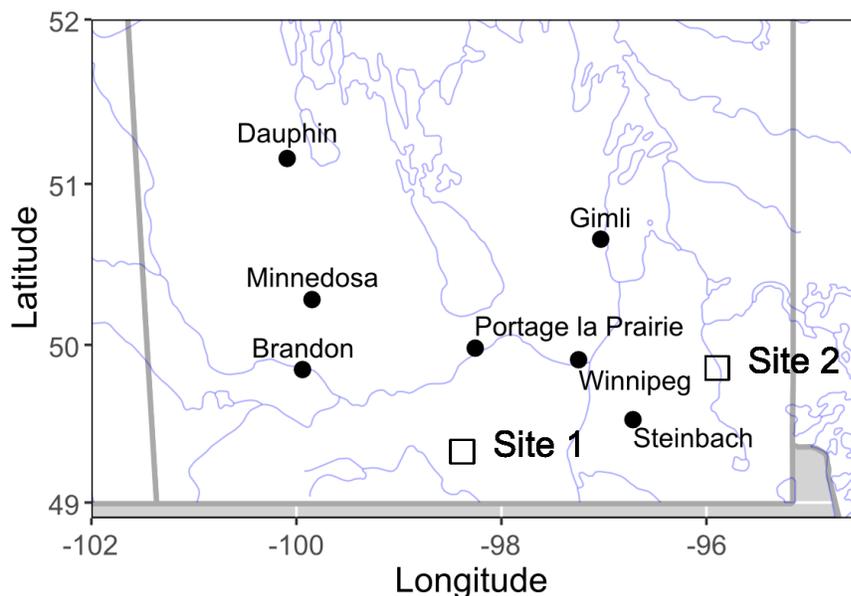


Figure 5.1: Map of southern Manitoba, showing the locations of the two study sites.

#### 5.3.1.1 Particle size analysis

The soil samples were weighed (~ 10 g) placed in 100 mL beakers and deionized water was added to make a 1:5 (soil:water, by volume) slurry. The samples were disaggregated using an ultrasonic probe (Misonix S-4000, Qsonica, Newtown, CT, USA) with a power output of 45 W and the duration of sonication for each sample was adjusted so

that the amount of energy delivered was  $300 \text{ J mL}^{-1}$  (based on the total sample volume) (Yang et al. 2009). The samples were sonicated while in an ice bath and the sonication energy was pulsed (2 min on, 1 min off) to prevent the over heating of the sample and probe. Samples were washed through a  $63 \mu\text{m}$  sieve and transferred into a 1000 mL beaker and oven-dried. All further analyses described below were confined to the  $< 63 \mu\text{m}$  fraction.

Each soil sample ( $< 63 \mu\text{m}$ ) was subsampled for particle size, organic carbon (Section 5.2.1.2) and geochemical analyses (Section 5.2.1.3). For the absolute particles size analysis, samples were digested with hydrogen peroxide (35 %) to remove organic matter and an aliquot of a solution of sodium hexametaphosphate and sodium carbonate was added following the procedure of Kroetsch and Cang (2007). The samples were re-sonicated following the same procedure outlined above. The median particle size ( $d_{50}$ ) of the samples were measured using a laser diffraction system (Malvern Mastersizer 3000, Malvern, UK) (0.01 – 3500  $\mu\text{m}$  diameter measurement range).

#### *5.3.1.2 Soil organic carbon analysis*

Organic carbon (C) was measured as the C contained within the  $< 63 \mu\text{m}$  size fraction. Similar to Vandenbygaart et al. (2012), no pretreatment was used to remove inorganic forms of carbon as test samples did not effervesce with the addition of 10 % hydrochloric acid and the pH (1:2 ratio of soil to water) of the soils were  $< 7.5$  which indicate that carbonates were not present in significant quantities. Therefore, total C was used to estimate organic C content. Total C analysis was measured using an elemental analyzer (Elemental Combustion System ECS-4010, Costech Analytical Technologies Inc, Valencia, CA, USA).

### 5.3.1.3 Geochemical analysis

Samples were analyzed for a broad suite of geochemical elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn and Zr) using ICP-MS following a microwave-assisted digestion with aqua-regia (ALS Mineral Division, North Vancouver, BC, Canada). Of the 51 elements investigated seven (Au, B, T, W and Ge) were below the detection limit in one or more of the samples and were removed from all analyses.

### 5.3.2 Site 2

Site 2 was originally sampled and investigated by Lobb (2012) as part of a larger study assessing the efficacy of riparian zones to filter sediment and phosphorus from agricultural runoff. The site is situated in south-eastern Manitoba (MB), Canada, near the town of Elma (Fig. 5.1). The soils in the region are Gleyed Dark Gray Luvisols with a loam soil texture (Smith and Ehrlich 1967). A soil profile was excavated at several points along a transect that ran along the dominant flow path from the mid-slope landscape position through to the riparian zone. Soil samples were collected in 5 cm intervals throughout the entire depth of the A horizon. The field was characterized as an oil seed and cereal cropping system and the riparian zone was comprised predominately of grass and sedge.  $^{137}\text{Cs}$  radioactivity was measured, and total  $^{137}\text{Cs}$  inventories in each profile were calculated (data from Sheppard et al. 2012), using the same methodology described for site 1 (Section 5.2.1). The particle size analysis methods are described below.

### *5.3.2.1 Particle size analysis*

For the absolute particles size analysis, samples were digested with hydrogen peroxide (35 %) to remove organic matter and an aliquot of a solution of sodium hexametaphosphate and sodium carbonate was added following the procedure of Kroetsch and Cang (2007). The samples were washed through a 500- $\mu\text{m}$  sieve to remove coarse sands. The median particle size (d50) of the samples were measured using a Malvern Mastersizer 2000 laser diffraction system (Malvern, UK) (0.02 – 2000  $\mu\text{m}$  diameter measurement range) and the range of the analysis was limited to the  $< 63 \mu\text{m}$  to be consistent with the particle size analysis for site 1.

### **5.3.3 Data analysis**

All statistical analysis was undertaken using R Statistical Software v3.2 (R Core Team 2015) through RStudio Integrated Development Environment v0.98.1103 (RStudio 2016). All graphical plots were created using the R package ggplot2 v0.9.3.1 (Wickham 2009). The Kruskal-Wallis H-test was used to select elements that showed a significant difference (p-value  $< 0.05$ ) in concentrations between the sample groups (i.e., landscape position and surface/subsurface samples). Principle component analysis (PCA) was then used to analyze variance in the resulting multi-element dataset to reduce the dimensionality in an effort to see how the different sample types differentiated based on the geochemical composition. Plots show both the score and loading for the first two principal components. Pearson correlation coefficients were also calculated to assess the relation between geochemical concentration, d50, SOC and depth for site 1.

## 5.4 Results

### 5.4.1 Patterns of soil erosion and deposition

The  $^{137}\text{Cs}$  inventories (Figs. 5.2a and 5.3a) can be used to identify the patterns of soil erosion and deposition, as a result of both tillage and water erosion processes, by comparing inventories along the transect with a reference level (inventory at a location that has experienced no or minimal erosion and deposition). Site 1 (Fig. 5.2a) shows a small amount of net soil erosion (i.e.,  $^{137}\text{Cs}$  inventory below the reference inventory) in the upper landscape position and a small net accumulation of soil in the mid position (i.e.,  $^{137}\text{Cs}$  inventory above the reference inventory). The lower landscape position had the greatest net accumulation of soil with significant quantities of soil also being deposited within the riparian zone, as illustrated by the  $^{137}\text{Cs}$  inventory. The patterns of soil erosion and deposition have resulted in a fairly simple topographic hillslope profile (Fig. 5.2b). Site 2 shows slight net soil erosion in the upper and mid landscape position and net accumulation from the lower position through to, and extending in to, the the riparian zone (Fig 5.3a). The greatest amount of soil accumulation occurs near the edge of field, where the hillslope profile (Fig 5.3b) shows the presence of a topographical step at the field edge (caused by tillage erosion). Part of this step is within the riparian zone and this is thought to be the result of the fence line (edge of field) being moved ~3 m at some point during the last ~60 years.

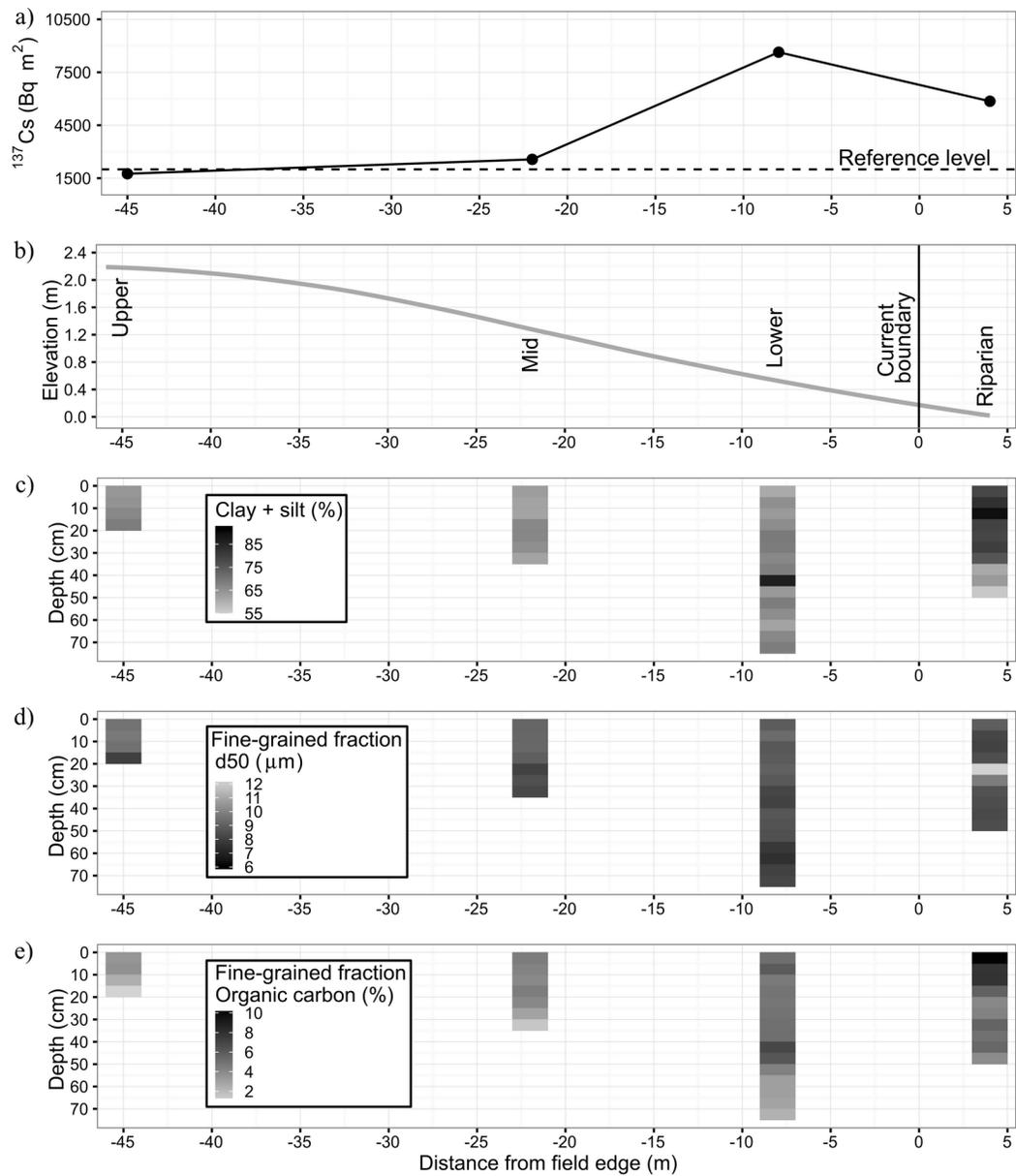


Figure 5.2: Soil profiles in site 1 showing: a) total  $^{137}\text{Cs}$  inventory; b) elevation profile and landscape position; c) percentage clay + silt; d) median particle size ( $d_{50}$ ;  $\mu\text{m}$ ) within the  $< 63 \mu\text{m}$  fraction; and e) soil organic carbon concentration (%) within the  $< 63 \mu\text{m}$  fraction.

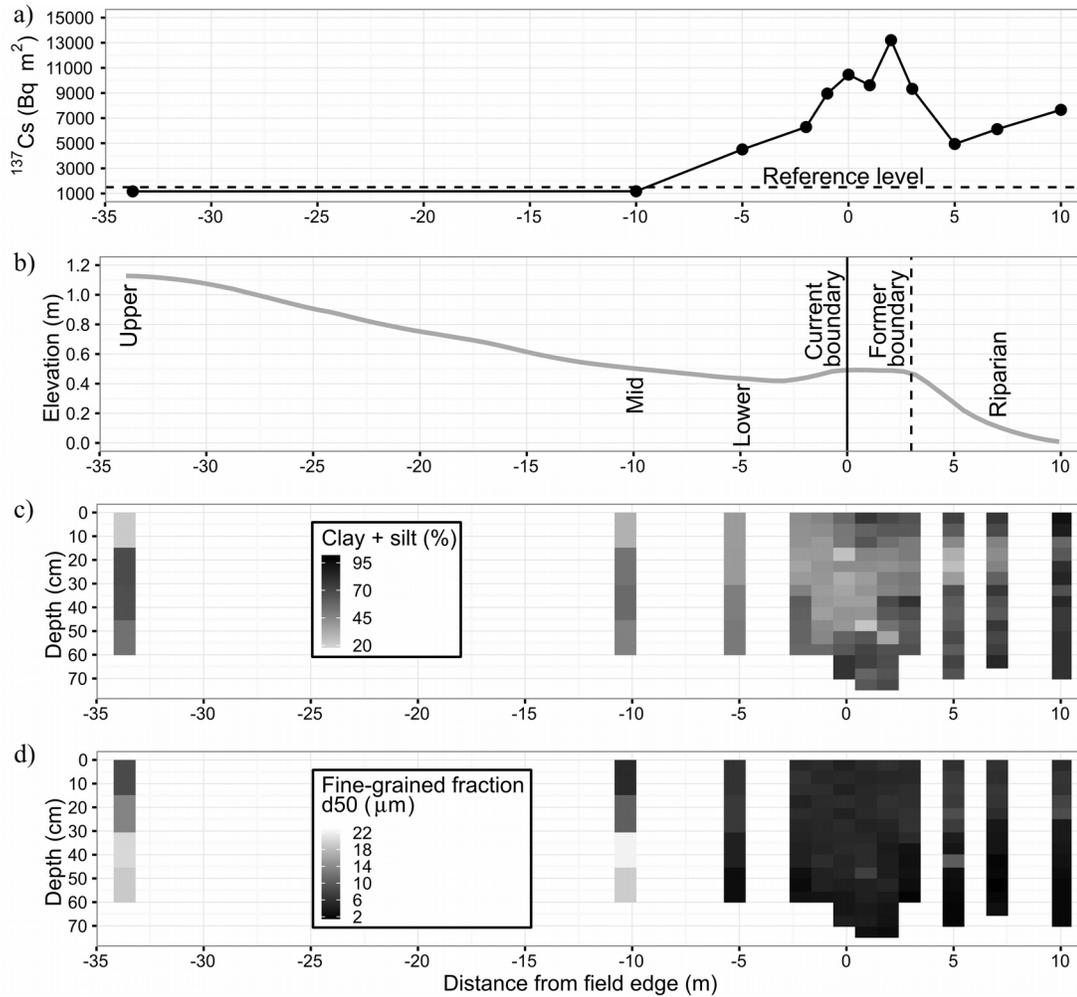


Figure 5.3: Soil profiles in site 2 showing: a) total  $^{137}\text{Cs}$  inventory; b) elevation profile and landscape position; c) percentage clay + silt; d) median particle size ( $d_{50}$ ;  $\mu\text{m}$ ) within the  $< 63 \mu\text{m}$  fraction; and e) soil organic carbon concentration (%) within the  $< 63 \mu\text{m}$  fraction.

#### 5.4.2 Particle size and organic carbon

Averaging across all depths within a soil profile, both sites demonstrated an overall increase in the percentage of clay and silt ( $< 63 \mu\text{m}$ ) in the down-slope direction with the riparian positions consisting of the greatest proportion of fine-grained material (Figs. 5.2c and 5.3c). For the upper, mid and lower slope position the soils became finer-grained with depth but within the riparian zone this trend was reversed. However, once sand-sized

particles are removed from the analysis, the patterns of particle size become less defined (Figs, 5.2d and 5.3d). Interestingly, within the soil profiles in site 1 there were instances which showed an abrupt change in particle size. For example, in the lower landscape position at a depth of 40 – 45 cm (Fig 5.2c) the percentage of clay and silt was 87.1 % while the samples above and below were 68.9 % and 61.5 %, respectively. Similar to the patterns of the particle size analysis, averaging across all depths within a soil profile, site 1 demonstrated that the concentration of SOC, within the < 63 µm fraction, increased in the down slope direction (Fig 5.2e ). For the upper, mid and riparian positions the SOC concentration generally decreased with depth, but within the lower landscape position there was a significant spike in the SOC concentration (7.0 %) at a depth of 40 – 45 cm which is consistent with the data reported in Vandenbygaart (2012).

#### **5.4.3 Geochemical analysis**

The geochemical analysis for site 1 it was demonstrated that there was no consistent trend in geochemical concentrations, for all elements, either across the transect or with depth. Generally, the riparian position showed the most variation in geochemical concentrations, across the transect and with depth, as compared with the other landscape positions; however, the magnitude and direction of the changes in concentration was element specific. Within the riparian zone, the change in concentration with depth of Cu (Fig. 5.4), Ce, Mg, Re, Sb, and Se was greater as compared to the other landscape positions. The elemental concentrations of Co (Fig. 5.4), Mn and Mo had an overall lower concentration and decreased with depth at a greater rate as compared to the other landscape positions. Furthermore, elements including Sr (Fig. 5.4) and Ca did not vary much with depth but had an overall higher concentration as

compared the other landscape positions. Overall, the concentrations of P (Fig. 5.4) and K, two commonly used agricultural inputs, were the highest in lower landscape position. The remainder of the elements (e.g., Ga; Fig. 5.4) showed no discernible trends across the landscape or with depth.

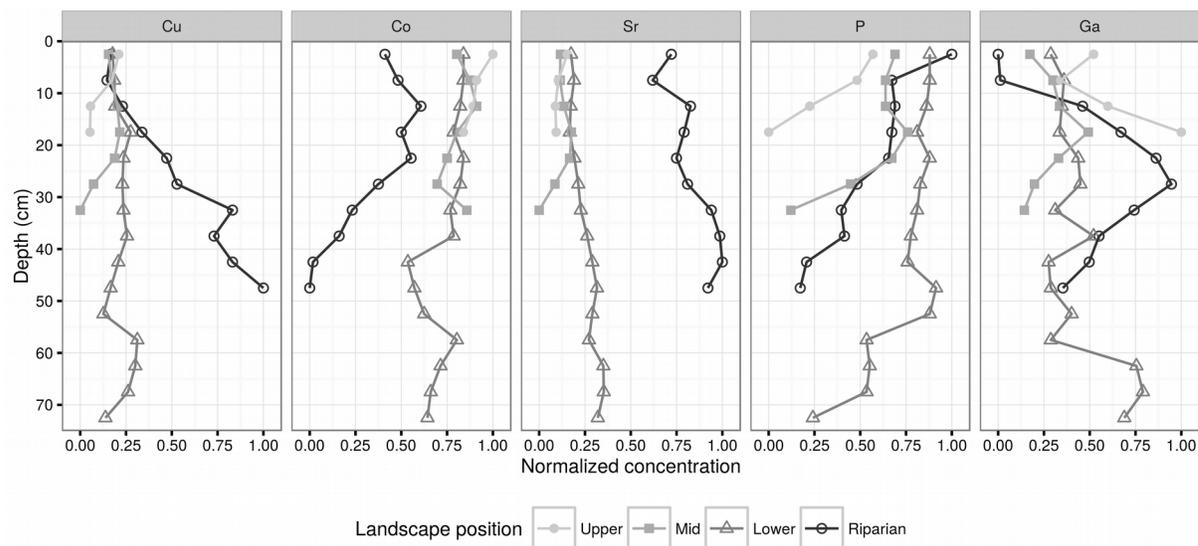


Figure 5.4: Examples of the geochemical concentrations in different landscape positions and with depth for site 1. Concentration have been normalized between 0 and 1 so direct comparisons can be made between elements.

Overall, 26 geochemical elements showed a significant correlation between elemental concentration and SOC, while only two elements showed a significant correlation between elemental concentration and d50 at site 1 (Table 5.1). The direction of these correlations was element specific with 16 and 10 elements showing negative and positive correlations, respectively. In addition, both Te and U had a significant negative correlation between concentration and d50. Separating the soil samples into different groupings provided some additional information on the observed trend in the geochemical analysis. Comparing the within-field to riparian samples and surface to subsurface samples it is clear that the significance of the relation between particle size and SOC was dependent on both landscape

position and depth. Within the landscape position grouping, the direction (i.e., positive or negative) of the significant correlations of both SOC and d50 was similar between riparian and within-field groups (with the exception of As, Cd and Cu). Similarly, for the depth grouping, Hf is the only element where the direction of both the SOC and d50 correlations was not the same between the surface (0 – 15 cm) and subsurface (15 cm +) soil samples.

Table 5.1: Pearsons correlation coefficients, for different sample groupings, between elemental concentrations soil organic carbon (SOC), median particle size (d50) and depth at site 1. Bold indicates significant correlation (p-value < 0.05).

Element	Landscape position									Depth			
	All samples			Riparian			Within field			Surface (0–15 cm)		Subsurface (0–15 cm)	
	SOC	d50	Depth	SOC	d50	Depth	SOC	d50	Depth	SOC	d50	SOC	d50
Ag	0.21	0.16	-0.21	-0.02	0.17	-0.22	<b>0.59</b>	0.26	-0.24	-0.31	0.00	<b>0.50</b>	0.16
Al	<b>-0.47</b>	0.15	0.33	<b>-0.79</b>	0.58	0.39	<b>-0.45</b>	-0.32	0.34	<b>-0.82</b>	0.45	-0.25	0.29
As	<b>-0.47</b>	-0.21	0.00	<b>0.76</b>	-0.14	<b>-0.70</b>	<b>-0.58</b>	-0.20	0.05	<b>-0.87</b>	<b>0.65</b>	<b>-0.53</b>	-0.38
Ba	0.10	-0.03	-0.14	<b>0.67</b>	-0.09	<b>-0.88</b>	<b>0.80</b>	0.27	-0.13	<b>-0.72</b>	0.38	0.31	-0.15
Be	<b>-0.46</b>	0.07	<b>0.46</b>	<b>-0.89</b>	0.45	<b>0.68</b>	<b>-0.46</b>	-0.35	<b>0.43</b>	<b>-0.70</b>	0.55	-0.27	0.15
Bi	-0.23	-0.31	0.05	0.18	-0.54	-0.11	0.03	-0.11	0.05	<b>-0.60</b>	0.09	-0.09	<b>-0.42</b>
Ca	<b>0.66</b>	-0.01	0.00	0.17	-0.55	0.28	<b>0.88</b>	0.02	0.07	<b>0.96</b>	<b>-0.74</b>	<b>0.57</b>	0.21
Cd	<b>0.76</b>	0.01	<b>-0.46</b>	<b>0.72</b>	<b>-0.73</b>	-0.17	<b>0.82</b>	<b>0.56</b>	<b>-0.55</b>	<b>0.90</b>	<b>-0.59</b>	<b>0.79</b>	-0.04
Ce	<b>-0.73</b>	0.24	-0.01	<b>-0.90</b>	0.28	<b>0.85</b>	<b>-0.61</b>	0.27	<b>-0.45</b>	<b>-0.92</b>	<b>0.75</b>	<b>-0.54</b>	0.08
Co	<b>-0.36</b>	0.11	<b>-0.34</b>	0.42	0.34	<b>-0.85</b>	-0.29	<b>0.53</b>	<b>-0.73</b>	<b>-0.93</b>	<b>0.73</b>	-0.36	-0.12
Cr	<b>-0.68</b>	0.15	0.22	<b>-0.97</b>	0.42	<b>0.74</b>	<b>-0.61</b>	-0.12	0.05	<b>-0.96</b>	<b>0.63</b>	<b>-0.46</b>	0.16
Cs	<b>-0.54</b>	-0.07	-0.10	-0.40	-0.10	0.54	<b>-0.59</b>	-0.02	-0.19	<b>-0.68</b>	0.42	<b>-0.60</b>	-0.13
Cu	0.13	0.04	0.28	<b>-0.73</b>	-0.06	<b>0.97</b>	<b>0.46</b>	-0.19	0.23	0.27	-0.27	0.34	0.16
Fe	<b>-0.47</b>	0.22	-0.10	-0.12	<b>0.64</b>	-0.46	<b>-0.54</b>	-0.12	-0.01	<b>-0.92</b>	0.57	-0.40	0.19
Ga	<b>-0.43</b>	0.16	0.31	<b>-0.75</b>	0.52	0.42	<b>-0.47</b>	-0.32	0.32	<b>-0.68</b>	0.39	-0.22	0.28
Hf	<b>0.59</b>	0.29	<b>-0.47</b>	0.09	-0.16	-0.39	<b>0.55</b>	<b>0.47</b>	<b>-0.59</b>	<b>0.88</b>	<b>-0.81</b>	<b>0.57</b>	<b>0.44</b>
Hg	<b>0.48</b>	-0.17	0.01	0.49	-0.40	-0.61	0.10	-0.32	0.28	<b>0.88</b>	<b>-0.82</b>	0.26	0.01
In	-0.18	0.15	0.06	-0.57	0.57	0.14	-0.05	-0.12	0.04	-0.47	0.20	-0.02	0.21
K	0.13	0.08	<b>-0.35</b>	<b>0.74</b>	0.17	<b>-0.95</b>	<b>0.53</b>	0.27	-0.38	-0.09	0.05	0.11	-0.01
La	<b>-0.78</b>	-0.21	<b>0.51</b>	<b>-0.84</b>	0.42	<b>0.64</b>	<b>-0.75</b>	<b>-0.58</b>	<b>0.49</b>	<b>-0.86</b>	<b>0.58</b>	<b>-0.80</b>	-0.27
Li	-0.25	0.22	0.16	<b>-0.94</b>	0.38	<b>0.81</b>	<b>-0.59</b>	-0.17	-0.01	-0.51	0.29	-0.10	0.35
Mg	0.02	0.02	0.22	<b>-0.68</b>	-0.10	<b>0.89</b>	-0.35	-0.23	0.10	0.55	-0.55	0.10	0.14
Mn	-0.09	-0.03	-0.31	<b>0.79</b>	-0.12	<b>-0.94</b>	<b>0.52</b>	<b>0.76</b>	<b>-0.74</b>	<b>-0.86</b>	<b>0.72</b>	-0.08	-0.26
Mo	-0.03	-0.08	-0.27	<b>0.91</b>	-0.32	<b>-0.88</b>	<b>0.56</b>	<b>0.43</b>	<b>-0.47</b>	<b>-0.68</b>	0.56	0.03	-0.29
Na	-0.13	0.16	0.04	-0.48	0.04	<b>0.78</b>	<b>-0.52</b>	0.20	-0.30	0.00	0.45	-0.15	0.16
Nb	<b>0.39</b>	0.19	-0.05	0.16	0.03	-0.20	<b>0.64</b>	0.32	-0.04	-0.15	0.06	<b>0.68</b>	0.13
Ni	-0.30	0.24	0.10	<b>-0.70</b>	0.40	0.47	<b>-0.51</b>	-0.08	-0.01	<b>-0.84</b>	0.50	-0.09	0.31
P	<b>0.64</b>	0.15	-0.28	<b>0.75</b>	0.20	<b>-0.96</b>	<b>0.90</b>	0.20	-0.13	<b>0.67</b>	-0.41	<b>0.63</b>	0.21
Pb	<b>0.56</b>	0.11	<b>-0.59</b>	<b>0.87</b>	-0.33	<b>-0.81</b>	<b>0.48</b>	<b>0.46</b>	<b>-0.54</b>	<b>0.62</b>	-0.45	<b>0.46</b>	0.08
Rb	<b>-0.54</b>	0.00	-0.06	-0.44	0.47	0.04	<b>-0.42</b>	-0.19	-0.13	<b>-0.67</b>	0.40	<b>-0.51</b>	-0.05
Re	0.08	-0.09	0.23	-0.47	-0.30	<b>0.85</b>	0.02	-0.04	0.16	<b>0.59</b>	-0.54	0.19	-0.02
Sb	0.09	-0.06	0.11	-0.46	-0.33	<b>0.89</b>	0.06	0.36	<b>-0.57</b>	0.25	-0.50	0.20	-0.01
Sc	<b>-0.67</b>	0.05	0.23	<b>-0.90</b>	0.39	<b>0.67</b>	<b>-0.68</b>	-0.22	0.11	<b>-0.86</b>	<b>0.60</b>	<b>-0.56</b>	0.04
Se	<b>0.43</b>	-0.15	0.10	-0.03	-0.61	0.56	0.37	-0.11	0.24	<b>0.83</b>	<b>-0.84</b>	0.35	0.01
Sn	-0.07	-0.31	<b>0.33</b>	0.03	-0.44	0.08	-0.09	-0.38	0.36	0.47	-0.46	-0.10	-0.23
Sr	<b>0.46</b>	0.02	0.18	-0.50	-0.27	<b>0.86</b>	0.34	<b>-0.50</b>	<b>0.77</b>	<b>0.90</b>	<b>-0.79</b>	0.37	0.28
Te	-0.24	<b>-0.37</b>	0.10	0.17	-0.47	0.13	-0.32	-0.15	0.06	-0.17	0.15	-0.37	<b>-0.51</b>
Th	<b>-0.76</b>	-0.15	0.11	<b>-0.84</b>	-0.05	0.92	<b>-0.82</b>	-0.18	-0.01	<b>-0.90</b>	<b>0.65</b>	<b>-0.81</b>	-0.25
Ti	<b>-0.64</b>	-0.14	0.26	-0.09	0.47	-0.28	<b>-0.63</b>	-0.26	0.37	<b>-0.91</b>	0.57	<b>-0.63</b>	-0.28
Tl	-0.32	0.10	<b>-0.47</b>	-0.43	-0.35	<b>0.79</b>	<b>-0.43</b>	0.28	<b>-0.61</b>	<b>-0.84</b>	<b>0.69</b>	-0.34	-0.04
U	-0.14	<b>-0.41</b>	<b>0.80</b>	-0.16	-0.53	0.57	-0.27	<b>-0.58</b>	<b>0.85</b>	<b>0.76</b>	<b>-0.83</b>	-0.24	-0.31
V	<b>-0.67</b>	-0.18	0.25	<b>-0.70</b>	-0.11	<b>0.97</b>	<b>-0.67</b>	-0.21	0.03	<b>-0.96</b>	<b>0.66</b>	<b>-0.55</b>	-0.27
Y	<b>-0.57</b>	-0.15	0.60	<b>-0.85</b>	0.49	0.61	<b>-0.64</b>	<b>-0.68</b>	<b>0.61</b>	<b>-0.58</b>	0.25	<b>-0.61</b>	-0.05
Zn	<b>0.60</b>	0.19	<b>-0.47</b>	<b>0.70</b>	-0.36	-0.28	<b>0.58</b>	<b>0.44</b>	<b>-0.50</b>	<b>0.72</b>	-0.33	<b>0.59</b>	0.20
Zr	0.27	0.19	<b>-0.39</b>	-0.51	-0.37	0.62	0.05	0.33	<b>-0.58</b>	<b>0.72</b>	<b>-0.85</b>	0.19	0.31
# neg.	16	2	8	15	1	8	19	4	11	22	8	11	2
# pos.	10	0	3	7	1	14	13	7	5	12	10	8	1

The results of the Kruskal-Wallis H-test showed that 25 elements (As, Ba, Bi, Ca, Co, Cs, Cu, Hf, Hg, K, Li, Mg, Mn, Mo, Na, Nb, P, Rb, Re, Sb, Se, Sr, Ti, U, and Zr) had a significant difference ( $p$ -value  $< 0.05$ ) in concentration between one or more of the landscape positions. The subsequent PCA analysis showed that the geochemical composition of the riparian zone, considering all depths, was different than other landscape positions (Fig. 5.5a). The first principal component separated the landscape positions based on the concentrations of As, Ba, Ca, Co, Cu, K, Mg, Mn, Mo, Re, Sb, Se and Sr. The second principal component separated the landscape positions based on the concentrations of Ca, Cs, Cu, Mg, Na, Re, Sb, Se, Sr and Ti.

The results of the Kruskal-Wallis H-test showed that 11 elements (Al, Be, Co, Cu, Ga, K, Mn, Pb, Sn, U, and Y) had a significant difference ( $p$ -value  $< 0.05$ ) in concentration between surface (0 – 15 cm) and subsurface (15 cm +) soil samples. In contrast, differences in the geochemical composition between groups was not clear as most surface soil samples grouped close together, but subsurface samples were more spread out across both principle component axes (Fig 5.5b). The first principal component separated the sample groups based on the concentrations of Co, K, Mn and Pb. The second principal component separated the sample groups based on the concentrations of Co, Cu, K, Mn, Pb and Sn.

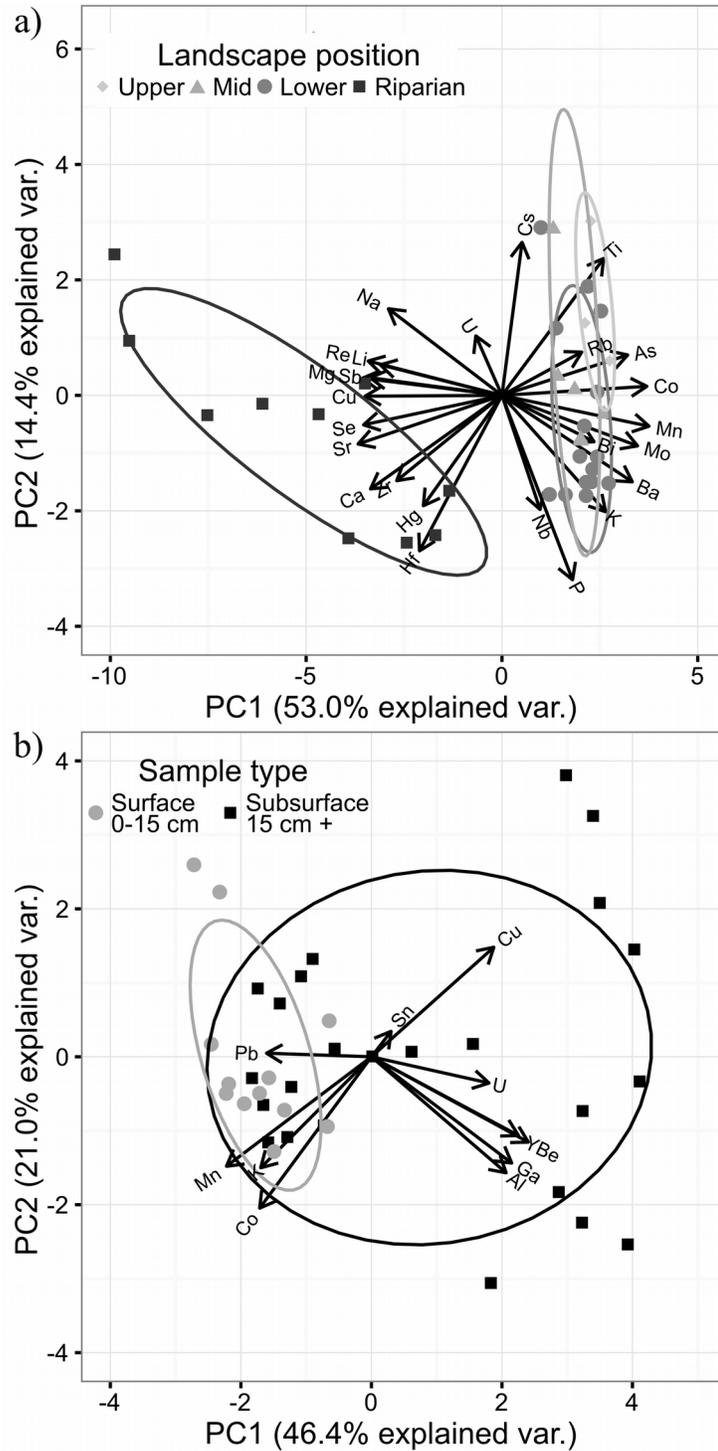


Figure 5.5: Principal components analysis (PCA) score and loading plots of the first two principal components (PC1 and PC2) for site 1 depicting the differences in geochemical composition between: a) landscape positions; and b) surface and subsurface samples.

## 5.5 Discussion

### 5.5.1 Particle selectivity

The lower landscape and field edge positions in both sites showed the greatest net accumulation of soil (Figs 5.2b and 5.3b). There was also considerable net accumulation of soil in the riparian zone; however, this soil within the riparian zone was composed of a greater fraction of fine-grained material as compared to the lower landscape position. These results suggest that there is either; 1) a preferential deposition of coarse-grained material in the lower landscape positions; or 2) there is a secondary erosional process that is preferentially mobilizing and transporting fine-grained soil deposited in the lower position and transporting it off field into the riparian zone. Since both sites are under annual crops there is frequent soil disturbance through both seeding and tillage operations. Research has shown that these types of soil disturbances can result in significant amounts of soil being translocated down slope and that tillage erosion may transport significantly more soil in the upper landscape positions as compared to water erosion (e.g., Li et al. 2007; Li et al. 2008). Furthermore, soil texture in the lower position is more similar to that of the upper and mid positions as compared to the riparian zone (Figs 5.2c and 5.3c), which is supported by the fact that tillage erosion is not typically a particle size selective process (Xiaojun et al. 2013). The process of tillage erosion typically did not deposit soil within the riparian zone; for example, the presence of the topographic step along the edge of field in site 2 is evidence that tillage erosion does not transport significant amounts of soil past the field boundary. Therefore, tillage erosion cannot explain the net accumulation of fine-grained soil within the riparian zone, which suggesting that a secondary process may be responsible for the observed

trends in both the net accumulation and texture of the deposited soil within the riparian zone.

It is likely that water erosion is remobilizing and transporting soil that had previously deposited in the lower position by tillage into the riparian zone. In this scenario there is an interaction between two different types of erosion where tillage erosion is acting as a delivering mechanism for the water erosion process (Lobb et al. 2004). For example, previously formed rills may be filled in by the frequent tillage operations. This soil is then eroded away as the rills re-form during the next significant rainfall event. This sequence of events may be repeated several times a year. Water erosion has been shown to be a selective process which preferentially mobilizes and transports fine-grained particles (e.g., Issa et al. 2006; Armstrong et al. 2011). This may explain the accumulation of finer-grained particles within the riparian zone. The topographic step in site 2 provides an interesting case whereby any runoff that converges within the landscape and moves down slope will accumulate behind the step, encouraging the infiltration of the runoff into the soil and decreasing its transport capacity. This would result in deposition of coarse-grained soil in the lower slope position and any runoff that does overtop the step and is transported to the riparian zone would be enriched in fine-grained soil.

It is also interesting to note some of the abrupt changes in particle size that occur at depth in both the lower and riparian positions in site 1 (Figs. 5.2c and 5.2d). For example, there is a thin lens of soil with a high  $d_{50}$  (20 – 25 cm) within the riparian landscape zone. This layer of soil may have been deposited during an intensive precipitation event whereby a large amount of coarser-grained soil was deposited and subsequently buried by finer-grained sediment. However, the importance of up-stream contributions, in contrast to up-slope contributions, of sediment to the riparian positions during flooding events cannot be

discounted as these episodic events may have also contributed to the abrupt changes observed.

At site 1, there was a higher concentration of SOC within the riparian zone relative to the other landscape positions. There are a few possibilities that could explain this trend: 1) in-field losses of SOC, or the homogenization of the soil profile, due to agricultural practices; 2) preferential erosion of carbon-rich particles from up slope; 3) higher carbon input from riparian vegetation; or 4) a combination of processes.

In the case of the first possibility, cultivation, or mixing of the soil profile, can increase the loss of C to the atmosphere by promoting decomposition because as the vegetative residues are incorporated into the soil the amount of vegetation in contact with the soil increases, which makes the residue more readily available for decomposition (Reicosky and Lindstrom 1993). Cultivation will also result in the homogenization of the tillage layer as the high C content surface soil is mixed with the lower C content subsurface soil, resulting in the lowering of the overall maximum SOC concentration within a profile (Gregorich et al. 1998). Both of these processes act to reduce the in-field SOC concentrations relative to the uncultivated riparian area.

Secondly, previous research, by Vandenbygaart et al. (2012), at site 1 demonstrated that there was a higher total SOC inventory within the lower and riparian positions relative to the upper and mid positions. This was found to be the result of a loss of C-rich soil in the upper and mid positions and the subsequent accumulation in lower and riparian landscape positions. While erosion of SOC results in greater SOC inventory in the lower and riparian landscape positions, it had effectively buried C-rich soil to a depth at which the rate of decomposition was low (Vandenbygaart et al. 2012). This may account for the fact that

maximum SOC concentration were located at a depth of 40 – 45 cm in the lower slope position (Fig 5.2e ). The lower rates of soil accumulation within the riparian zone may also be less effective at burying C-rich soil. This may be due to the fact that the mechanism for transporting C-rich soil particles across the field edge boundary may be predominately water erosion (e.g., Schiettecatte et al. 2008).

Finally, in contrast to the other landscape positions, the maximum SOC concentration within the riparian zone was at the surface which may reflect inputs from the perennial vegetation and the lack of harvesting biomass.

### **5.5.2 Geochemistry and implications for sediment fingerprinting**

The geochemical analysis from site 1 showed that there was significant spatial and vertical variability for most elements (Fig. 5.4). For many elements, it has been previously demonstrated that for in-stream sediment there is a negative correlation between concentration and d50 and a positive correlation between concentration and SOC (e.g., Horowitz 1991) which serves as the basis for particle size and organic matter correction factors. If the upper and mid landscape positions are considered to be the source of the deposited soil within the lower and riparian landscape positions, it would be expected that the same correlations described above would hold true. However, very few elements showed this expected correlations and many of the elements had correlations in the opposite direction (Table 5.1). Furthermore, it is generally accepted that particle size exerts a larger influence on concentration as compared to SOC (e.g., Horowitz 1991), but in this study more elements had a significant correlation with SOC than with the d50. Here correlations between both SOC or the d50 and concentrations appear to explain some of the observed vertical

variability. The lack of consistency in the direction of the correlations may suggest that the effects of SOC and d50 are not additive. Alternatively, other properties, including Al-, Fe- and Mn-oxides, might be more important in controlling the distribution of elements both with depth and across the landscape. This material, similar to clay, has a high SSA and is chemically reactive and geochemical elements can concentrate in this fraction. Furthermore, the differences in concentration with depth or across the hillslope may also be due to biogeochemical transformations or translocation within the soil profile.

Hydrology is very different within riparian zones compared to upper, mid and lower landscape positions. Soil in riparian zones tend to have both an overall higher moisture status due to proximity to the channel and a frequent change in redox conditions as a result of seasonal changes in the water table (Burt et al. 2002; Vidon et al. 2010). Redox sensitive elements such, As, Cr, Cu, Fe, Mn, and U, are of particular interest, as the mobility of these elements within the soil profile are linked to the redox potential of the environment (Borch et al. 2010). For example, a laboratory study by Rezanezhad et al. (2014) compared a soil column with a static water table to a column with a fluctuating water table and found that the concentration of several metals (Fe, Mn, Si and K) changed with depth. The likely mechanism was thought to be due to chemical transport associated with the rise and subsequent draw-down of the water table. These hydrological conditions may, in part, be responsible for the differences observed in elemental concentration between landscape positions in this study. However, further study at site 1 is needed to fully evaluate the role of hydrology, particle size and SOC on the distribution of geochemical elements within the riparian zone.

Effectively characterizing potential sources of sediment is a key part of the sediment

fingerprinting approach (Davis and Fox 2009). In many agricultural case studies, surface soils are identified as potential sources, but there is no clear approach on how best to characterize this type of source. In some case studies, surface scrapes are taken near the edge of the field or within the riparian zone (i.e., sediment deposits along the delivery pathway), and this material is identified as having a high potential to be eroded and subsequently transported to surface waterways (e.g., Collins et al. 2012). Another strategy is to composite soil samples collected as part of a grid or transect pattern, in an effort to capture some spatial variability (e.g., Gellis and Noe 2013). In other case studies, samples are taken along transects extending from the upper slope position down and through the riparian zone, and this material is identified as a contributing source area (e.g., Koiter et al. 2013a). In the latter two examples, the depth of sampling becomes important. In cultivated areas samples can be taken to the depth of tillage as this layer is homogenized regularly through tillage. The appropriate depth to sample in the riparian zone is less clear, but the depth of observed erosional features (e.g., rills) should be considered.

At site 1, taking into consideration the entire depth of the A-horizon, there are many elements that had concentrations that were significantly different between one or more of the landscape positions (i.e., results of the Kruskal-Wallis H test) and the results of the PCA show there were some clear differences in the geochemical composition of riparian soil as compared to within-field soil (Fig. 5.5a). In contrast, there were few elements that had concentrations that were significantly different between surface and subsurface soil samples and differences in geochemical composition between the two groups were less clear (Fig. 5.5b). Overall, these results suggest that geochemical composition of the soils within the riparian is driven more by *in-situ* biochemical processes than by particle selectivity resulting

from soil erosion processes.

## **5.6 Conclusions**

In both sites it was found that there was net soil erosion in the upper and mid landscape positions and a subsequent net accumulation in the lower/field edge and riparian positions. However, the maximum net accumulation occurred in the lower/field edge position. There was evidence of particle size selectivity, as soil in the riparian zone was found to have a greater percentage of clay and silt compared to the soils within the field. However, the difference in particle size became less obvious when the analysis was restricted to the < 63  $\mu\text{m}$  fraction. Similarly, the riparian zone had higher SOC concentrations, but it was not clear whether this was a result of preferential deposition of C-rich particles within the riparian zone or a overall reduction in C within the fields due soil mixing from tillage. The geochemical composition within site 1 varied both spatially and vertically but it was difficult to attribute this variability to particle size or SOC content. Other biogeochemical processes were also likely to contribute to the observed patterns.

The soils within the riparian zone had unique particle size, SOC and geochemical composition characteristics, which can have implications for the sediment fingerprinting approach. Specifically, it has implications on how potential terrestrial sources of sediment are characterized and more importantly whether or not to include riparian soils as a unique source or as part of up-slope sediment source is key. Furthermore, this research suggests that careful consideration is needed when designing a sampling campaign and developing sampling protocols to effectively characterize potential sources of sediment.

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## **6 The role of gravel channel beds on the particle size and organic matter selectivity of transported fine-grained sediment: implications for sediment fingerprinting and biogeochemical flux studies**

### **6.1 Abstract**

The preferential erosion, delivery and transport of sediment within a drainage basin can result in downstream changes in both particle size and organic matter content. The physical and biological properties of transported and deposited sediment are important considerations in many sediment management and investigative tools, including sediment fingerprinting, and aid in the interpretation of sediment-associated nutrient and contaminant data. A recirculating flume (2m x 2 m x 40 m) was used to assess the changes in particle size, organic matter content and geochemical composition of fine-grained sediment (< 125  $\mu\text{m}$ ) over a 31 hr period (representing a travel distance of  $\sim$ 24 km) under three contrasting channel bed conditions. The three channel gravel bed conditions investigated were 0-, 5-, and 40-cm gravel bed depths. Suspended sediment samples were collected throughout the duration of the experiment and gravel-stored sediment were collected along the length of the flume at the end of the experiment. Both suspended and gravel-stored sediment were analysed for particle size and organic matter content. In addition, suspended sediment samples were analysed for a broad suite of geochemical elements. The channel bed characteristics had a significant effect on both the particle size and organic matter selectivity of the transported suspended sediment.

Furthermore, it was shown that a smooth planer channel bed compared to a planar gravel bed (i.e., 0- vs 5-cm gravel treatments) introduced small-scale roughness which resulted in the preferential deposition of larger particles into the channel bed. Increasing the gravel bed from 5- to 40-cm increased the amount of intra-gravel flow and reduced the potential for resuspension resulting in a further reduction in the particle size as well as resulting in a significant increase in the organic matter content of the suspended sediment. The relationship between geochemical concentrations and particle size of the suspended sediment, in terms of linearity, magnitude and direction, were not consistent between the different elements investigated. This research helps to understand the processes that control the particle size and organic matter selectivity of fluvial transported sediment. This information is an important part of many sediment management tools, including sediment fingerprinting, as it provides context when selecting sampling sites and interpreting the data they provide. The inconsistent relationship between particle size and different geochemical elements highlights the uncertainty associated with commonly used particle size correction factors.

## **6.2 Introduction**

### **6.2.1 Sediment management tools and approaches**

Particle size and organic matter selectivity, in the context of sediment transport, refers to the preferential detachment, entrainment, transfer and deposition of sediment based on particle size and organic matter content. The sediment cascade is the concept that sediment eroded from hillslopes can followed though a series of connected unique geomorphic units to the watershed outlet. Along the sediment cascade, sediment mobilization on the hillslopes, storage within the riparian zones and the fluvial transport in downstream rivers are all

selective processes (Slattery and Burt 1997; Koiter et al. 2013a). Information on the processes of particle size and organic matter selectivity is needed for watershed management tools including, sediment budgets, geomorphic connectivity and sediment fingerprinting (Stone and Walling 1997; Di Stefano and Ferro 2002; Fryirs 2013). Many of the watershed tools commonly used can be considered blackbox concepts because there is little consideration as to the processes that link the inputs to the outputs, and in particular, the process of particle selectivity is often overlooked (Walling 1983; Koiter et al. 2013a).

The sediment source fingerprinting technique uses naturally occurring physical and biogeochemical properties as tracers to discriminate between sediment sources and to subsequently estimate the contribution from each sediment source to sediment collected downstream (see Davis and Fox (2009) for a review of sediment fingerprinting). Ideally, the sediment properties selected as tracers do not change (i.e., exhibit conservative behaviour) between the source of sediment and the downstream sediment collection so that a direct comparison can be made. However, particle size and organic matter transport selectivity can result in the non-conservative behaviour of sediment properties as selectivity tends to result in downstream fining and an enrichment of organic matter content. Both of these properties have been shown to have an effect on geochemical and radionuclide tracer concentrations within the sediment and this is primarily due to the increase in specific surface area (SSA) and chemical reactivity (Horowitz 1991). The importance of this phenomenon has been recognized within the sediment source fingerprinting community as correction factors for both particle size and organic matter are commonly used. These correction factors are typically based on the ratio of SSA and organic matter content between collected in-stream sediment and potential sediment sources (e.g., Collins et al. 1997). However, the use of these

correction factors are increasingly being criticized as they have not been widely tested and have little basis in watershed processes (Koiter et al. 2013a; Smith and Blake 2014).

The importance of incorporating process-based understanding of the changes in physical and biogeochemical properties of sediment during transport through watersheds have been increasingly recognized as a critical step in linking sediment sources to in-stream sediment in a reliable and robust manner. The special issue, *Advances in Sediment Fingerprinting*, in the *Journal of Soils and Sediments*, is evidence of this as many of the research articles focus on the testing of assumptions that link sources to sediment. For example, Pulley et al. (2015) investigated the use of different groups of tracers (e.g., geochemistry, radiochemistry, mineral magnetics) on the apportionment results; Lacey et al. (2015) compared a statistical and geological approach to the tracer selection process; Sherriff et al. (2015) examined the uncertainty with respect to changes in particle size and organic matter content as well as geochemical transformations on the apportionment results; Wilkinson et al. (2015) incorporated the erosional history in characterizing sediment source tracer concentrations. This research compliments the other contributions in this special issue by investigating the particle size and organic matter selectivity of fluvial transported sediment and its subsequent influence on the geochemical concentrations of suspended sediment.

The sediment delivery ratios for watersheds are particle size dependent as smaller particle size classes tend to have higher delivery ratios as the coarser sediment fraction is preferentially deposited. For example, Walling (1983) found that within the Jackmoor Brook watershed (9.8 km<sup>2</sup>) located in Devon, England, very fine-grained sediments (<1 µm) had a delivery ratio of 100 % while coarser sediment (20 – 63 µm) had a delivery ratio of only 30

%). Furthermore, the suspended sediment within the Jackmoor Brook watershed was also found to be enriched in organic matter by 60 % as compared to the sources of sediment. Stone and Walling (1997) describe the importance of particle size distribution and selectivity in assessing the delivery and transport patterns of different particle size fractions and its subsequent importance in constructing and interpreting sediment budgets for watersheds. For example, Bainbridge et al. (2014) constructed a suspended sediment budget for three different particle size classes (< 2, 4 – 16 and >16  $\mu\text{m}$ ) for the Burdekin River watershed (130,400  $\text{km}^2$ ) located in north-east Queensland, Australia. It was found that a dam, located mid-catchment, trapped approximately 66 % of the total incoming sediment, however, the dam resulted in the preferential trapping of the coarsest sediment size class (92 % trapped) as compared to the finest sediment size class (33 % trapped). This preferential deposition of the coarser sediment resulted in 80 % of the total sediment being exported at the outlet of the watershed being comprised of sediment < 16  $\mu\text{m}$  despite coarser sediment inputs from tributaries downstream of the dam. This research highlights the importance of considering watershed characteristics when selecting in-stream sediment sampling locations and interpreting the data.

The process of particle size and organic matter selectivity also needs to be considered when assessing data on carbon, nutrient, contaminant and geochemical fluxes at the watershed scale. The fluvial transport of organic and inorganic carbon are key parts of the global carbon (C) and nutrient cycles. Approximately  $1.9 \times 10^{12}$  kg of C (inorganic/organic and dissolved/particulate forms) from terrestrial sources are delivered to surface waterways on an annual basis (Cole et al. 2007). However, only half of this amount is delivered to the ocean, a further ~ 40 % is returned to the atmosphere and the remaining ~ 10 % is stored as

deposited sediment in lakes, reservoirs and rivers. The predominant form of sediment-stored carbon in freshwater systems is particulate organic C (POC) and lakes represent the largest and the most understood and quantified C storage compartment. In contrast, the role of C storage in rivers is smaller and is less understood and quantified (Cole et al. 2007; Tranvik et al. 2009). The particle size and organic matter content of transported sediment are important components of the overall characterization of the spatial and temporal patterns of C storage as these properties drive the settling velocities of sediment (e.g., Young and Huryn 1997). For example, in a 75 km<sup>2</sup> catchment, located in south-eastern Queensland, Australia, Garzon-Garcia et al. (2015) found that there were changes in the C content of the sediments for different flow magnitudes. This indicates that there was particle size and organic matter selectivity occurring which resulted in higher C content sediment being transported during lower flow events as compared to higher flow events.

Sediment-associated nutrients, particularly phosphorus (P), are an important nutrient source in the external and internal loading of lakes and rivers and can result in eutrophication (Withers and Jarvie 2008). The concentration of bioavailable P is correlated with particle size, with smaller particles having higher concentrations of P; this coupled with the preferential transport of fine-grained sediment has important implications for the linking of terrestrial P sources to surface waterways and its management (Kerr et al. 2011). For example, Ockenden et al. (2014) found that both the total nitrogen (N) and P concentrations of sediment trapped in 10 on-farm constructed wetlands were inversely related to median particle size. However, the total mass of accumulated N and P within the wetlands was dependent on the total mass of sediment trapped. Similar to nutrients, many contaminants including metals, organic chemicals, pathogens and pharmaceuticals, also tend to be

concentrated in the fine-grained and organic rich sediment (Oliver et al. 2007; Maskaoui and Zhou 2010; Zheng et al. 2012).

### **6.2.2 Fluvial transport of fine-grained sediment**

Within the fluvial environment, fine-grained sediment ( $< 63 \mu\text{m}$ ) transport and depositional patterns, are primarily driven by the settling velocity of sediment particles (Naden 2010). The settling velocity of sediment is mainly influenced by the size of the particles as the smaller particles tend to remain in suspension as the mass of the particles are counteracted by the upward momentum created by eddies and turbulence. The composition, specifically the clay and organic matter content, of sediment is also an important factor controlling the settling velocity as these components can act as binding agents aggregating individual particles into larger aggregate particles. Aggregation can influence the settling velocity though changes in size, density, shape and internal structure of sediment particles (Droppo et al. 1997).

In addition to particle size, other important aspects of fine-grained sediment hydrodynamics include the velocity and transport capacity of the flow. As there is generally an overall downstream reduction in these two fluvial characteristics the capacity of streams to entrain and transport larger particle is reduced, therefore, a downstream fining/gradation of sediment is often observed as the coarser particles are preferentially deposited upstream (i.e., hydraulic sorting). In addition to hydraulic sorting, abrasion and breakage of sediment particles can also result in the downstream reduction in particle size. This is an important process in watersheds containing low strength material (e.g., shale deposits) and it can be difficult to separate the processes of selectivity from abrasion and breakage (Koiter et al.

2013b). There can also be temporal variation in the selective nature of fluvial transport processes due to increases in precipitation and runoff which result in greater flow velocities and transport capacity (Walling et al. 1992). Similar to changes in the particle size distribution, there is generally an overall downstream increase in the organic matter content of the sediment (Rhoton et al. 2006). The preferential transport of organic matter is largely due to the lower density and the subsequent slower settling velocity of organic-rich particles as compared to mineral particles of a similar size.

Reach-scale features can also have a local influence on fine-grained sediment dynamics. These features include longitudinal (e.g., pool and riffle sequence, change in slope), lateral (e.g., flow characteristics around a meander, changes in channel width) and vertical (e.g., due to channel bed roughness, armoured layers) variations in flow velocities. These local variations result in the deposition of fine-grained sediments in features including, alluvial fans, channel bars, floodplains and infiltration into the interstices of gravels. Much of the literature focuses on the infiltration of sand-sized particles into the gravel matrix (e.g., Wooster et al. 2008; Grams and Wilcock 2014) and less on the infiltration of fine-grained sediment ( $< 63 \mu\text{m}$ ) as this material is often considered to move through a river system unimpeded (i.e., wash load). However, fine-grained sediment storage within the gravel bed is an important consideration as it can reduce hyporheic exchange, compromise invertebrate and fish habitat, and act as a legacy source of sediment-associated nutrients and contaminants (Rehg et al. 2005; Rex and Petticrew 2008; Albers and Petticrew 2012).

In this study, the particle size and organic matter selectivity of fluvial transported fine-grained sediment was investigated under three contrasting gravel channel bed conditions using a large recirculating flume. The objectives of this research were to investigate: 1) the

changes in the concentration, particle size distribution and organic matter content of suspended and bed sediment over distance travelled; 2) the relationship between particle size and organic matter content of the suspended sediment; 3) the changes in the geochemical composition of the suspended sediment; and 4) the ability of a particle size correction factor to account for the changes in suspended sediment geochemistry.

## **6.3 Methods**

### **6.3.1 Flume characteristics**

A recirculating flume located at the Quesnel River Research Centre (QRRC), Likely, British Columbia (BC), Canada, (52°37'08.2"N 121°35'33.3"W) was used to investigate the change in physical and biogeochemical properties of fine-grained sediment over time (distance travelled) under three different channel bed conditions. The recirculating flume was constructed from concrete and had dimensions of 2 m x 2 m x 40 m with a gradient of 0.05 % (see Fig. 6.1 for a schematic of the flume setup). Water was recirculated using two centrifugal pumps (Goulds, Model 3656 LH 54 BF, ITT Industrial Process, NY, U.S.A.) with a discharge of 4500 L min<sup>-1</sup> and large aluminium screens (1 mm opening) were placed at the front and back of the flume to direct the flow of water and dissipate turbulence caused by the pumping of water. The flumes were filled with water to a depth of 15 to 20 cm (above the channel bed) and had a velocity of 25 to 20 cm s<sup>-1</sup> (at 60 % of the depth from the surface) measured with a propeller driven flow meter (Swoffer Instruments Inc., WA, U.S.A.) at 9 and 27 m from the front of the flume, respectively. The water was supplied from on-site groundwater wells and had a neutral pH (7.15), low conductivity (180 µs cm<sup>-1</sup>) and was devoid of any measurable particulate matter.

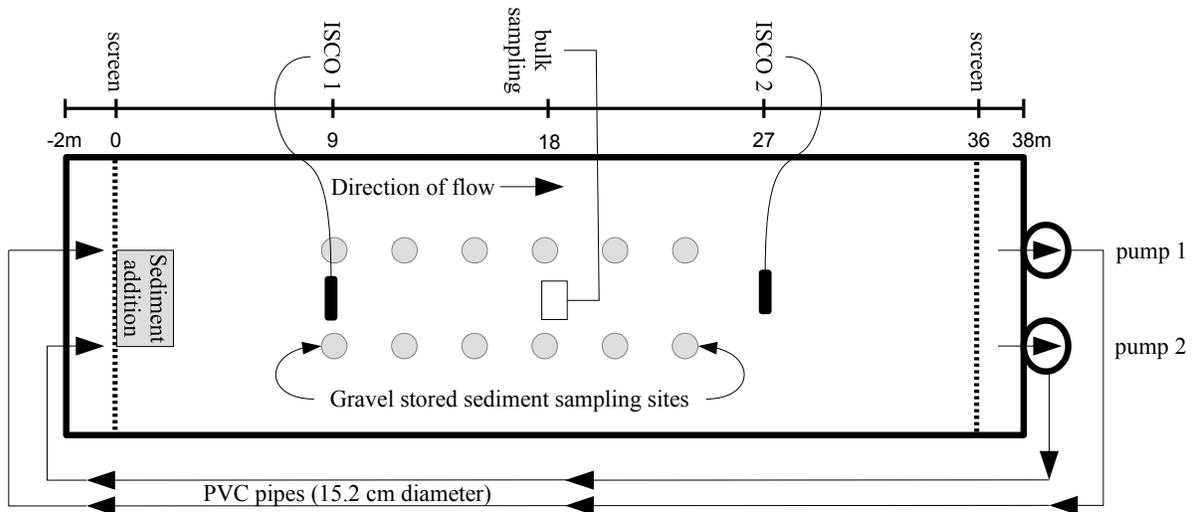


Figure 6.1: Recirculating flume schematic showing the setup of the flume and sampling locations for suspended sediment and gravel-stored sediment (not drawn to scale).

The gravel used for the channel bed material was sourced from a local aggregate quarry and the shape was characterized by selecting 100 stones at random and measuring the three axes of each stone. The gravel were determined to be uni-modal and spherical to slightly discoid in shape using the Zingg classification (Zingg 1935) with a mean diameter (intermediate-axis;  $D_{50}$ ) of  $3.2 \pm 0.7$  cm ( $\pm 1$  SD). The porosity of the channel bed gravel was 30 % and was measured using the water displacement method (12 L gravel sample). The gravel was washed prior to placement in the flume to remove any fine-grained sediment; as well, the gravel and the flume were cleaned in between experiments. The lack of fine-grained sediment within the gravel may represent conditions after flushing flows or recent movement of the channel bed. The three channel bed treatments investigated were: 1) 0-cm gravel bed ( $0 D_{50}$ ); 2) 5-cm gravel bed ( $1.5 D_{50}$ ); and 3) 40-cm gravel bed ( $12.5 D_{50}$ ) which can be considered as representing end-members in terms of channel bed porosity and sediment storage capacity. This allowed for the examination of bed surface roughness, intra-gravel flows and sediment storage capacity on particle selectivity. The gravel depth was uniform

throughout the length of the flume creating a flat/planar bed form.

### **6.3.2 Sediment addition description**

The fine-grained sediment that was added to the flume were soil surface scrapes (0 – 5 cm) collected in the lower slope position at the edge of an agricultural field next to the riparian area, in the Beaver Valley near Likely, BC (52°30'27.8"N 121°52'14.0"W), to represent sediment likely to be eroded and delivered to surface waterways. The soil was air-dried and passed through a 2 mm sieve to remove stones and vegetation (e.g., grasses). The air-dried soil (200 g aliquots) was slaked in water for 10 min prior to being placed in a 125 µm stainless steel sieve and raised and lowered by hand in a vertical motion with an approximate displacement of 10 cm in a container with 15 L of water for 10 min to obtain water-stable aggregates < 125 µm in size (methods based on Angers et al. 2007). For each treatment, a total of 6.5 kg of air-dried soil was wet sieved which resulted in  $2.7 \pm 0.1$  kg of fine-grained sediment (oven-dry weight) being added to each of the three flume treatments.

The fine-grained sediment was delivered in four 15 L aliquots spaced 15 min apart to a stock container at the head of the flume (Fig. 6.1) that had a 800 cm<sup>2</sup> grid of 0.6 cm holes in the front and rear central portion of the container. The downstream grid was screened with 200 µm Nitex mesh (Sefar Inc. QC, Canada) to prevent particles > 200 µm from entering the channel (similar to the method used by Rex and Petticrew 2010). The rapid but finite addition of sediment, as described above, may be characteristic of a channel bank failure or a small mass wasting event; channel banks have been identified as a common source of fluvial sediment (e.g., Walling 2005; Koiter et al. 2013b).

### 6.3.3 Sampling and analysis

The flume simulations were run for 31 hrs, corresponding to approximately 24 km of total distance travelled. The first samples were collected 15 min after the last sediment addition (i.e., 1 hr after the initiation of the flume simulation) to ensure complete mixing within the flume environment. Suspended sediment samples (1 L) were collected using two Isco automatic water samplers (model 3700; Teledyne Isco, Inc, NE, U.S.A.) located at 9 and 27 m (Fig. 6.1) with the intake at 50 % of the flow depth. The suspended sediment samples were split and measured for particle size distribution, suspended sediment concentration and organic matter content (Section 2.3.1). Bulk (20 L) suspended sediment samples, for geochemical analysis, were collected mid-flume at 18 m at 1, 2, 4, 7 and 13 hrs and these samples were allowed to settle at room temperature ( $\sim 20$  °C) for 48 hrs and the clear supernatant was decanted and the sediment samples were air-dried.

No bed sediment was collected for the 0-cm of gravel treatment as patterns of deposited sediment were assessed visually. A total of 12 sediment traps were used to collect gravel-stored sediment for the 5- and 40-cm gravel treatments. The sediment traps were placed in six rows and within a row traps were spaced equidistant from each other and the sidewalls of the flume. Each row was 3 m apart beginning 9 m from the front of the flume (Fig. 6.1). For the 5-cm gravel channel bed, gravel-stored sediments were collected using a sediment trap consisting of a plastic disk (35 cm diameter), with a small lip around the edge (1 cm high) which was placed on the bottom of the flume and covered with 5 cm of gravel. For the 40-cm gravel channel bed, gravel-stored sediments were collected using sediment traps that consisted of a waterproof bag (20 cm diameter and 35 cm long) secured to a metal

ring and buried 20 cm deep into the gravel bed and covered with gravel (Rex and Peticrew 2008). At the end of the flume simulation run the sediment traps were collected and the sample (including gravel) was placed in a 125  $\mu\text{m}$  sieve and the fine-grained sediment separated from the gravel by rinsing with water. A subsample of the fine-grained sediment was taken for particle size analysis and organic matter content (Section 2.3.1), with the remainder being allowed to settle. The clear supernatant was then decanted and the sediment was oven-dried and weighed.

#### *6.3.3.1 Particle size and organic matter content*

The SSA of the sediment samples were measured using a Malvern Mastersizer 3000 laser diffraction system (Malvern, UK) (0.01 – 3500  $\mu\text{m}$  diameter measurement range) assuming a constant particle density of 2.65  $\text{g cm}^{-3}$ . The SSA of sediment samples was used as the primary measure of particle size as opposed to median particle size because comparisons of the median particle size would require that the distributions have similar shapes (e.g., normal distribution). However, it is important to note that increases in SSA correspond to a reduction in the median particle size diameter ( $D_{50}$ ). The added, suspended, and gravel-stored sediment were measured for the non-dispersed or effective SSA (E-SSA) and the dispersed SSA (D-SSA); the latter following 2 min of in-line sonication at 90% power (45 W). The suspended sediment samples were filtered using pre-ashed glass fibre-filters (0.7  $\mu\text{m}$  pore size) to determine the suspended sediment concentration and ashed at 550  $^{\circ}\text{C}$  for 1 hr to determine the organic matter content. Suspended sediment concentrations were corrected using a dilution factor to account for the additional pore water within the gravel bed matrix. The dilution factors were calculated using the measured gravel porosity and the depth of the gravel bed and were 1, 1.07 and 1.53 for the 0-, 5- and 40-cm gravel bed

treatments, respectively. Similarly, subsamples of the added sediment and gravel-stored sediment were ashed to determine organic matter content.

The bulk suspended sediment samples were analyzed for a broad suite of geochemical elements (51 elements in total) using ICP-MS following a microwave-assisted digestion with aqua-regia (ALS Mineral Division, North Vancouver, BC, Canada). Subsamples of the bulk suspended sediment were also measured for the absolute SSA (A-SSA) following digestion with 30 % hydrogen peroxide to remove organics and disaggregated chemically with a solution of sodium hexametaphosphate and sodium carbonate (Kroetsch and Cang 2007) and physically with 2 min of sonication at 45 W (Misonix S-4000, Qsonica, Newtown, CT, USA).

#### **6.3.4 Data analysis**

All statistical analysis was undertaken using R Statistical Software v3.1.2 (R Core Team 2015) through RStudio Integrated Development Environment v0.98.5 (RStudio 2015). All plots were created using the R package ggplot2 v0.9.3.1 (Wickham 2009) with non-transformed data. For the suspended sediment, the change in concentration, organic matter content and SSA over time, as well as differences between the three channel bed conditions, were assessed using linear regression with treatment contrasts using the 5-cm gravel treatment as the reference level. The relation between organic matter content and SSA for suspended sediment was nonlinear and a piecewise linear regression was used. The data were split based on the largest SSA for the 0-cm gravel treatment which corresponded to 990.2 and 1112.4 m<sup>2</sup>kg<sup>-1</sup> for the E-SSA and D-SSA, respectively.

Locally weighted regression, or LOESS, curves were used to help visualize the spatial patterns for the bed sediment characteristics and were generated using the `stat_smooth`

function and a spanning coefficient of 1.25 was used to prevent over-fitting.

The relation between geochemical concentrations and A-SSA for the bulk suspended sediment samples were assessed using linear regression. A hypothetical size-corrected concentration regression line was created using the common correction factor which was based on the ratio of A-SSA of suspended to the added sediment (Collins et al. 1997). Using the regression line for the measured suspended sediment geochemical concentrations it was assumed that at  $965 \text{ m}^2 \text{ kg}^{-1}$ , where the suspended and the original added sediment A-SSA are equal (i.e., correction factor = 1.00), the geochemical concentrations were also the equal. The concentration at this A-SSA was then multiplied by the calculated correction factors and plotted as the hypothetical size-corrected geochemical concentration.

## **6.4 Results**

### **6.4.1 Changes in concentration, particle size and organic matter content**

#### *6.4.1.1 Suspended and gravel-stored sediment concentrations*

Given the total mass of the added sediment to the volume of water in the flume (excluding the volume of water contained within the gravel bed), the calculated maximum suspended sediment concentration, if all sediment remained in suspension with no mixing with gravel pore water, was approximately  $170 \text{ mg L}^{-1}$  for each flume treatment. The suspended sediment concentrations were averaged between the two sampling locations (located at 9 and 27 m; Fig 6.1) prior to statistical analysis and the changes in the suspended sediment concentration over time are shown in Fig. 6.2a . The maximum recorded suspended sediment concentration (1 hr) was 92.3, 90.5, and  $57.5 \text{ mg L}^{-1}$  for the 0-, 5- and 40-cm gravel bed treatments, respectively. Overall, the concentration decreased over time (Table 6.1a) and

was characterized by a rapid decrease followed by a slow but continuous decline in concentration. At the termination of each flume simulation (31 hrs) the suspended sediment concentration was 25.7, 13.2 and 1.4 mg L<sup>-1</sup> corresponding to approximately 12.1, 6.0 and 0.6 % of the total added sediment remaining in suspension for the 0-, 5- and 40-cm gravel bed treatments, respectively (Fig. 6.2a). There was a significant interaction between sampling time and channel bed conditions. The rate of decline in concentration was the lowest for the 0-cm gravel treatment followed by the 5-cm gravel treatment and the rate of decline was the highest for the 40-cm gravel treatment (Table 6.1a).

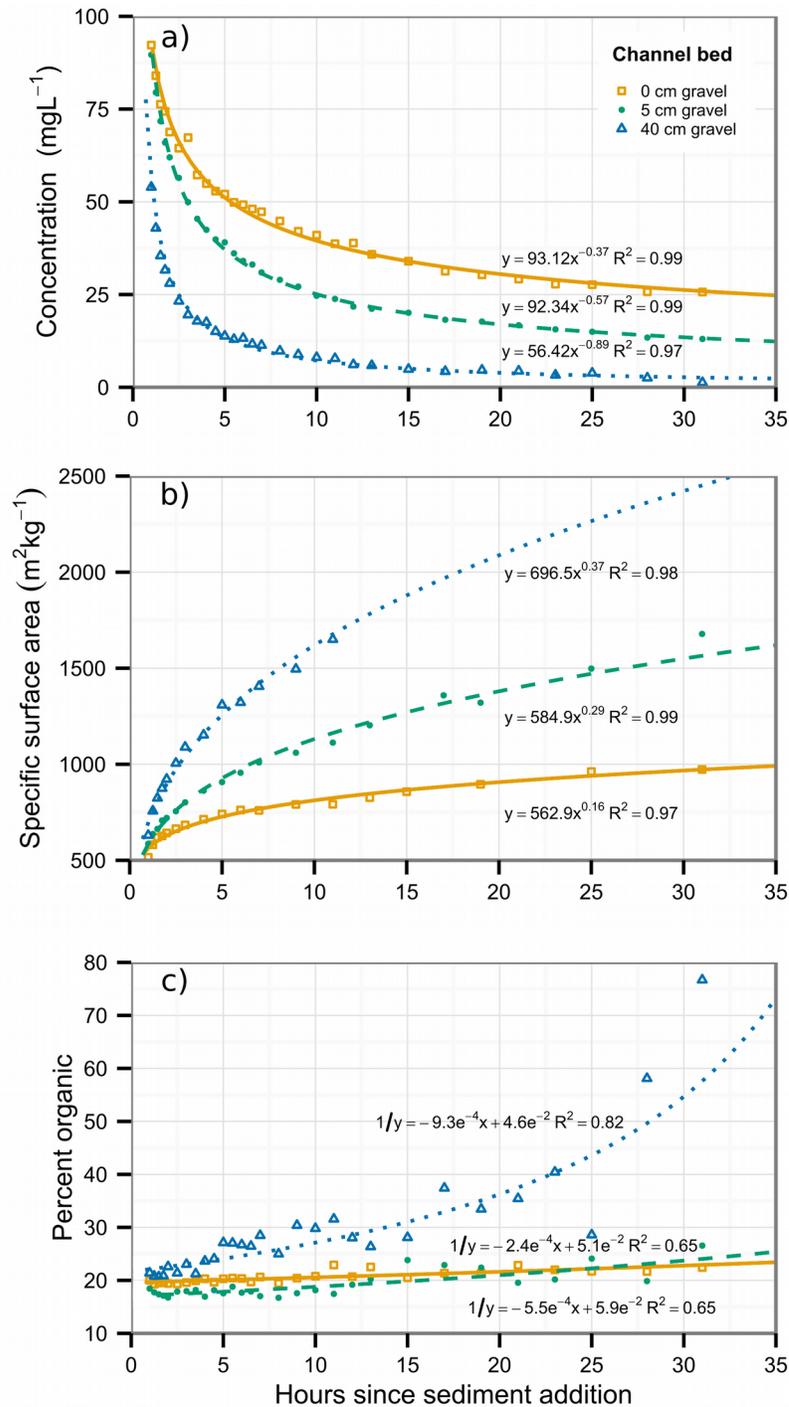


Figure 6.2: The change in: (a) suspended sediment concentration (corrected for dilution); (b) specific surface area (calculated using E-SSA); and (c) organic matter content of suspended sediment, with time (distance travelled) over three channel bed conditions. Dilution factors of 1, 1.07 and 1.53 were determined for the 0, 5, and 40 cm gravel beds, respectively.

Table 6.1: Results of linear models looking at the correlation in concentration (a), specific surface area (b) and organic matter content (c) of suspended sediment with hour (distance travelled), channel bed and particle type. Channel bed contrasts compares 0 cm to 5 cm gravel (1) and 40 cm to 5 cm gravel (2).

Analysis	Parameter	Estimate	Std. Error	DF	t value	P(> t )
<b>(a) Concentration</b> log <sub>10</sub> (mg L <sup>-1</sup> )	(Intercept)	1.965	0.018	81	109.34	< 0.001**
	log <sub>10</sub> (hour)	-0.566	0.019	81	-29.41	< 0.001**
	0 cm vs. 5 cm gravel	0.004	0.025	81	0.14	0.887
	40 cm vs. 5 cm gravel	-0.214	0.025	81	-8.42	< 0.001**
	log <sub>10</sub> (hour) x channel bed (1)	0.193	0.027	81	7.11	< 0.001**
	log <sub>10</sub> (hour) x channel bed (2)	-0.327	0.027	81	-12.01	< 0.001**
<b>(b) Specific surface area</b> log <sub>10</sub> (m <sup>2</sup> kg <sup>-1</sup> )	(Intercept)	2.827	0.004	91	646.21	< 0.001**
	log <sub>10</sub> (hour)	0.278	0.005	91	57.33	< 0.001**
	0 cm vs. 5 cm gravel	-0.019	0.006	91	-3.20	0.002*
	40 cm vs. 5 cm gravel	0.072	0.006	91	11.36	< 0.001**
	Particle type (E-SSA vs. D-SSA)	-0.055	0.003	91	-20.37	< 0.001**
	log <sub>10</sub> (hour) x channel bed (1)	-0.123	0.007	91	-17.92	< 0.001**
log <sub>10</sub> (hour) x channel bed (2)	0.088	0.009	91	9.43	< 0.001**	
<b>(c) Organic matter content</b> 1/(% <sub>organic</sub> )	(Intercept)	0.0588	0.0009	81	63.38	< 0.001**
	hour	-0.0006	0.0001	81	-7.97	< 0.001**
	0 cm vs. 5 cm gravel	-0.0078	0.0013	81	-5.92	< 0.001**
	40 cm vs. 5 cm gravel	-0.0126	0.0013	81	-9.61	< 0.001**
	hour x channel bed (1)	0.0003	0.0001	81	3.23	0.002*
	hour x channel bed (2)	-0.0004	0.0001	81	-3.81	< 0.001**

\*\* indicates P < 0.001

\* indicates P < 0.01

DF represents degrees of freedom

No measurement of gravel-stored sediment was made for the 0-cm gravel treatment, however, visual observations showed that the amount of sediment on the bottom of the flume increased towards the back of the flume (i.e., the majority of sediment accumulated between 25 and 36 m; Fig. 6.1). The amounts of gravel-stored sediment for the 5- and 40-cm gravel beds are shown in Fig. 6.3a. There is a small difference between the two treatments with an average of  $28.1 \pm 5.4$  ( $\pm 1$  SD) and  $35.6 \pm 5.4$  g m<sup>-2</sup> for the 5- and 40-cm of gravel treatments, respectively. There was no consistent trend in the amount of gravel-stored sediment along the length of the flume, however, there was evidence of a difference along the width (i.e., left to right) of the flume. This was especially evident in the 5-cm gravel treatment near the front (9

– 12 m; Fig. 6.3a) of the flume and these observations suggest that the flow patterns were not linear along the entire length of the flume.

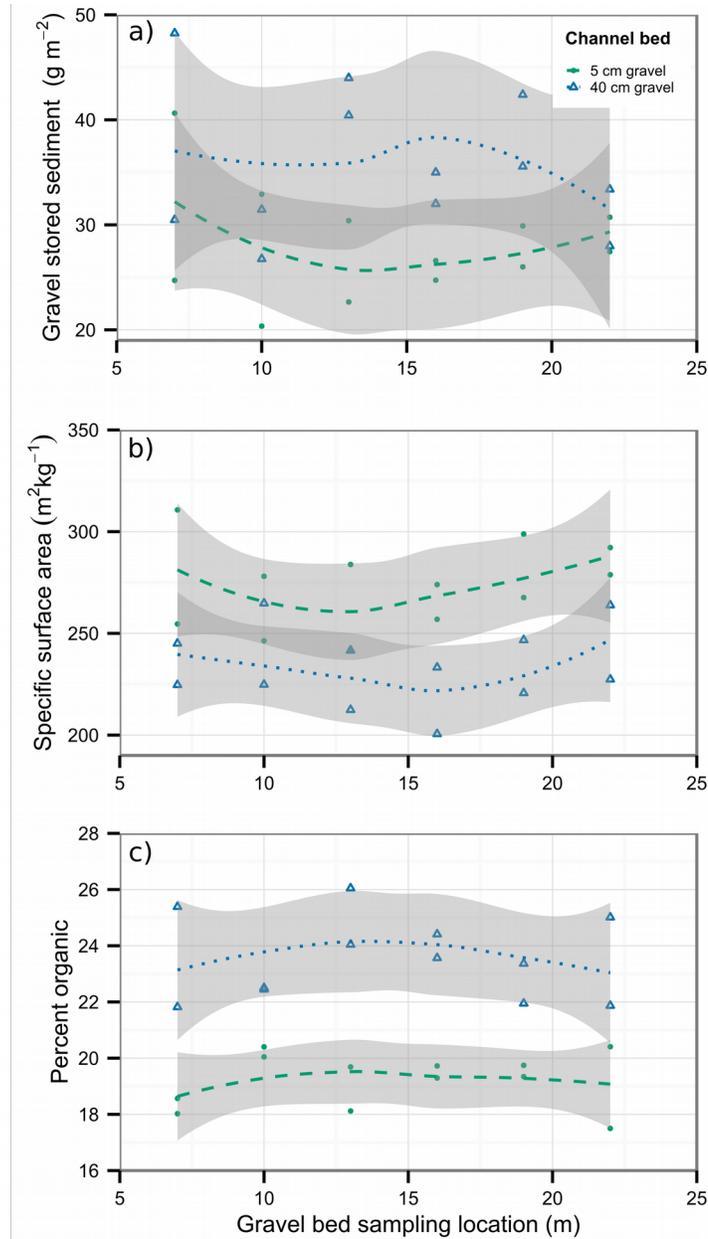


Figure 6.3: Properties of the gravel-stored fine-grained sediment along the length of the flume for the 5 and 40 cm gravel bed treatments. Sediment properties measured include: (a) total stored mass; (b) specific surface area (calculated using E-SSA); and (c) organic matter composition. See Fig. 6.1 for sampling locations.

#### 6.4.1.2 Particle size

The added sediment had an average E-SSA and D-SSA of  $312.3 \pm 89.7$  ( $D_{50}$ ;  $19.9 \pm 8.1 \mu\text{m}$ ) and  $450.3 \pm 78.1 \text{ m}^2 \text{ kg}^{-1}$  ( $D_{50}$   $11.9 \pm 2.4 \mu\text{m}$ ) ( $\pm$  range), respectively. The D-SSA is larger than the E-SSA due to the effect of particle aggregation. The SSA data were averaged between the two sampling locations (9 and 27 m; Fig. 6.1) prior to statistical analysis and the E-SSA data are shown in Fig. 6.2b. The changes in the particle size had an inverse trend, but a similar rate of change, to the suspended sediment concentration. Overall there was a significant increase in the SSA (i.e., decrease in particle size) over time (Table 6.1b) and it was characterized by an immediate and large increase in E-SSA following the addition of sediment as observed during the first suspended sediment measurement (1 hr) with a measured E-SSA of 515.3, 586.2 and  $630.2 \text{ m}^2 \text{ kg}^{-1}$  ( $D_{50}$ ; 8.62, 7.13 and  $6.24 \mu\text{m}$ ) for the 0-, 5- and 40-cm of gravel treatments, respectively. There was an initial rapid increase in the E-SSA over the first few hours and then the rate of change slowed as the flume simulation progressed. For the 40-cm gravel treatment there was insufficient suspended sediment after 10 hrs to make reliable particle size measurements. There was no significant interaction between particle type (E-SSA or D-SSA) and sampling time (hrs) (i.e., the relations between E-SSA or D-SSA and sampling time had similar characteristics) and this interaction term was removed from the analysis. The rate of increase in SSA was less for the 0-cm compared to the 5-cm gravel bed and the rate of increase in SSA was greater for 40-cm compared to the 5-cm gravel bed (Table 6.1b).

The E-SSA and D-SSA for the gravel-stored sediment for both 5- and 40-cm gravel beds was coarser than the added sediment (shown in Fig. 6.3b). The gravel-stored sediment is coarser in the 40-cm gravel treatment as compared to the 5-cm gravel treatment. Both the E-

SSA and D-SSA showed a similar amount of variation with a range in the E-SSA of 69.2 and 64.2  $\text{m}^2 \text{kg}^{-1}$  and a range in the D-SSA of 65.5 and 54.9  $\text{m}^2 \text{kg}^{-1}$  for the 5- and 40-cm gravel treatments, respectively. The E-SSA of the stored fine-grained bed sediment showed little change along the length of the flume (Fig. 6.3b).

#### *6.4.1.3 Organic matter content*

The organic matter content of the added sediment ranged between 19.5 and 20.4 % with an average of 19.9 %. The organic matter contents of the suspended sediment were averaged between the two sampling locations (located at 9 and 27 m; Fig. 6.1) prior to statistical analysis and the changes in organic matter content over time are shown in Fig. 6.2c. Initially, the organic matter of the suspended sediment was similar to the added sediment for all three treatments. Overall, as the flume simulations progressed there was an increase in the suspended sediment organic matter content (Table 6.1c). At the termination of the flume simulation (31 hr), there was only a small (< 10 %) increase in the organic matter content compared to the start of the flume simulation (1 hr) for the 0- and 5-cm gravel beds, however, there was a large increase in the organic matter content for the 40-cm gravel treatment. There was a significant interaction between sampling time and channel bed conditions. The rate of increase in organic matter content was less for the 0-cm gravel compared to the 5-cm gravel and the rate of increase in organic matter content was greater for 40-cm gravel compared to the 5-cm gravel (Table 6.1c). The organic matter content of the bed sediment for the 5- and 40-cm gravel beds were both similar to the added sediment and show no spatial trends along the length of the flume with average values of  $19.2 \pm 1.0$  % and  $23.5 \pm 1.5$  % for the 5- and 40-cm gravel treatments, respectively (Fig. 6.3c).

#### 6.4.2 Relation between particle size and organic matter

The relation between organic matter content and E-SSA was non-linear (Fig. 6.4) over the range investigated. Overall there was no significant relation for particles below the E-SSA threshold of  $1000 \text{ m}^2 \text{ kg}^{-1}$  and a significant positive relation for particles above the E-SSA threshold (Table 6.2). For the particles below the  $1000 \text{ m}^2 \text{ kg}^{-1}$  threshold, there was a significant interaction between E-SSA and channel bed conditions with the 0-cm gravel bed having a steeper positive slope compared to the 5-cm gravel bed (Table 6.2a). The relation between organic matter and E-SSA was the same for the 5- and 40-cm channel beds for above the threshold value (Table 6.2b). There was no significant interaction between particle type (effective or dispersed sediment) and the SSA and this interaction term was removed from the analysis.

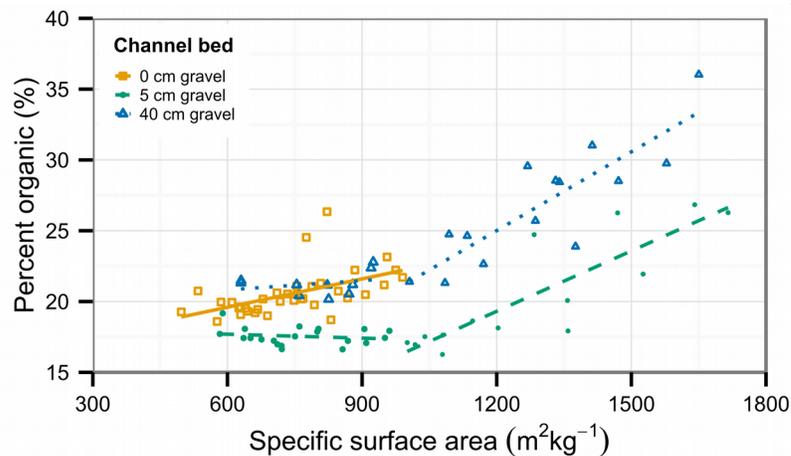


Figure 6.4: The relation between specific surface area (calculated using E-SSA) and organic matter content for the suspended sediment over three channel bed conditions.

Table 6.2: Results of piecewise regression looking at the correlation in organic matter content for small SSA (a) and large SSA (b) with specific surface area, channel bed and particle type for suspended sediment. Channel bed contrasts compares 0 cm to 5 cm gravel (1) and 40 cm to 5 cm gravel (2).

Analysis	Parameter	Estimate	Std. Error	DF	t value	P(> t )
<b>(a) Organic matter content (%)</b> Small specific surface area (< 1000 m <sup>2</sup> kg <sup>-1</sup> )	(Intercept)	17.832	1.141	125	15.63	<0.001 *
	SSA	0.000	0.001	125	-0.09	0.932
	0 cm vs. 5 cm gravel	-2.099	1.357	125	-1.55	0.124
	40 cm vs. 5 cm gravel	1.534	2.119	125	0.72	0.471
	Particle type (E-SSA vs. D-SSA)	-0.377	0.208	125	-1.81	0.073
	SSA x channel bed (1)	0.006	0.002	125	3.88	<0.001 *
	SSA x channel bed (2)	0.003	0.002	125	1.03	0.306
<b>(b) Organic matter content (%)</b> Large specific surface area (> 1000 m <sup>2</sup> kg <sup>-1</sup> )	(Intercept)	2.841	2.203	51	1.29	0.203
	SSA	0.014	0.002	51	8.53	<0.001 *
	40 cm vs. 5 cm gravel	2.444	3.362	51	0.73	0.471
	Particle type (E-SSA vs. D-SSA)	-2.514	0.603	51	-4.17	<0.001 *
	SSA x channel bed (2)	0.002	0.002	51	1.01	0.317

\* indicates P < 0.001

DF represents degrees of freedom

### 6.4.3 Sediment geochemistry

Only the bulk suspended sediment samples collected in the 0-cm gravel bed treatment for the first 13 hrs had enough mass for geochemical analysis (0.5 g needed for analysis). The A-SSA of the added sediment was 959.3 m<sup>2</sup> kg<sup>-1</sup> (D<sub>50</sub>; 4.21 μm) and the range of A-SSA for the suspended sediment was 964.7 – 1237.0 m<sup>2</sup> kg<sup>-1</sup> (D<sub>50</sub>; 2.77 - 3.96 μm). The ratio between the A-SSA of the collected suspended sediment to the added sediment corresponds to a particle size correction factor ranging between 1.01 and 1.29 over the first 13 hrs of the flume simulation. The relationship between geochemical concentration and SSA was not consistent between the different elements in terms of linearity and the direction and magnitude of the slope. Out of the 51 elements investigated, six elements were below detection limits in one or more of the sediment samples and were removed from the analysis. Of the remaining 45 elements, 16 elements had a positive slope and two elements had negative slopes that were

significantly different than 0 ( $P < 0.1$ ;  $n = 5$ ). Fig. 6.5 shows examples of a positive (As), negative (La) and no clearly defined relationship (Cd) between A-SSA and geochemical concentration. The hypothetical size corrected concentration is also plotted to highlight some of the potential errors associated with size corrected geochemical concentrations. For example, at 13 hours where the A-SSA of the suspended sediment was  $1237 \text{ m}^2 \text{ kg}^{-1}$ , there is the potential of an overestimation of the concentration of As and La of 9.5 % and 43.0 %, respectively.

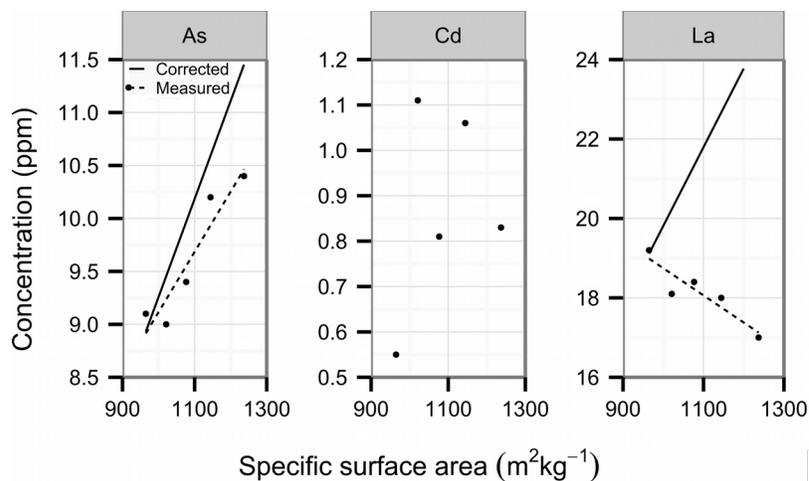


Figure 6.5: Three examples of the different relations between geochemical concentration and specific surface area (calculated using A-SSA), including the hypothetical size corrected concentration. Arsenic, positive relation ( $p < 0.1$ ); Cadmium, nonlinear relation; and Lanthanum, negative relation ( $p < 0.1$ ).

## 6.5 Discussion

### 6.5.1 Suspended sediment concentration and particle size selectivity

The effective particle size is typically a more relevant measure of particle size when investigating fluvial transport processes as it is the overall size, along with shape, composition, density and internal structure of sediment particles that determines the settling

and entrainment velocities (Droppo 2001). However, results showed that the patterns of change in the particle size distribution over time (i.e., distance travelled) did not significantly differ between the E-SSA and D-SSA (Table 6.1b). This suggests that the particles were transported as dense water-stable aggregates with similar hydrodynamic behaviour as compared to discrete particles. However, it is unclear whether the stability of the aggregates reflects the properties of the added sediment, the flow characteristics within the flume or the duration of the experiment. To assess whether flocculation was occurring along the length of the flume the difference for both E-SSA and D-SSA between the two sampling locations (9 and 27 m; Fig. 6.1) were calculated for each treatment. There was not a significant ( $p < 0.05$ ) difference in either the E-SSA or D-SSA between the 9 and 27 m suspended sediment sampling locations (data not shown). Overall, there was a very small average difference in SSA between the two sampling locations of  $-15.1$  and  $-1.9 \text{ m}^2 \text{ kg}^{-1}$  for the E-SSA and D-SSA, respectively. The reduction in both the E-SSA and D-SSA suggests there is some small degree of disaggregation or selective deposition of larger particles between the two sampling locations. The idea of selective deposition is supported by the small decrease in suspended sediment concentration (average difference of  $0.4 \text{ mg L}^{-1}$ ) between the two sampling locations.

Regardless of channel bed conditions there was a significant reduction in suspended sediment concentration and a decrease in the particle size and an increase in the organic matter content of the suspended sediment over time (i.e., distanced travelled). The presence of lower water velocities along the walls of the flume, due to the frictional resistance, and the greater depth of water and corresponding lower velocities at the rear of the flume will have played a role in promoting sediment deposition of the coarser sediment particles.

Furthermore, the cohesive nature of the added sediment would have reduced the re-entrainment of deposited sediment. The Shields (1936) diagram shows that for inorganic particles  $< 200 \mu\text{m}$ , higher velocities and shear stress thresholds are needed for entrainment as the particle size decrease. For example, the median diameter (effective) of the added sediment was  $20 \mu\text{m}$  and the corresponding lower limit of entrainment, according to the Hjulsström (1936) curve is approximately  $40 \text{ cm s}^{-1}$ , compared to the velocities of  $20 - 25 \text{ cm s}^{-1}$  in this study.

Comparing the 0- to the 5-cm gravel bed treatments presents an opportunity to look at the effect of channel bed roughness and gravel bed pore volume on the preferential trapping of sediment. The addition of 5 cm of gravel significantly reduced the overall suspended sediment concentration, resulted in smaller particle sizes and increased the organic matter content of the suspended sediment compared to the 0-cm gravel bed. The roughness elements created by the gravel changes the vertical velocity profile by slowing the water velocity near the bed surface due to drag forces (increased fluid contact at the channel bed boundary) (Kirkgöz 1989). The Manning's roughness coefficient for straight uniform concrete channel ranges between  $0.012 - 0.018$  as compared to  $0.028 - 0.035$  for a gravel bed (Arcement and Schneider 1989). The resulting reduction in near bed velocity would allow for smaller grains of sediment to settle. In many natural settings the channel bed is not composed of grains of a single size class (uniform) but rather composed of a wide range in particle size from clay and silts through to coarse sands and gravels. The entrainment of particles from non-uniform beds tend not to follow the Shields diagram and fine-grained sediments of non-uniform channel beds are more difficult to entrain compared to the same sized particles in a uniform channel bed (Xu et al. 2008). Within the flume simulation, the addition of a gravel bed created a bed

with a bimodal grain size distribution (i.e., the added fine-grained sediment and the coarse gravel), and the gravel would have acted as a protecting layer preventing the erosion of the fine-grained sediment. Furthermore, the addition of the gravel would have increased the amount of turbulence near the channel bed. Turbulence can penetrate below the channel surface and can result in the resuspension of sediment stored near the channel bed surface (Packman and Salehin 2003). However, this effect diminishes with depth and may, in part, explain the lower concentrations and smaller particles in the 40-cm as compared to the 5-cm gravel beds.

The comparison of the 40- to the 5-cm gravel channel bed allows for the investigation of the effects of intra-gravel flow on the dynamics of suspended sediments. Previous research (Slager 2014), using salt as a tracer in a similar QRRC flume, under similar flow and gravel bed conditions, showed that the water residence time quickly increased with depth. The residence time within the gravel matrix was approximately 5 and 55 times greater at a depth of 5 and 15 cm, respectively, compared to the channel bed surface (Slager 2014). Intra-gravel flows exhibit a sieve-like removal of all but the very fine-grained sediment as the tortuous flow pathways through the gravel would slow the velocity of the flow allowing for a greater amount of sediment deposition. For example, Petticrew et al. (2007) demonstrated through the use of lidded and non-lidded channel bed sediment traps that a significant amount of fine-grained sediments can be deposited by lateral flows through gravel. With larger grain sizes (e.g., sand), particles can become trapped among the pore spaces near the surface of the gravel creating a seal, or cap, preventing the downward migration of sediment, however, given the fine-grained nature of the added sediment and the high porosity of the gravel in this study it is likely that the added sediment would penetrate deep into the gravel bed. The fine-

grained sediment stored deeper in the gravel bed is less exposed to turbulence, which would limit the amount of sediment being resuspended (Gibson et al. 2011; Hamm et al. 2011).

The nature of the sediment supply is important to consider as it will influence the particle size and organic matter selectivity of fluvial transported sediment. For example, a sediment pulse, as demonstrated in this study, will be different as compared to a more continuous supply of sediment (e.g., surface erosion). The latter would maintain a higher and more consistent suspended sediment concentration resulting in a higher fluid density which will change the settling velocity of sediment particles. In addition, the continuous deposition of sediment will eventually exceed the storage capacity of the gravel bed or create a surface seal changing the boundary conditions from a rough and porous to a smooth and impermeable surface, similar to the 0-cm gravel treatment.

### **6.5.2 Organic matter selectivity**

All three flume treatments show an increase in the organic matter content of the suspended sediment over time. This is likely due, in part, to the difference between the density of organic matter ( $0.9 - 1.3 \text{ Mg m}^{-3}$ ) and mineral particles ( $2.6 - 2.75 \text{ Mg m}^{-3}$ ) (Brady and Weil 2001). The decrease in density generally lowers the settling velocity allowing for the preferential transport of organic-rich particles. The aggregated sediment particles may have been breaking apart due to the pumps within the recirculating flume setup and breaking down the aggregates into their primary organic and inorganic components. The more dense mineral fraction preferentially settles while the organic component remains in suspension which results in the organic-rich sediment remaining in suspension.

The relation between E-SSA and organic matter content of the suspended sediment

was not linear over the range of E-SSA investigated. Only suspended sediment particles over a E-SSA threshold value of  $1000 \text{ m}^2 \text{ kg}^{-1}$  showed a significant positive relation between E-SSA and organic matter content. This suggests that the selective process involved in fluvial transport is different, in terms of magnitude of the effect and the trend over time, between particle size and organic matter. This was also evident with respect to changes over time for each property as particle size had a log-log relation (Fig. 6.2b) while organic matter had a reciprocal relation (Fig. 6.2c). Furthermore, making generalizations about the organic matter content based on particle size may depend on the range of E-SSA being investigated; i.e., the relation may be considered linear over small ranges of E-SSA. Small sample masses prevented the investigation of the relationship between A-SSA and organic matter which is needed to fully understand the particle size and organic matter dynamics.

### **6.5.3 Implications for geochemical composition of suspended sediment**

The lack of any consistent trend between the different geochemical elements suggests that the mineralogy of the inorganic fraction of the sediment is not uniform across particle sizes (Fig. 6.5). The distribution of geochemical elements within sediment, whether it is part of the crystalline structure (e.g., primary or secondary minerals) or absorbed onto the surface (e.g., exchangeable), may affect the relation between A-SSA and geochemical concentrations. Other sediment properties may also influence the A-SSA and geochemical concentration relation, for example, Fe-oxides have been shown to increase soil aggregation (e.g., Duiker et al. 2003) as well as have a large influence on the geochemical composition of soils due to their high A-SSA (Horowitz 1991). Therefore, a larger single aggregate will have a lower E-SSA than the sum of the A-SSA for all the individual particles that the aggregate is composed

of. When these larger aggregates are preferentially deposited they may sequester a disproportional amount of other elements compared to the smaller aggregates or discrete particles remaining in suspension. The dissolution and desorption of elements from the added sediment once entering the flume environment would have also contributed to the range of trends observed. The organic matter content of the sediment may have also influenced the geochemical composition, however, the added effects of organic matter may have been limited as there was only a small change (1 – 13 hrs) in organic matter content for 0 cm gravel bed treatment for which the geochemistry of the suspended sediment was investigated (Fig. 6.2b). Further investigation of the partitioning of geochemical elements into various fractions (e.g., exchangeable, bound to organic matter and residual) is needed to fully understand the relation between A-SSA, organic matter content and geochemical concentrations.

This study highlights the importance of the particle size selectivity process on geochemical (e.g., trace metals) flux and transport studies. It is important to establish the relations between particle size and elemental concentrations for each element of interest as the results from this study show that the relation between particle size and elemental concentration can vary between elements. Once the particle size and elemental concentration relation has been established this information can be used in conjunction with both the suspended sediment concentration and particle size distribution to estimate total load. Furthermore, the results from this study demonstrate that both the particle size and organic matter content selectivity can change according to the channel bed conditions, specifically the channel bed roughness and the presence of high porosity gravels. Fig. 6.6 depicts a conceptual diagram showing the changes in particle size, organic matter content,

suspended sediment concentration and gravel bed sediment storage with changing gravel bed depth as observed in this study. This is important to consider as the channel bed conditions can change over time from high flow events that flush out gravel-stored fine-grained sediment or result in gravel bed movement. In addition, channel bed condition can also vary longitudinal from headwaters towards the watershed outlet as channels transition between bed types, for example, from bedrock to gravel through to sand channel bed types. The spatial and temporal variations in particle size and organic matter selectivity needs to consider when selecting sampling locations and timing and interpreting the data (Koiter et al. 2013a).

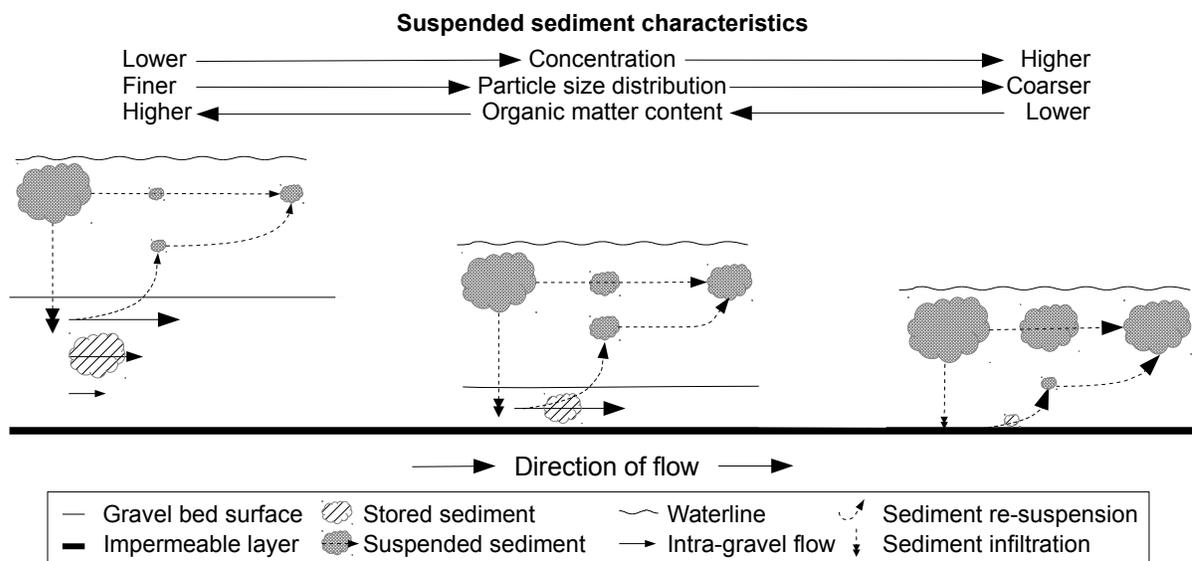


Figure 6.6: Conceptual diagram showing the influence of gravel beds on the deposition, storage and resuspension of fine-grained sediment. The gravel bed increases bed roughness slowing the velocity near the channel bed which promotes deposition. Increasing the depth of the gravel bed modifies the intra-gravel flow resulting in greater storage and limiting the resuspension of sediment.

The relation between particle selectivity and geochemical composition is an important aspect of many sediment fingerprinting studies. Typically there is a difference in both particle size distribution and organic matter content between potential sources of sediment and

downstream collected sediment that is corrected for by using simple correction factors based on ratios of A-SSA and organic matter content between source and sediment. However, Smith and Blake (2014), demonstrated that the particle size and organic matter correction factors can have a large influence in the final source apportionment results. Therefore, it is important to test the validity of such correction factors prior to using them. The results from this study, although limited, support the conclusions of Koiter et al. (2013a) for the need to carefully consider particle size correction factors and the elements selected as tracers in sediment fingerprinting studies, as not all elements have the same A-SSA and concentration relation. The range in ratios found between the different geochemical elements in this study are similar to the research by others (e.g., Russell et al. 2001; Smith and Blake 2014) and draws attention to the assumption made when using particle size correction factors. This research highlights the continued need for research and empirical evidence for the processes of particle size and organic matter selectivity and their subsequent influence on geochemical properties if the sources and sinks are going to be linked in a robust and reliable manner. Fluvial transport is one of the last steps of the sediment cascade and further work is needed to investigate the additional influences of particle selectivity of the erosional and sediment delivery processes when linking sediment sources to downstream collection.

## **6.6 Conclusions**

Using a recirculating flume it was demonstrated that the distance travelled (i.e., transport time), and channel bed characteristics both had a significant effect on the particle size and organic matter selectivity of the transported suspended sediment. Furthermore, it was shown that a gravel bed (0- vs 5-cm gravel treatments) introduced small-scale roughness

which resulted in the preferential deposition of larger particles into the channel bed as compared to a smooth planer channel bed. The change from the 5- to 40-cm the gravel bed treatments increased the amount of intra-gravel flow and reduced the potential for resuspension resulting in further reduction in the particle size of the suspended sediment. This information demonstrates that the channel bed conditions are an important factor to consider when selecting sediment sampling sites and interpreting the data they provide. The geochemical properties of the suspended sediment changed as a result of fluvial transport but it was difficult to properly account for these changes based on particle size alone. There are other confounding factors, including the relation of aggregate size and stability to sediment geochemistry, that need to be considered. This research helps to understand the process of particle selectivity, in terms of particle size and organic matter content, which is an important part of many sediment management tools as well as aiding in the interpretation of sediment-associated nutrient and contaminant transport dynamics.

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## **7 Investigating the role of connectivity and scale in assessing the sources of sediment in an agricultural watershed in the Canadian prairies using sediment source fingerprinting**

### **7.1 Abstract**

Sediments adversely impact the quality of surface waters and are a significant source of contaminants such as nutrients and pesticides in agricultural watersheds. The development of effective Beneficial Management Practices (BMPs) to minimize these impacts requires a sound understanding of the sources of sediments. The objectives of this study were: (1) to determine the sources of sediment in an agricultural watershed in the Canadian prairies using sediment source fingerprinting; and (2) to assess the results of the sediment fingerprinting study within the context of the scale of observation and the hydro-geomorphic connectivity of the watershed. Geochemical and radiochemical fingerprints were used to discriminate between the three potential sediment sources identified: topsoil, streambanks and shale bedrock. Suspended and bed sediment samples were collected over the course of three years at six locations along the main stem of the creek, ranging from 3<sup>rd</sup> order (48 ha) to 7<sup>th</sup> order (7441 ha) drainage basins. Four sediment fingerprint properties were selected that met statistical- and process-based selection criteria and the Stable Isotope Analysis in R (SIAR) program was used to estimate the proportion of sediment derived from each source at each sampling location in the watershed. The suspended sediments in the upper reaches were dominated by topsoil sources (85 – 64 %) while the suspended sediments moving through the lower reaches and being exported from the watershed had a higher proportion of sediment

coming from streambank and shale bedrock sources. The results of this sediment fingerprinting study demonstrate that there is a switch in sediment sources between the headwaters and the outlet of the watershed. This research highlights the importance of the sampling location, scale and connectivity on the interpretation of results derived from the sediment fingerprinting technique.

## **7.2 Introduction**

### **7.2.1 Lake Winnipeg Basin**

In many river basins, agricultural activities have been identified as a significant source of sediment and associated nutrients and contaminants (e.g., pathogens, pesticides). Agriculture in Canada covers approximately 7% (6.8 million ha) of the total land area with 80% situated in the prairie region of the country (i.e., the provinces of Manitoba, Saskatchewan and Alberta) (Statistics Canada 2012). The agricultural landscape of the prairies is a mosaic of arable cropland, pasture and forage. The Lake Winnipeg basin covers more than 1,000,000 km<sup>2</sup> and drains a significant portion of this agricultural region. The basin encompasses portions of four Canadian provinces (Alberta, Saskatchewan, Manitoba and Ontario) and parts of four U.S.A states (Montana, North Dakota, South Dakota and Minnesota). Lake Winnipeg is the 10<sup>th</sup> largest lake by surface area (24,500 km<sup>2</sup>) in the world, and has experienced a significant decline in water quality over the past several decades. Of particular concern is the increase in frequency and extent of algal blooms (i.e., eutrophication) and its subsequent effect on the aquatic ecosystem and human health (Schindler et al. 2012). The eutrophication of Lake Winnipeg is largely due to excessive nutrient loading from urban, industrial and agricultural sources. It has been estimated that

agriculture in Manitoba contributes approximately 5% of the total nitrogen and 15% of the total phosphorus loading into Lake Winnipeg (Lake Winnipeg Stewardship Board 2006). This represents approximately 11% and 32% of Manitoba's contribution of nitrogen and phosphorus, respectively, to Lake Winnipeg. Because P has a high affinity to soil particles much of the total loss of P from farmland is due to soil erosion and sediment delivery. Therefore, identifying the sources of sediment and understanding the interaction of sediment with nutrients within agricultural river basins of the Canadian prairies will play an important part of the mitigation and protection of Lake Winnipeg.

### **7.2.2 The use of sediment fingerprinting in assessing the sources of sediment in river basins**

The development and targeting of effective Beneficial Management Practices (BMPs) to minimize the impacts of agriculture on water quality requires a good understanding of the sources of sediments. However, issues of excessive sediment and nutrient pollution in agricultural watersheds often arise from diffuse, or non-point sources. With no clearly defined entry points, high spatial and temporal variability, large land base, and multiple stakeholders, this type of pollution is difficult to attribute to a specific location and to control. Effective river basin management strategies to address these issues increasingly rely on sediment fingerprinting to identify sediment sources at the river basin scale (Owens 2008; Mukundan et al. 2012). In brief, sediment fingerprinting utilizes the natural physical and biogeochemical properties of sediment as tracers. A suite of sediment properties are selected that can differentiate between potential sediment sources (e.g., cropland, streambanks, forests). These unique sediment properties, which comprise the fingerprint, are measured in

both the source and sediment samples and a statistical and mixing model approach is subsequently used to estimate the contribution of sediment from each potential source (for an overview of the methodology and application of sediment fingerprinting, see Gellis and Walling (2011)).

In many sediment fingerprinting studies, sediment is collected only at the river basin outlet and conclusions based on these samples on the sources of sediment are then often extended to the entire river basin. However, there can be a significant disconnect in the sediment cascade between the head waters and the outlet of a river basin. The transport of sediment through a river basin has been described as a “jerky conveyor belt” owing to the continual cycles of deposition and the subsequent reworking of sediment. Within the sediment fingerprinting literature, the processes that link the sources of sediments to the collected sediments have been described as a black-box. The black-box approach is viewed in terms of its inputs (sediment sources) and outputs (collected sediments) with very little knowledge of how processes (e.g., erosion and transport processes) within the black-box influence the relationship between the inputs and outputs (Koiter et al. 2013). To help overcome the problems associated with the black-box approach, there needs to be further assessment of the location of sediment sampling sites in relation to the sediment sources and how this may influence the interpretation and conclusions made.

### **7.2.3 (Dis)Connectivity in river basin sediment cascades**

It has been well documented that only a small proportion of eroded sediment within a river basin makes it through to the outlet (i.e., the sediment delivery ratio) (Walling 1983). This is the result of the net storage of sediment within different compartments (e.g., hillslope,

floodplain, river channel) of a river basin. The sediment delivery ratio is dependent on the scale of observation due to the non-linearity of river basin processes at different scales. The sediment delivery ratio generally decreases with increasing drainage area, as the magnitude and residence times of sediment storage increases and there is a decline in the connectivity (i.e., a disconnect) between the hillslopes and the river channel (Walling 1983; Fryirs 2013). Although the concept of connectivity between different compartments is difficult to define and quantify, it remains an important part of our understanding of river basin processes and system behaviour (Michaelides and Chappell 2009).

Within the context of the sediment cascade at the river basin scale, connectivity refers to the physical connection or linkages between compartments and their effect on sediment transfer. The degree of connectivity refers to how efficiently and unobstructed the transport of sediment is throughout the river basin. There are three main types of linkages: longitudinal, lateral and vertical and when these linkages become blocked, the compartments become disconnected and the flow of sediment is disrupted (Fryirs 2013). Fryirs (2013) identified three types of blockages: buffers, barriers and blankets and the spatial arrangement of these features will exert an influence on the connectivity and subsequently the pattern of sediment transport and storage (Kuo and Brierley 2013). It is also important to consider that different grain-sizes will have different storage and transport patterns. Furthermore, there is also considerable temporal variability in connectivity of the landscape (Parsons 2012). Sediment transport processes operate at different time-scales which can create a disconnect as one process can supply sediment at a faster rate than another can remove it. In addition, blockages can be breached and connectivity restored during periods of high flow. Thus, the connectivity of a river basin has a large influence on sediment dynamics and needs to be

considered at all spatial and temporal scales of observation.

When developing a sediment fingerprinting study it is important to identify where blockages occur within the river basin and determine how they may disrupt the linkages between sediment sources and transported sediment in order to properly select sediment sampling locations and interpret the data they provide. For example, Smith and Dragovich (2008), using multiple sediment sampling locations, found a rapid transition from hillslope to channel source dominated sediment with increasing distance downstream in a small (1.6 km<sup>2</sup>) catchment in New South Wales, Australia. Therefore, sediment collected at the river basin outlet may not accurately represent processes affecting sediment dynamics elsewhere in the river basin. Despite this, many sediment fingerprinting studies do not fully address the influence of basin geomorphology, topography and connectivity on sediment dynamics, and therefore the importance of the location of sediment sampling sites, and samples are typically collected at outlet locations alone. This can lead to poor management decisions based on the incorrect assessment of the relative contributions of different sediment sources in different parts of the basin.

The present study is located in the South Tobacco Creek watershed in south-central Manitoba, Canada, which has been the subject of numerous research projects investigating the impacts of agricultural practices on crop yield, hydrology, soil erosion and sediment and nutrient dynamics (Li et al. 2007a,b, 2008, 2011; Tiessen et al. 2010, 2011; Liu et al. 2013). This study builds upon the existing body of knowledge by providing observations of the sources of sediment at the watershed scale using sediment fingerprinting. The objective of this study was to assess the sources of sediment at multiple spatial scales using sediment fingerprinting within a nested sampling approach (longitudinal study). This type of sampling

approach allows for an assessment of the influences of scale, connectivity and basin characteristics – including geomorphology, topography and hydrology – on sediment dynamics.

### **7.3 Study catchment**

The 7441 ha (74.41 km<sup>2</sup>) South Tobacco Creek (STC) watershed (49° 22' N, 98° 14' W) is located near the town of Miami, Manitoba, and is part of the Lake Winnipeg basin (Fig. 7.1a). This is a predominately agricultural landscape that includes both annual cropping (cereal and oilseed) and perennials (forage and pasture). The annual and perennial cropland account for approximately 60% and 12% of the watershed area, respectively, and the remainder is mostly forested valley walls that are unsuitable for cultivation, with some roads and yard sites (Hope et al. 2002). The watershed was part of a national program aimed at assessing the economic and water quality impacts of different agricultural practices across Canada (Agriculture and Agri-Food Canada 2012). The watershed extends over the Manitoba Escarpment; its upper reaches lay in undulating glacial tills and its lower reaches lay in the lacustrine sediments of glacial Lake Agassiz. Beyond the STC watershed, the creek joins the Tobacco Creek and continues to flow eastward reaching the Red River which flows northwards to Lake Winnipeg then onwards to Hudson Bay via the Nelson River. The Manitoba Escarpment is a major physiographic feature of the Canadian prairie landscape extending for more than 600 km from the Pasquia Hills in Saskatchewan, through southwestern Manitoba, to the Pembina Hills in North Dakota (McNeil and Caldwell 1981). Within the STC, watershed the elevation drops dramatically (~200 m) as the creek incises through the escarpment and exposes the underlying shale bedrock (Fig. 7.1b). As the point of

incision (knickpoint) migrates upstream it has produced steep valley walls and actively eroding cut-bank shale bedrock outcrop features (small bluffs) along the channel (some exceeding 20 m in height). The Cretaceous shale bedrock is mainly the Pierre Shale and Niobrara Formations. This shale is relatively friable (i.e., low strength) and fluvial processes, coupled with freeze-thaw and wetting-drying cycles, quickly break down this material into fine-grained sediment. The dominant soil series above the escarpment are Dark Grey Chernozems with a primarily clay-loam texture, while below the escarpment are Black Chernozems with a primarily clay texture (Hope et al. 2002).

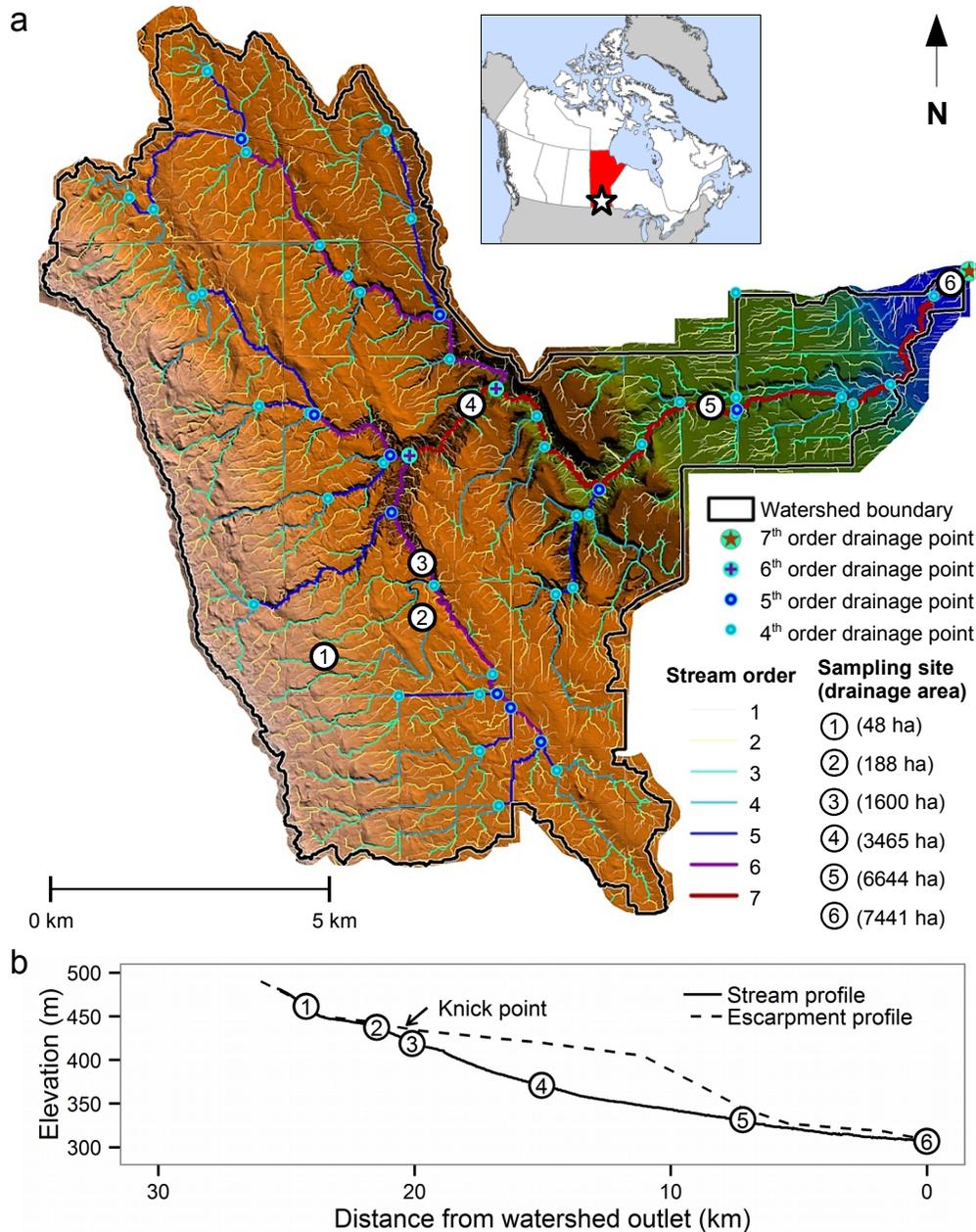


Figure 7.1: (a) Stream network extracted from the 5-m LIDAR DEM of the South Tobacco Creek watershed (Manitoba, Canada) using the FlowMapR program (Li 2011). Also shown are the locations of sediment sampling sites and their associated drainage areas (ha). (b) Longitudinal profile showing the elevation and sediment sampling sites along the stream and the Manitoba Escarpment.

The climate of the region is classified as sub-humid with a mean annual precipitation of 550 mm, with approximately 30% falling as snow, and has warm summers and cold winters (+30 to -30 °C) with a mean annual temperature of 3 °C (1971-2000 climate normals; Environment Canada 2013a). Daily discharge is measured at two locations (gauging stations operated by the Water Survey of Canada (WSC); Environment Canada 2013b), the first below the escarpment (site 4, WSC station 05OF023) and the second at the outlet of the watershed (site 6, WSC station 05OF017) (Fig. 7.2). The hydrology is dominated by snow-melt runoff events in the spring, ~80% of which occurs over frozen soils, with episodic rainstorms in the summer and autumn months (Fig. 7.2). Many of the lower order streams in the headwaters are ephemeral and become dry during the summer months. In contrast, during high runoff and discharge there can be significant flooding throughout the watershed. Due to concerns over damaging floods downstream of the STC watershed, 26 small dams and reservoirs were constructed between 1985 and 1996 in the headwaters (30% of the total drainage area) to reduce peak flows and flooding (Yarotski 1996). In addition, there is also considerable natural damming throughout the watershed due to beaver (*Castor canadensis*) activity. The hydrology of the STC watershed has also been modified extensively through surface drains, especially in the lower reaches, as these surface drains have improved the drainage by increasing the hydrological connectivity.

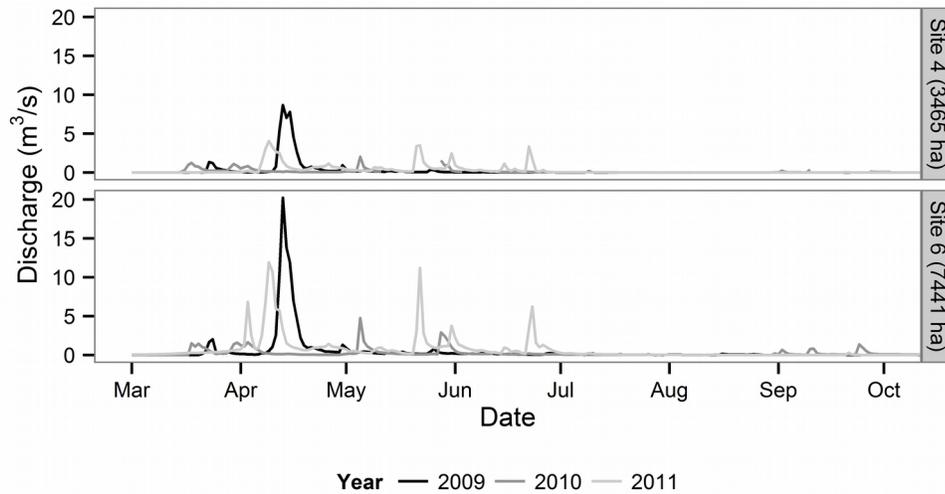


Figure 7.2: Daily discharge measurements for 2009 – 2011 at two locations in the South Tobacco Creek watershed (data from Environment Canada 2012)

The climatic, hydrological, topographical and geomorphological characteristics of the STC watershed influence sediment dynamics at different spatial scales. Therefore, sampling at the outlet alone may provide insufficient information to support a meaningful conclusion on the sources of sediment for the entire watershed. The hydrologic network of the STC watershed was extracted from a 5 m LIDAR Digital Elevation Model (DEM) of the watershed (see Fig. 7.1a) (Li 2011). A summary of the watershed characteristics can be found in Table 7.1. To provide information on the sources of sediment at various spatial scales and to isolate the effects of geomorphic features, including the escarpment, six fluvial sediment sampling sites were established along the main stem of South Tobacco Creek ranging from third order (48 ha; 0.48 km<sup>2</sup>) to seventh order (7441 ha; 74.41 km<sup>2</sup>) drainage basins (see Fig. 7.1).

Table 7.1: Summary of the hydrological characteristics of the South Tobacco Creek watershed (from Li 2011)

Stream order	Counts	Total stream length (km)	Direct catchment area (ha)	Total contributing area (ha)	Average contributing area (ha)
1	3790	398	4412	4400	1
2	890	191	1300	4355	5
3	208	107	814	4560	22
4	51	56	438	4719	93
5	13	25	210	4355	335
6	3	17	161	5158	1719
7	1	17	107	7441	7441
<b>Total</b>	<b>4956</b>	<b>812</b>	<b>7441</b>	---	---

## 7.4 Methods

### 7.4.1 Collection of sediment and source samples

In an effort to assess the impacts of agricultural activities on soil erosion and the delivery of sediment and sediment-associated nutrients to surface waterways, three main potential sediment sources were identified based on field observations. These sources were: (1) topsoil from agricultural fields and riparian zones adjacent to the creek; (2) streambanks; and (3) shale bedrock material. Topsoil and streambank samples used to characterize the fingerprint of the potential sources were taken upstream at approximately the same locations as the fluvial sediment samples (see Fig. 7.1). Several (2 – 4) transects were established at each sampling site extending from the edge of the streambank through the riparian zone and into the adjacent fields. The sampling transects were established along a toposequence parallel to the dominant slope gradient and extended from the edge of the streambank to the hilltop. Each transect consisted of 4 – 8 individual sampling points, and at each, the surface horizon (e.g., A horizon) was sampled using a 3.18 cm (diameter) soil probe over a depth of 5 – 20 cm, depending on the depth of the horizon. Typically, surface scrapes (0 – 5 cm) are collected to characterize topsoil sources, however, in cultivated landscapes the surface soil

horizon is regularly mixed and in the riparian zones there is continuous erosion and deposition of soil from upstream and upslope. Therefore, to accommodate these processes the full horizon was sampled. It should be noted, however, the sampling of the full surface horizon may misrepresent the topsoil sources due to the depth dependency of some fingerprint properties (e.g.,  $^{137}\text{Cs}$ ) as sheet and rill erosion are generally limited to the top 0 – 5 cm. Transects were used to collect soil samples in order to characterize surface soils, as opposed to the often used 'likely to erode' approach (i.e., sampling areas identified as susceptible to erosion and that are well connected to the channel) as the latter approach is subjective and there is little empirical evidence to support that it adequately characterizes the potential sources (Davis and Fox 2009). The transect approach is more systematic and captures variation in fingerprint properties due to differences in management, vegetation, relief and drainage. It also recognizes that connectivity can be difficult to detect and evaluate, and it does not assume that areas that are not well connected do not directly contribute to the sediment load, which may not be the case during periods of high runoff and flooding (Thompson et al. 2012). One transect from each sampling location was included in the characterization and each topsoil sample ( $n = 28$ ) was analyzed separately for geochemistry and radionuclides (see section 3.2 for details) in an effort to fully characterize the topsoil as a source of sediment.

Three streambank profiles were also sampled at each of five of the six sites (site 3 has not yet been sampled as this sediment sampling location was established in 2011). During a period of low flow, samples were collected at 10 - 30 cm increments down the bank profile using a box-core sampler inserted perpendicular to the streambank face. Detailed profiles were collected, as opposed to aggregating samples, in order to better understand the vertical

distribution of the fingerprint properties of this sediment source, as this helps with the process-based interpretation of the fingerprint properties (see section 4. 1). A total of 75 individual streambank samples were analyzed, however, prior to fingerprint selection and the application of a mixing model, the geochemical and radionuclide properties for the streambank sources were first averaged across the depth of each profile giving equal weight to individual profiles regardless of the height of the streambank ( $n = 15$ ). Averaging was used as the entire bank profile contributes to the sediment load through the undercutting and slumping of banks as well changes in the height of erosion due to changing flow levels.

A large outcrop (15 m in height) of the shale bedrock along the channel (between sites 3 and 4) was sampled in a similar manner to the streambanks which was possible in this region due to the friable nature of the bedrock shale; material was collected from five different layers of bedrock ( $n = 5$ ).

Samples of both suspended and channel bed sediment were collected at each site 2-3 times per year, during the ice-free period (April to November), between 2009 and 2011 (see Table 7.2 for a description of the sampling dates). Suspended sediment was collected using a passive time-integrated sediment sampler designed by Phillips et al. (2000) and evaluated by Russell et al. (2000). The samplers were fixed to the channel bed by anchoring them to concrete paving stones using chains. Two samplers were used at each location to ensure a representative sample could be collected as these samplers can become clogged, buried, destroyed or lost by high flows, debris in flows, ice build-up, animal activity and/or vandalism. The sediment samplers were inspected for maintenance two to four times per month depending on stream flow conditions with more frequent inspections during periods of high flow. Sediment from the two samplers (if available) were combined prior to analysis.

The amount of sediment collected at each sampling site ranged from 9 to 578 g with an average of 104 g. The channel bed consists largely of unconsolidated sediment and shale fragments. Field observations indicated that there was considerable bedload transport as the pattern of channel bars changed between site visits. Therefore, to complement the suspended sediment data, channel bed sediment was also collected using a small trowel to a depth of 5 cm (see Table 2). The combination of suspended and bed sediment sampling allowed for a more complete assessment of the sediment dynamics within the watershed.

Table 7.2: Summary of suspended and bed sediment sampling.

Sampling period			Sediment sampling site					
Season	Months		1	2	3	4	5	6
2009	Spring	April – June	SS <sup>1</sup> + BS <sup>2</sup>	SS + BS	no data	SS + BS	SS + BS	SS + BS
	Summer/Fall	July – October	SS + BS	SS + BS	no data	SS + BS	SS + BS	SS + BS
2010	Spring	April – June	SS + BS	SS + BS	no data	SS + BS	SS + BS	SS + BS
	Summer/Fall	July – November	SS + BS	SS + BS	no data	SS + BS	SS + BS	SS + BS
2011	Spring	April – June	SS	SS	SS	SS	SS	SS
	Summer	July – August	SS + BS	SS + BS	SS + BS	SS + BS	SS + BS	SS + BS
	Fall	Sept – Nov	SS	SS	SS	SS	SS	SS

<sup>1</sup>SS – suspended sediment

<sup>2</sup>BS – bed sediment

#### 7.4.2 Laboratory analysis

All soil and streambank source material was air-dried, disaggregated by hand or gently with a mortar and pestle, and sieved to < 2 mm to remove stones. The shale bedrock source material was not sieved but aggressively disaggregated and ground to a powder with a mortar and pestle. Analysis was conducted on whole shale bedrock source samples because it is assumed that, due to the friable nature of this material, the entire sample may contribute to the sediment load. The suspended sediment samplers were emptied and washed out into 20 l buckets and allowed to settle, and the clear supernatant was decanted, dried at room temperature and disaggregated by hand. Similarly, the bed sediments were dried at room

temperature and disaggregated by hand. In many sediment fingerprinting studies analysis is limited to the < 63 µm grain-size fraction to facilitate a comparison between sources and sediment by reducing the differences in grain-size. However, there are issues regarding the representativeness of this material (Koiter et al. 2013) as it does not consider downstream attrition (i.e., disintegration of large particles during fluvial transport) to be a factor influencing the relationship between sources and sediment. Within the STC watershed there is considerable evidence of the attrition of the shale bedrock through abrasion and repeated freeze/thaw and wet/dry cycles, therefore, the range of analysis was increased to < 2 mm and whole shale rock was included in the analysis.

Both fallout radionuclides and geochemistry have been widely used in sediment fingerprinting studies to discriminate between potential sediment sources. <sup>137</sup>Cs radioactivity was detected at 662 keV using Broad Energy Germanium Gamma spectrometers (Canberra BE3830, Landscape Dynamics Laboratory, University of Manitoba, Canada) with a counting time ranging from 24 to 48 hours. The concentrations of a suite of geochemical elements (56 in total) were determined using ICP-MS following a microwave-assisted digestion with nitric acid (Northern Analytical Laboratory Service, University of Northern British Columbia, Canada).

All statistical analysis was undertaken using R Statistical Software v2.15.3 (R Core Team 2013) through RStudio v0.97 (RStudio 2013). Plots were created using the R package ggplot2 v0.9.3 (Wickham 2009).

#### **7.4.3 Tracer selection and source apportionment model**

Tracers, especially geochemical and radionuclide properties, are often selected on the

basis of their ability to statistically differentiate between multiple sediment sources. A purely statistical approach may not be the most appropriate method as the conservative behaviour of sediment properties and the underlying processes that lead to their ability to discriminate between sources are not considered (Koiter et al. 2013). For this study, a combination of statistical- and process-based selection criteria was used to determine appropriate sediment properties to include in the mixing model. Similar to Walling et al. (1999), the first step involved using the Kruskal Wallis H-test to select properties that showed a significant difference ( $p < 0.01$ ) between the potential sediment source groups. Since the Kruskal Wallis H-test is based on ranks and not measures, in the second step, the list of selected properties was further reduced to include only properties that showed a difference in the mean property values by a factor of  $> 2$  between at least one pair of sediment sources. The remaining properties were then further assessed (i.e., third step) as to whether prior knowledge of watershed geology or physical and biogeochemical processes could explain the differences in properties found between sediment sources; i.e., did their selection make sense. As sediment fingerprinting works most effectively when large, well-defined differences between fingerprints exist, properties were excluded in cases where there was no clear explanation for the differences found. Furthermore, many fingerprinting studies use particle size correction factors to account for difference in particle size between sediment and sources. However, the relationship between particle size and tracer property concentration is complex (Russell et al. 2001) and there is no standardized approach, such that some studies choose to not use correction factors (e.g., Martínez-Carreras et al. 2010). Thus, given the friable nature of the shale bedrock and the evidence for significant attrition in the watershed, no effort was made to correct for differences in particle size, as it was felt that use of particle size correction

factors could inappropriately manipulate the raw tracer property concentration data. Furthermore, textural analysis was not conducted on soil or sediment samples as textural analysis on low strength materials (e.g., shale) are strongly affected by analytical operating procedures and, therefore, it can be difficult to get reliable data (Storti and Balsamo 2010). The physical or chemical dispersion pre-treatment of the soil or sediment would break apart the friable shale particles and as a result it would be difficult to relate the particle size information to erosion or fluvial transport processes.

Stable Isotope Analysis in R (SIAR; v 4.1.3) (Parnell et al. 2010; Parnell and Jackson 2011), a Bayesian isotopic mixing model available as an open source R package, was used to estimate the relative contribution of the potential sediment sources at each sediment sampling site. Sediment samples were grouped by sampling site only as the changes in the relative contributions in sediment sources between years or seasons are outside the scope of this study. SIAR was developed for use within ecological studies, however, it is a basic mixing model and can be used with any fingerprint property (tracer) as long as the assumptions of linear mixing are met. The SIAR model uses the mean value and the standard deviation of sediment fingerprint properties and is fit using Markov Chain Monte Carlo (MCMC) methods producing simulations of possible values of sediment proportions of the various potential sediment sources via a Dirichlet prior distribution consistent with the data (Parnell et al. 2010). Dirichlet distributions are commonly used as the prior distribution in multivariate Bayesian mixture models (Evans et al. 2000; Jackson et al. 2009). The model was run using 200,000 iterations with a burn-in of 50,000. In addition, since this is not an ecological study, the trophic enrichment and concentration dependence correction factors were omitted from the model (i.e., set to 0). The proportion results from the mixing model are

reported as the range between the 25<sup>th</sup> and 75<sup>th</sup> percentiles.

## **7.5 Results and discussion**

### **7.5.1 Source discrimination**

The first step of the sediment fingerprint (tracer) selection process based on the Kruskal Wallis H-test ( $P < 0.01$ ) identified 13 out of the 56 sediment properties analyzed as showing good discrimination potential (Table 7.3). The second step, based on the difference in the mean concentrations between sediment sources (see section 3.3), removed an additional three elements. Of the 10 elements remaining ( $^{137}\text{Cs}$ , Na, Ti, Mn, Ga, As, Se, Ba, U, Rb) four were selected to be used in the mixing model ( $^{137}\text{Cs}$ , Ti, As, U) and the reasons for their inclusion in the mixing model are described below.

Both  $^{137}\text{Cs}$  and Ti showed higher concentrations in surface soils compared to subsurface sediment sources (streambank and shale bedrock) providing good discrimination between the two main groups of potential sources (Fig. 7.3 and 7.4). This finding is consistent with current knowledge of the environmental behaviour of these two properties. For example,  $^{137}\text{Cs}$  is an artificial fallout radionuclide derived from the atmospheric nuclear weapons testing in the 1950s and 1960s, that effectively tags surface sediments as it is quickly and strongly adsorbed to clays and organic matter such that the activity concentration declines markedly with depth (Ritchie and McHenry 1990).  $^{137}\text{Cs}$  has been widely used in previous studies as a fingerprint to discrimination between surface and subsurface sediment sources (e.g., Wallbrink et al. 1998; Owens et al. 2012). Similarly, Ti is often used to estimate the rate of weathering, as it is highly resistant to weathering and has low mobility in soils (e.g., Taboada et al. 2006). The process of weathering often leads to higher concentrations of

Ti in the surface soils compared to subsurface materials because the more mobile elements are leached through the soil profile (i.e., the process of negative enrichment) (Kabata-Pendias 2000; Dąbkowska-Naskręket and Jaworska 2001). The higher concentration of Ti within the topsoil may also be the result of the cycling of the element by vegetation which would limit the downward movement of Ti through the profile (Cornu et al. 1999). Further work is being undertaken to investigate the processes underlying Ti as a source fingerprint in this watershed.  $^{137}\text{Cs}$  and Ti are ideal properties to use in sediment fingerprinting due to their low mobility in soils, although there may be exceptions to this that require further investigation (Parsons and Foster 2011). The concentration of  $^{137}\text{Cs}$  and Ti are particle-size dependent with higher concentrations found in the fine-grained fraction of the soil (He and Walling 1996; Taboada et al. 2006).

Table 7.3: Mean values for sediment fingerprint properties and sediment source discrimination procedure

Fingerprint Property	Topsoil (mg kg <sup>-1</sup> )	Streambanks (mg kg <sup>-1</sup> )	Shale (mg kg <sup>-1</sup> )	P-value	Process/prior knowledge used in the source discrimination process
Ti <sup>a</sup>	70.30	54.78	26.63	< 0.01*	Enriched in topsoil due to weathering processes
<sup>137</sup> Cs <sup>a</sup>	13.15 <sup>b</sup>	4.21 <sup>b</sup>	0 <sup>b</sup>	< 0.01*	Fallout radionuclides label surface soils
As <sup>a</sup>	7.96	9.97	18.31	< 0.01*	Previously known to be enriched in the shale bedrock
U <sup>a</sup>	2.49	3.37	7.23	< 0.01*	Previously known to be enriched in the shale bedrock
Ba	203	242	112	< 0.01*	No prior knowledge or process could explain the trend
Ga	24.55	22.50	12.23	< 0.01*	No prior knowledge or process could explain the trend
Mn	1460	1929	394	< 0.01*	No prior knowledge or process could explain the trend
Na	165	257	1020	< 0.01*	No prior knowledge or process could explain the trend
Sb	0.01	0.02	0.03	< 0.01*	No prior knowledge or process could explain the trend
Se	1.73	2.28	7.75	< 0.01*	No prior knowledge or process could explain the trend
Rb	32.33	28.24	20.73	< 0.01*	Difference in property values by a factor of < 2
Si	606	454	352	< 0.01*	Difference in property values by a factor of < 2
W	0.01	0.01	0.01	< 0.01*	Difference in property values by a factor of < 2
Lu	0.18	0.24	0.26	0.01	
Sr	53.94	89.21	212.13	0.02	
La	21.73	24.91	29.18	0.02	
Li	16.86	21.67	35.57	0.02	
Gd	3.82	4.72	4.84	0.02	
Eu	0.84	1.03	1.09	0.02	
Pr	5.16	5.97	6.79	0.02	
Nd	19.29	22.63	24.63	0.03	
K	3732	3052	3006	0.03	
Hf	0.32	0.29	0.45	0.04	
Sm	3.94	4.72	4.84	0.04	
Tm	0.22	0.27	0.28	0.04	
Dy	2.98	3.70	3.67	0.05	
Ca	14713	27505	67613	0.05	
Yb	1.31	1.66	1.72	0.05	
Er	1.62	2.05	2.10	0.05	
Mg	4644	5364	3425	0.06	
Zr	16.04	15.69	27.26	0.06	
Fe	16906	15880	12491	0.07	
Ho	0.58	0.73	0.73	0.08	
Al	17168	15393	17312	0.13	
Bi	0.24	0.26	0.33	0.13	
Hg	0.13	0.15	0.20	0.16	
Ce	43.97	48.97	54.37	0.16	
Sn	0.03	0.03	0.02	0.18	
Ni	33.75	42.30	39.13	0.23	
Th	6.72	7.10	10.00	0.24	
Ag	0.15	0.15	0.20	0.33	
Cu	22.82	26.33	39.67	0.34	
B	23.33	18.40	24.67	0.37	
Cs	1.56	1.57	1.12	0.37	
Pb	13.58	14.84	18.15	0.38	
Co	9.07	10.67	9.67	0.40	
Tl	0.56	0.72	0.84	0.40	
Ge	1.11	1.16	1.26	0.44	
Be	0.76	0.76	0.91	0.49	
Nb	0.34	0.31	0.34	0.56	
Mo	0.77	1.67	1.55	0.60	
Cd	1.52	2.07	1.62	0.67	
Te	0.04	0.04	0.05	0.72	
P	794	803	731	0.84	
Zn	96.09	93.85	106.54	0.86	
Cr	31.83	31.32	47.24	0.86	
V	81.21	90.64	128.59	0.91	

\*p < 0.01 (Kruskal-Wallis H test), statistically significant at P < 0.01 (Kruskal-Wallis test)

<sup>a</sup> Properties selected for the mixing model; <sup>b</sup> (Bq kg<sup>-1</sup>)

<sup>b</sup>In Bq Kg<sup>-1</sup>

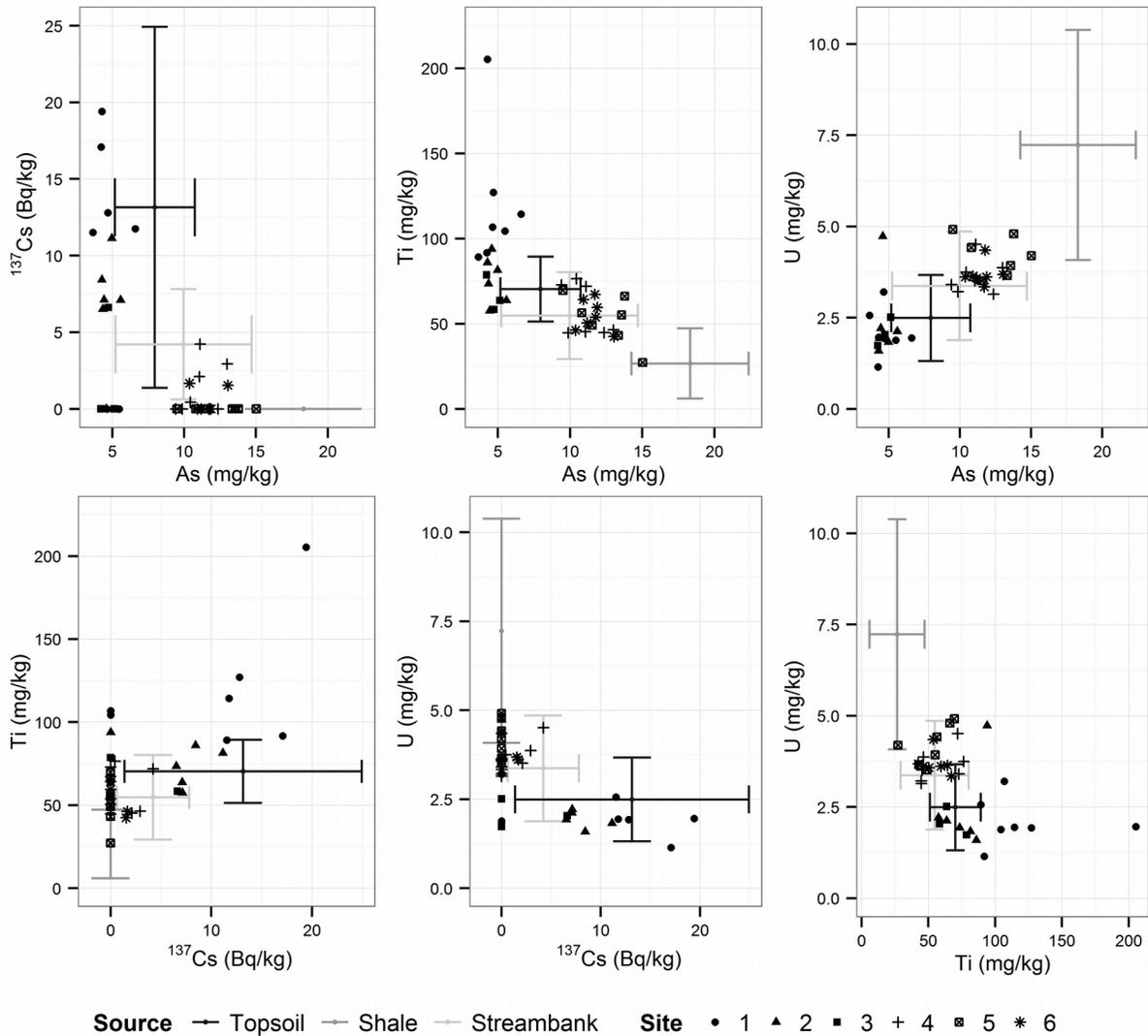


Figure 7.3: Geochemical and radionuclide fingerprints for the three potential sediment source types and for the suspended sediment collected from the six sampling sites along the South Tobacco Creek (error bars represent  $\pm 1$  standard deviation).

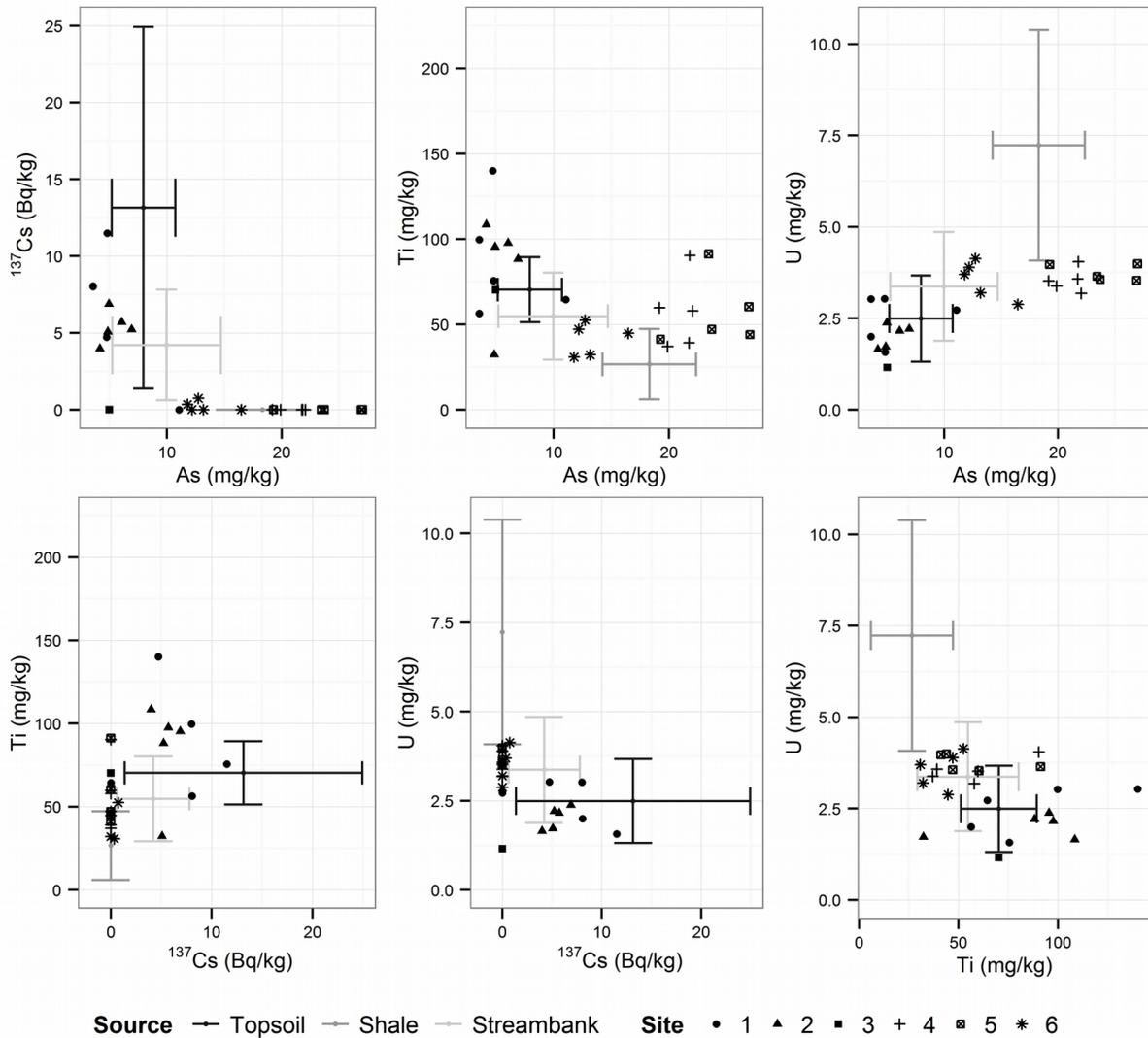


Figure 7.4: Geochemical and radionuclide fingerprints for the three potential sediment source types and for the bed sediment collected from the six sampling sites along the South Tobacco Creek (error bars represent  $\pm 1$  standard deviation)

The data provided by the transect sampling strategy showed the concentration of  $^{137}\text{Cs}$  and Ti in surface soils was lower in the fields compared to the riparian areas and the concentration generally increased from the edge of the field through the riparian area towards the streambank. This is consistent with the fact that mixing of the soil through tillage will homogenize the plow layer resulting in lower  $^{137}\text{Cs}$  and Ti concentrations in the field samples

and that erosional processes will move topsoil enriched in  $^{137}\text{Cs}$  and Ti (itself enriched in the fine-grained fraction) from the hillslope and deposit it in the riparian zone.

The streambank profiles showed a high  $^{137}\text{Cs}$  concentration in the top 0 – 20 cm, with similar values to riparian soils, followed by a sharp decline to 0 Bq kg<sup>-1</sup> for the remainder of the profile. This is reasonable considering that the top of the streambank can be considered as the extreme edge of the riparian zone soil. This is important to note because low-order streams in the headwaters have very small streambanks (< 40 cm in height) and it can be difficult to discriminate between the streambank and riparian soils as they have similar  $^{137}\text{Cs}$  fingerprints. This is the reason that the  $^{137}\text{Cs}$  fingerprint for the streambank source shows large variation as it includes banks from both the low- and high-order streams which have varying profile depths (see Figs. 7.3 and 7.4). The concentrations of Ti in the streambank profiles did not follow the same trend as  $^{137}\text{Cs}$ , and this may relate to differences in the processes and time-scales that lead to fingerprint formation. The  $^{137}\text{Cs}$  fingerprint has developed over approximately 60 years through the processes of fallout and subsequent soil redistribution, while the Ti fingerprint has slowly been developing since the last glacial retreat through the process of weathering.

Both As and U showed higher concentrations in the shale bedrock compared to the topsoil and streambank sources providing good discrimination between the potential source groups (see Figs 7.3 and 7.4). Shale deposits are often enriched in trace elements as shale is comprised of clay which acts as a sink for trace elements. Previous work on the shale in the Manitoba Escarpment has shown that it has high concentrations of both As and U (Haluschak et al. 1998; Garrett and Thorleifson 1999; Nicolas and Bamburak 2011). Under oxidizing environmental conditions and a pH < 8.5, As is strongly adsorbed to soil particles making it

an ideal sediment fingerprint. However, under reducing conditions there is a change in oxidation state, from As(V) to As(III), and As can become more mobile. Under oxidizing environmental conditions, U is moderately well adsorbed to soil particles with Fe-, Al- and Mn-oxides and organic matter accounting for the majority of the adsorption and accumulation in soils (Choi and Park 2005). The adsorption of U on soil surfaces is strongly related to pH and mobility can increase in the presence of dissolved carbonates through the formation of U-carbonate complexes. It is currently unclear how the environmental conditions, in particular the presence of carbonates, in the watershed will influence U dynamics. As research in the watershed continues it will be necessary to re-evaluate the inclusion of U in the mixing model. The concentration of As and U are both particle-size dependent with higher concentrations found in the fine-grained fraction of the soil (Horowitz 1991; Du et al. 2012).

Overall, these four sediment fingerprints provide good discrimination between the three potential sediment sources identified (see Figs 7.3 and 7.4). Topsoil (field and riparian) sources are characterized by high  $^{137}\text{Cs}$  and Ti and low As and U concentrations. Streambank sediment sources are characterized by intermediate  $^{137}\text{Cs}$  and Ti and low As and U concentrations. The shale bedrock sources are characterized by low  $^{137}\text{Cs}$  and Ti and high As and U concentrations.

The SIAR model assumes that the variability associated with the sources is reasonably normally distributed (Parnell et al. 2010). This assumption was met for the majority of the sediment source fingerprints, however, in some cases it was not. This may be due to low sample numbers or the fact that sediment fingerprints for potential sources are not always uniform across the watershed. Violating the assumption of normality may result in a

misrepresentation of sediment fingerprint variability in the mixing model. Furthermore, as described in section 3.3, there are additional sources of error due to the particle size dependency of fingerprint properties, which can make a reliable comparison between sources and sediment difficult to make. Therefore, emphasis should be placed on the order of magnitude of the sediment source contributions.

### **7.5.2 Identifying the sources of sediment**

Some of the fingerprint properties for both the suspended and bed sediments fall towards the extreme range of the potential sediment sources (see Figs 7.3 and 7.4) and this is likely due to differences in particle size as all of the fingerprints selected have been shown to have a strong relation between concentration and particle size. However, due to the significant attrition observed in the watershed, the development of a robust particle size correction factor would be difficult and potentially inappropriate (see Koiter et al. 2013). The concentrations of  $^{137}\text{Cs}$  and Ti in the suspended sediment samples (see Fig. 7.3) decrease from the low-order streams in the headwaters towards higher-order streams closer to the outlet of the watershed. The most dramatic decrease occurs at site 3 (6<sup>th</sup> order stream, 1600 ha drainage area) which is the beginning of the major incision (knickpoint) of the creek as it crosses the Manitoba Escarpment (Fig. 7.1b). Conversely, the concentrations of As and U in the suspended sediment increase from the headwaters towards the outlet of the watershed, again the transition occurring at the major incision point. The channel bed sediment samples show a similar trend although the changes in fingerprint properties are not as clear (Fig. 7.4). In comparison to the suspended sediment, the bed sediment had lower concentrations of both  $^{137}\text{Cs}$  and Ti in the headwaters, higher concentration of As towards the watershed outlet and

the concentrations of U were similar throughout the watershed. The distinctive change in the suspended sediment fingerprint from the headwaters to the watershed outlet suggests that there is a switch in sources of suspended sediment beginning at the incision point.

The SIAR model output using the suspended sediment samples confirms that there is a switch in the predominant sediment sources between the headwaters and the outlet of the watershed (Fig. 7.5). In low-order streams in the headwaters (site 1, 3<sup>rd</sup> order stream and 48 ha drainage area) topsoil is the predominant sediment source accounting for approximately 64 – 85% (25<sup>th</sup> – 75<sup>th</sup> percentile) of the suspended sediment while streambanks and shale bedrock sediment sources account for approximately 12 – 33% and 1 – 4% of the suspended sediment, respectively. As the scale of observation increased from 3<sup>rd</sup> order streams (site 1, 48 ha drainage area) to 7<sup>th</sup> order streams (site 5, 6644 ha drainage area) the proportion of topsoil sediment sources declines to 13 – 33%, the proportion of streambanks and shale bedrock sediment sources increased to 34 – 52% and 29 – 39%, respectively. The switch to a dominance of streambanks and shale bedrock sources is in keeping with the obvious signs of bank erosion in the downstream reaches. At the watershed outlet (site 6, 7441 ha drainage area) there is a small increase in topsoil sources to 31 – 44% with a corresponding decrease in the contributions of the streambank and shale bedrock sediment sources accounting for 29 – 43% and 22 – 30% of the suspended sediment, respectively. The SIAR model output using the channel bed sediment samples shows little change in sediment sources from the headwaters towards the watershed outlet (Fig. 7.6). The relative contributions of topsoil, streambanks and shale bedrock across the watershed were on average 18 – 42%, 33 – 59% and 12 – 33%, respectively.

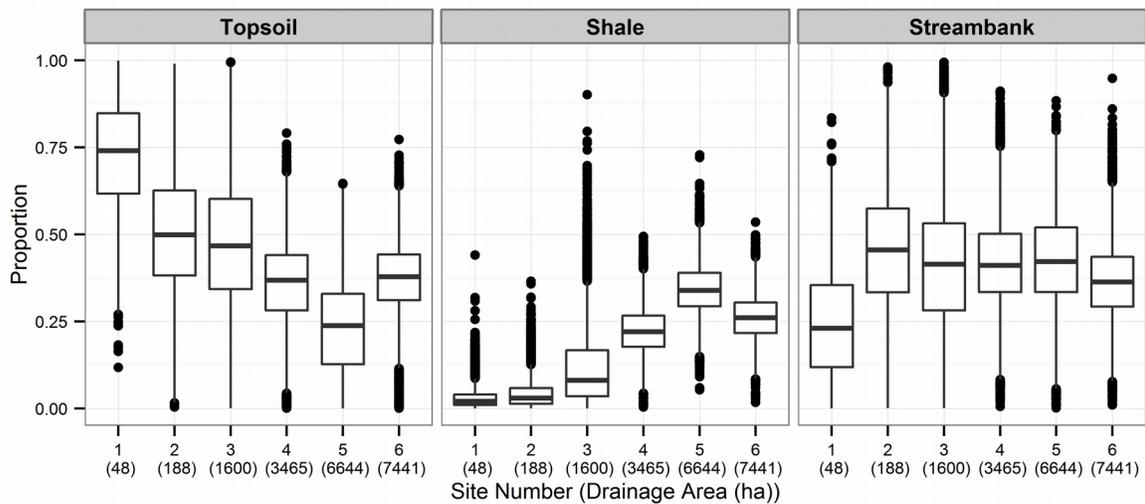


Figure 7.5: Box and whisker plots of values of sediment proportions of the three potential sediment source types for the suspended sediment collected from the six sampling sites along the South Tobacco Creek

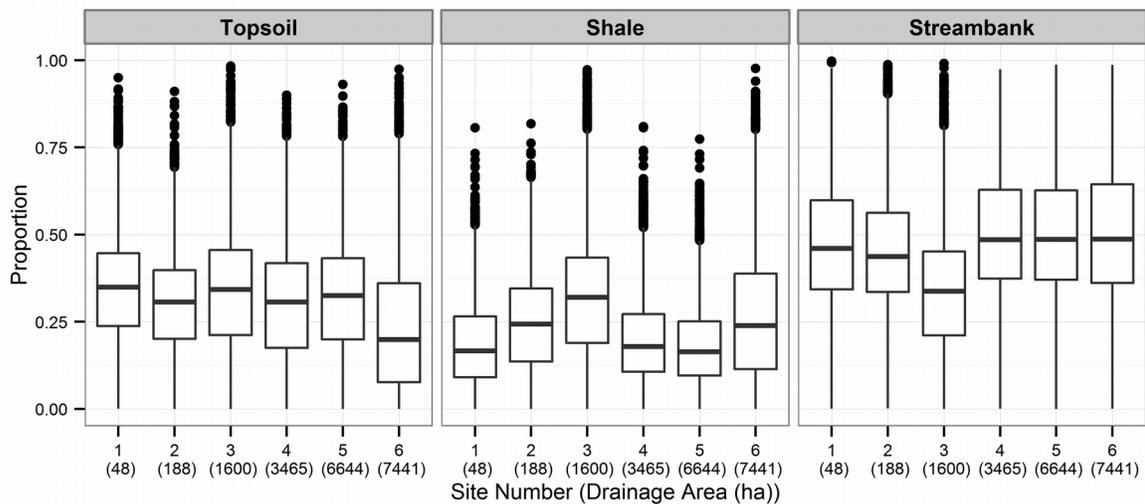


Figure 7.6: Box and whisker plots of values of sediment proportions of the three potential sediment source types for the bed sediment collected from the six sampling sites along the South Tobacco Creek

### 7.5.3 The role of scale and connectivity

The relative contributions of the three sediment sources to the suspended sediment

varied depending on the scale of observation. The switch in sediments found within the watershed is consistent with Fryirs (2013) conceptualization of the sediment cascade. In low-order streams in the headwaters the hillslopes are well coupled to the channel and become decoupled in higher-order streams closer to the outlet of the watershed. The change in the connectivity between hillslope and the channel can be seen in the summary of the watershed characteristics (Table 1) as the direct catchment area (i.e., the area that directly drains into a given stream order) decreases with increasing stream order. This corresponds well with the high contribution of topsoil found in the suspended sediments in the headwaters (see Fig. 7.5) followed by a rapid decline in the relative contribution downstream. It is important to note that the majority of the watershed is drained by low-order streams (see Table 7.1). Therefore, if the results from site 1 (3<sup>rd</sup> order stream, 48 ha drainage area) are extended to other streams of comparable size it would mean that considerable amounts of topsoil are being eroded.

Currently, it is unclear as to why the channel bed and suspended sediments show different trends (Fig. 7.6). The differences in the SIAR apportionment results may be related to differences in grain-size between bed and suspended sediment as all the fingerprints have a strong relationship to grain-size. In addition, the coarser grain-size of the bed sediments makes it more likely to be stored behind blockages in the sediment cascade (e.g., beaver dams) and as a result bed sediments are likely to have longer transit time compared to the suspended sediment. It may also reflect the fact that bed sediments may be the result of the slumping of local streambank material onto the channel bed. There are some shale outcrops in the headwaters above the major incision point which are likely contributing to the bed sediment and due to the friable nature of the shale bedrock and the process of attrition this channel bed sediment is likely a source of suspended sediment further downstream. This

process may account for the large difference in the proportion of the shale bedrock source between the suspended and bed sediment in the headwaters (Figs 7.5 and 7.6). In addition, the channel bed sediment may reflect long-term trends in sediment sources while the suspended sediment samples represent short-term trends. Further research is needed to understand the role of bed sediment and downstream attrition on sediment dynamics within the STC watershed.

Putting the suspended sediment apportionment results in a geomorphic context, the role of the Manitoba Escarpment on the sources of suspended sediment becomes evident. Above the escarpment in the undulating glacial till (sites 1 and 2) topsoil is the predominant sediment source. As the creek transitions over the escarpment (site 3) and begins to incise into the underlying shale bedrock (knickpoint) the relative contributions of the shale bedrock sediment source to the suspended sediment load increases. Previous research has also shown that significant amounts of sediment can be generated within this transition zone with limited opportunities for sediment storage (Belmont 2011; Belmont et al. 2011). There have also been significant changes in the hydrological network through the construction of small dams and reservoirs in the headwaters which have been shown to be net sediment sinks (Tiessen et al. 2011). This also may explain the decline in the contribution of topsoil sediment sources as the topsoil rich sediment is being stored in these features and not making it through to the outlet of the watershed.

Sedimentation also occurs at slope discontinuities along the main stem of the creek and, specifically, behind points of flow restriction such as culverts, bridges and weirs within the watershed. These structures can cause considerable sedimentation to occur upstream onto floodplains and result in the scouring of the streambanks and streambed (due to increase in

sediment transport capacity) downstream of these structures. This also may explain the decline in the contribution of topsoil sediment sources as the topsoil rich sediment may be stored in these features and not being transported through to the outlet of the watershed. Floodplains, constructed dams and beaver dams are common in the watershed, however, there is currently little information as to the location, frequency and size of these sediment storage features so it is difficult to quantify the effects they will have on the connectivity of the sediment cascade. The development of a sediment budget for the watershed will complement the fingerprinting study and help elucidate the role of these features on the sediment dynamics.

Improved drainage through surface drains in the lower reaches of the watershed may also increase the connectivity between the hillslope and the channel (Blann et al. 2009) and may explain the slight increase in topsoil sources at the watershed outlet (site 6). Field observations showed that tillage was moving topsoil directly into the surface drains as fields extended all the way to the edge. This would allow for the quick and efficient delivery of topsoil from the fields to the channel. The dredging of these surface drains to maintain capacity is a regular occurrence in the watershed and the dredged material is often put directly back on to the fields to replace the eroded soil. These observations suggest that surface drains coupled with tillage erosion may play an important role in the sediment cascade, and further work is needed to assess this.

## **7.6 Conclusions**

In summary, the results of the sediment fingerprinting study in the STC watershed based on three years (2009 – 2011) of sediment sampling, demonstrated that there was a

switch in suspended sediment sources between the headwaters and the outlet of the watershed. The suspended sediment in the upper reaches were dominated by topsoil sources while the suspended sediment moving through the lower reaches and being exported from the watershed had a higher proportion of sediment coming from streambank and shale bedrock sources. This research highlights the importance of the location of the sediment sampling sites. If the suspended sediment samples were solely collected at the watershed outlet the sediment sources would have been assessed as contributing approximately equal amounts opposed to identifying the switch in the dominant source of sediment. This type of sampling approach would have given an incomplete assessment of the sources of sediment as it would have led to the conclusion that the shale bedrock was a significant source of sediment throughout the watershed. Therefore, in the STC watershed, sediment collected at the river basin outlet does not accurately represent processes affecting sediment dynamics elsewhere in the river basin, and this can lead to poor management decisions. The observations over a range of spatial scales helped to isolate the major physiographic features and identify where changes in sediment source occur and provide information on the processes that drive these changes. Additional key aspects required to interpret the sediment source fingerprinting data include the need to: (1) understand the physical and geochemical processes controlling tracer property selection; and (2) incorporate knowledge of the hydro-geomorphological connectivity of the watershed. The utility of sediment fingerprinting can be improved by carefully considering which locations to sample and recognizing the effect this choice will have on data interpretation.

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## 8 Conclusion and synthesis

The current approach to sediment fingerprinting accounts for the input (i.e., sediment sources) and the output (i.e., downstream sediment) but the processes which link them are not well integrated into the approach. This is currently a major limitation of the approach (Fig. 8.1). Accounting for sediment and tracer fate (i.e., sediment fingerprints), as put forward by Davis and Fox (2009), is the methodological step that requires the most scientific inquiry with respect to advancement of the fingerprinting approach. This is due to the fact that this part of the fingerprinting approach presents a multidisciplinary research topic that has not been well studied. To develop a quantitative link the sources to sediment researchers will need to draw on the knowledge from a variety of disciplines including soil science, geomorphology, sedimentology, environmental science, analytical chemistry, statistics, hydrology, landscape ecology and aquatic ecology to develop process-based methods to account for changes in sediment properties. Research in this area will not only improve the understanding of how landscape processes influence sediment properties but it will also help clarify how the hillslope, riparian zone and stream channel environments are interconnected. Better accounting for sediment and tracer fate and other areas of uncertainty will improve the robustness and the utility of sediment fingerprinting approach.

The primary goal of this dissertation was the development and refinement of the sediment fingerprinting approach with an emphasis on the methods used to account for changes in sediment properties as sediment moves through a watershed. The first step was to review and assess the state of the science behind the sediment fingerprinting approach (Chapter 2). The review focused on the behaviour of sediment fingerprint properties as

sediment moves through the watershed from source to sink and the implications for sediment fingerprinting. It was found that the literature on sediment fingerprinting tends to assume there is a direct connection between sources and sediment, while much of the broader environmental and sedimentology literature identifies that numerous chemical, biological and physical transformations and alterations can occur as sediment moves through a watershed. Particle selectivity was found to be one of the main processes preventing a direct link between sources and sediment and, therefore, a major source of uncertainty within the sediment fingerprinting approach.

As a result, a series of experiments at the landscape-scale, represented by hillslope (Chapters 3 and 4), riparian (Chapter 5) and fluvial (Chapter 6) environments were undertaken to specifically investigate the particle selectivity of erosional, transportation and depositional processes within each of these key areas of the landscape. Finally, a watershed-scale application of the sediment fingerprinting approach was used to investigate the role of connectivity and scale on sediment dynamics (Chapter 7).

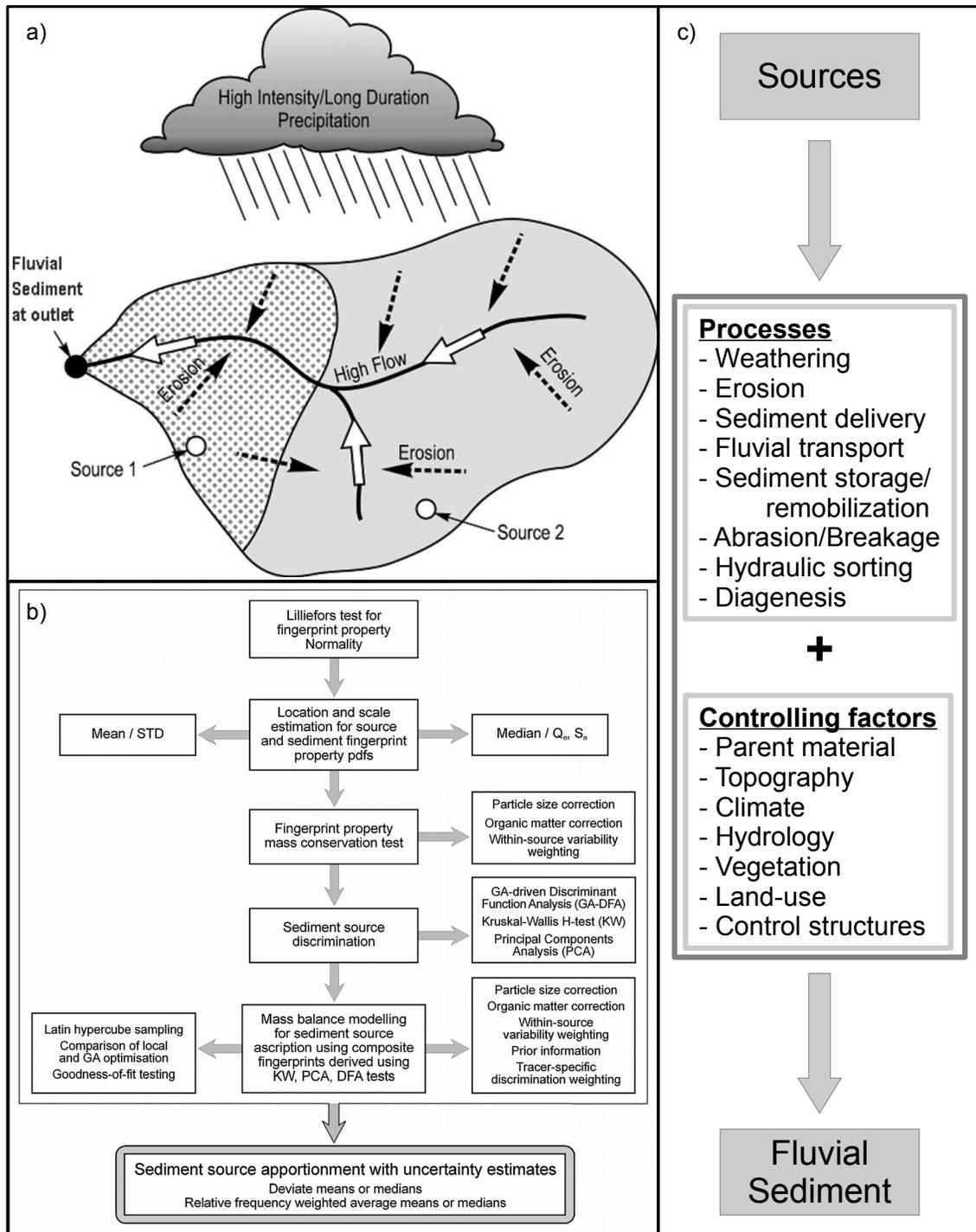


Figure 8.1: A conceptual model of the sediment source fingerprinting approach (a) (reproduced from Davis and Fox 2009), an approach for processing geochemical fingerprint data for sediment source apportionment (b) (reproduced from Collins et al. 2013) and the processes and controlling factors which are incorporated into the sediment fingerprinting approach (c) (adapted from Weltje and von Eynatten 2004).

## 8.1 Hillslopes

A rainfall simulator was used to generate runoff in two contrasting agricultural regions in British Columbia (BC) and Manitoba, Canada. The purpose of this experiment was to: 1) assess the importance of soil surface properties (e.g., vegetative cover, soil moisture) and their interactions with particle size and organic matter selectivity of interrill erosion; 2) assess the ability of commonly used correction factors to account for the differences in both particle size distribution and organic matter content and the concentrations of a broad suite of geochemical elements; and 3) examine the relation between the concentrations of a broad suite of geochemical elements and both particle size and organic carbon.

Overall, it was difficult to rank the relative importance of the individual soil surface properties on the particle size and organic matter selectivity of the soil erosion process as there were significant interactions between some of the soil surface properties. Furthermore, many of the soil surface properties measured in this study undergo seasonal changes, suggesting that the particle selectivity may also vary seasonally. This has implications for accounting for differences in particle size and organic matter content when case studies span multiple seasons or years. Consistent with other research, total sediment yield did correlate with particle selectivity as plots that generated higher amounts of sediment were less selective (e.g., Armstrong et al. 2011; Yang et al. 2013). However, the soil surface properties which affected the sediment yield were not the same as those which influenced particle selectivity. Therefore, predictions of particle size and soil organic carbon (SOC) enrichment based on sediment yield alone may not adequately describe the process of particle selectivity.

In comparing the geochemical composition of source soil to eroded sediment, it was

found that for many of the geochemical elements investigated there was a difference in concentration between the source soil and eroded sediment despite limiting the analysis to the <63- $\mu\text{m}$  fraction. These differences are typically thought to result from differences in particle size and organic matter (e.g., Horowitz 1991). As a result, correction factors are commonly applied to allow a more direct comparison between source and sediment (e.g., Collins et al. 1997). Concentrations in the source soil were adjusted using both particle size and organic matter correction factors. However, particle size correction factors tended to over-correct concentrations within the source soil relative to the eroded sediment and the further addition of the organic matter correction factor resulted in a significant over-correction. The magnitude of the over-correction was geochemical element-specific, which highlights that a single correction factor applied uniformly across a broad range of fingerprints may not be appropriate. The results of this study suggest that the commonly used correction factors may not be an adequate approach for accounting for differences in particle size and organic matter content. This has implications for the sediment fingerprinting approach as fingerprint data manipulation by these correction factors can influence the fingerprint selection process and ultimately the sediment source apportionment results. For example, in a sediment fingerprinting case study, Smith and Blake (2014) demonstrated that the conclusions changed depending on whether a particle size and an additional organic matter correction factor were applied to the data.

Further investigation revealed that the relation between elemental concentration and both particle size and organic matter were geochemical element-specific and were different between the two watersheds investigated. There were differences in the magnitude, direction and linearity of the relation and in some cases there was a significant interaction between

particle size and organic matter content. Furthermore, some elements required data transformations (e.g., log transformation) to meet the assumptions of a linear model. These results are consistent with Russell et al. (2001) where an analysis using different size fractions of source material revealed that the relation between particle size and concentration varied between elements and watersheds.

## **8.2 Riparian zones**

Soil profiles along transects that extended from the upper landscape position to the riparian zone, within two agricultural sites in southern Manitoba, Canada, were selected to investigate the particle selectivity and biogeochemical processes of riparian zones. While the greatest net accumulation of soil occurred in lower landscape positions there were still significant amounts of soil accumulation in the riparian zone. The soil within the riparian zone had a greater proportion of fine-grained material as compared to the other landscape positions. This presented evidence of a possible interaction between tillage and water erosion processes whereby tillage erosion (a non-particle size selective process) moves soil to the lower slope positions and water erosion (a particle size selective process) delivers soil particles into, and through, the riparian zone (Lobb et al. 2004). The soil in the riparian also had higher organic matter content as compared to the other landscape positions, which was likely related to differences in soil disturbance (i.e., tilled fields and non-till riparian zone) and not particle selectivity.

In addition to differences in particle size and organic matter content, there was also some evidence of biogeochemical transformation within the riparian zone. The changes in geochemical composition with depth were more prominent in the riparian zone and, overall,

the soils in the riparian zone had a unique geochemical composition relative to the other landscape positions. This is consistent with the literature which has characterized the riparian zone as a hot spot for biogeochemical processes due to the dynamic hydrologic conditions (e.g., fluctuating water table and redox conditions) (Vidon et al. 2010). Results of this chapter have implications for the sediment fingerprinting approach with respect to the sampling design and how best to characterize surface soil sources of sediment within agricultural watersheds. The soils within the riparian zone could be considered one of three ways: 1) included with samples from the other landscape positions as part of the hillslope continuum; 2) considered representative of contributions from the upper, mid or lower landscape positions; or 3) considered a unique source of sediment distinct from the other landscape positions.

### **8.3 Fluvial transport**

A large recirculating flume (2 x 2 x 30 m) at the Quesnel River Research Centre, BC, was used to investigate the particle selectivity of fluvial transported sediment under different channel bed conditions. There was strong evidence of both particle size and organic matter selectivity as a result of fluvial transport under all channel bed conditions as the smaller and organic-rich particles remained in suspension longer. The results of this experiment showed that compared to a planar gravel bed, a smooth planar channel bed introduced small-scale roughness which resulted in the preferential deposition of larger particles into the channel bed. Increasing the depth of the gravel bed increased the amount of intra-gravel flow and reduced the potential for resuspension resulting in a further reduction in the particle size as well as in a significant increase in organic matter content of the suspended sediment.

These results suggest that it is important to consider the channel bed conditions when interpreting particle size and organic matter information, high flow events that may flush out gravel-stored fine-grained sediment or result in gravel bed movement. In addition, channel bed condition can also vary longitudinally from headwaters towards the watershed outlet as channels transition between bed types (e.g., from bedrock to gravel through to sand channel bed types). These are important aspects to consider when selecting sites for sediment collection and interpreting the results they provide.

While the flume experiment (Chapter 6) demonstrated that the physical process of selectivity can influence fingerprint concentrations, the experimental setup eliminated the influence of many biogeochemical processes which would be present in a natural system. In particular, the hyporheic zone, where groundwater and surface water mix, will have an effect on both sediment and water geochemistry (Bencala 2000). The characteristics of groundwater reflect both inputs from the atmosphere and soils and bed rock (Alexakis 2008). Consequently, the ground water and surface runoff will have a different chemical profiles, including dissolved minerals, pH and dissolved oxygen. The movement of ground water into the stream (i.e., gaining streams) will result in a change in stream water chemistry and the fingerprint of sediment will adjust (e.g., adsorption/desorption of exchangeable ions) to compensate for the change in environmental conditions. Furthermore, the hyporheic zone is a hotspot for biogeochemical processes (e.g., denitrification) because of high solute residence times and steep gradients in dissolved oxygen and pH (Cardenas 2015). Therefore, there is a high potential for modification of fingerprint properties in sediment stored in the hyporheic zone. The consequences of both ground water exchange and hyporheic zone processes on the sediment fingerprinting approach are not well established.

## 8.4 Watersheds

A sediment fingerprint case study was conducted in the South Tobacco Creek watershed, a predominately agricultural region located in south-central Manitoba. A longitudinal sampling design was used and sediment samples were collected over the course of three years at six locations along the main stem of the creek, ranging from 3<sup>rd</sup> to 7<sup>th</sup> order streams (48 – 7441 ha catchment area). The results of the sediment fingerprinting study demonstrated that there was a switch in the source of sediment between the headwaters and the outlet of the watershed. The suspended sediment in the upper reaches were dominated by topsoil sources while the suspended sediment moving through the lower reaches and being exported from the watershed had a higher proportion of sediment coming from streambank and shale bedrock sources. This research highlights the importance of the location of the sediment sampling sites. If the suspended sediment samples were solely collected at the watershed outlet the, contributions of topsoil, streambank and shale bedrock sediment sources would have been assessed as contributing approximately equal amounts. This type of sampling approach would have given an incomplete assessment of the sources of sediment at the watershed scale as it would have led to the conclusion that the shale bedrock was a significant source of sediment throughout the watershed. Therefore, sediment collected at the watershed outlet does not necessarily accurately represent processes affecting sediment dynamics elsewhere in the river basin; failure to account for this can lead to poor management decisions. Observations over a range of spatial scales helped to isolate the major physiographic features, to identify where changes in sediment source occurred, and to provide information on the processes that drive these changes. Furthermore, bedrock

exposures are often not considered as potential sediment sources as they are often comprised of solid rock or high-strength consolidated sediment. However, the low-strength nature of the shale bedrock within the South Tobacco Creek watershed coupled with freeze-thaw and wet-dry cycles and abrasion produced significant amounts of fine-grained sediment. The rapid changes in particle size of the shale-derived sediment presents a challenging situation in which to account for changes in particle size between sediment sources and sediment collected downstream.

## **8.5 Implications for sediment fingerprinting**

The general introduction (Chapter 1) outlined the sediment fingerprinting approach and identified numerous areas of concern with respect to the robustness and reliability of the approach. The research and information presented in this dissertation can be used to help guide the sampling, sample preparation, data manipulation, fingerprint selection and interpretation of results (Table 8.1).

Table 8.1: Areas of concern with respect to the robustness and reliability of the sediment fingerprinting approach and protocol recommendations that can begin to address these concerns.

Area of concern	Protocol recommendations
<b>Sample collection and preparation</b>	
Sampling design	Clear objectives Complete documentation of design and methods Watershed characteristics to provide context for decisions Use prior knowledge of watershed processes as a guide
Sampling methods	
Sample storage	
Sample preparation	
Selecting analysis	
Analytical methods	
Order of analysis	
<b>Data manipulation</b>	
Particle size correction factor	Justification needs to be given for the use of corrections/weightings
Organic matter correction factor	Experimentation to confirm suitability
Fingerprint-specific weightings	Complete reporting of correction factor and weighting values
<b>Fingerprint selection</b>	
Below detection limits	Report basic statistics of fingerprint values and variability
Range test	Knowledge of the processes that led to fingerprint development
Non-conservative behaviour	Knowledge of fingerprint behaviour under changing environmental conditions
Statistical procedures	
<b>Interpretation of results</b>	
Watershed characteristics	Apportionment results need to be put in appropriate spatial and temporal context
Limitations and sources of error	Limitations and sources of error need to be taken into consideration when assessing the reliability and robustness of conclusions
Supporting information	Inclusion of multiple lines of evidence to support/constrain apportionment estimates

### 8.5.1 Sample collection and preparation

Sampling locations and method of collection of both source material and sediment are important aspects of the sediment fingerprinting approach. Locations for source sampling are often selected based on prior information (e.g., areas with high rates of soil erosion) and ease of access. In many sediment fingerprinting case studies the rationale behind the sampling locations for a given sediment source are not well documented, nor are the implications of the selected locations considered (e.g., bias sampling). Even within a location the sampling design and methodology are not standardized and a range of designs (e.g., transects or grid),

methods (e.g., surface scrapes or soil cores) and quantity of samples per source have been used. The goal of the sampling approach, within a spatially defined source area, is to be representative of the erosional processes that are transporting and delivering material to surface waterways, but this can be difficult to assess (Wilkinson et al. 2015). The lack of standardization in selecting and sampling sources of sediment has implications for fully characterizing the variability of fingerprints for a given source which introduces uncertainty that propagates through the remaining steps and ultimately the apportionment results (Du and Walling In press). The results from the rainfall simulation study (Chapters 3 and 4) demonstrated that there was a significant amount of spatial variability (i.e., inter-transect variability) in both the extent of particle size and organic matter selectivity and the concentration of geochemical fingerprints. Furthermore, the riparian zone study (Chapter 5) demonstrated that the riparian zone had a distinct particle size distribution, organic matter content and geochemical composition which raised questions as to whether the riparian zone should be considered a unique sediment source or part of the hillslope continuum. This information can be used to inform the sampling design to best suit the research needs of a particular case study as well as provide information that can be used to estimate the number of samples needed to achieve a given confidence level (e.g., power analysis). The development of methods of sample collection that better represent the sediment sources through the generation and collection of mobilized sediment (e.g., rainfall simulations; Motha et al. 2002) may be an option but further research is required to assess this.

Clear objectives of the sediment fingerprinting study need to be in place prior to collection of sediment, as the information they provide is directly linked to where the sampling sites are situated. The consideration of watershed characteristics, at a range of

spatial and temporal scales is essential when selecting in-stream sediment sampling locations. The results of the watershed-scale sediment fingerprinting case study (Chapter 7) demonstrated that the sediment collected at the outlet of a watershed was not reflective of processes occurring in the upper reaches (head waters), and that the sampling location was important to consider when interpreting the apportionment results. At the watershed-scale, concepts including the spatial arrangement of sources and the geomorphic connectivity of these sources relative to the site of downstream sediment collection (i.e., proximity to sediment sources and sinks) will help to define appropriate sampling sites that best suit the objectives of the study (Wethered et al. 2015). The next step is to consider the reach-scale properties, including abrupt changes in stream gradient, confinement and other modifications (e.g., culverts) as these features can create local patterns of channel erosion and deposition and, in many cases, the effects of these features are not considered in the overall study objectives. Finally, at the hydraulic unit scale, the flow characteristics (e.g., depth and velocity) and channel bed properties (e.g., type of substrate) are important to consider for the placement of sampling equipment. For example, the results from the flume study (Chapter 6) clearly showed that the extent of particle selectivity and subsequently the geochemical composition of the suspended sediment was sensitive to the channel bed substrate conditions.

Of equal importance is the influence of temporal characteristics of the watershed as this also needs to be considered when making decisions regarding the length of the study period or the frequency and method of sediment collection. As with sediment sampling location, clear objectives need to be in place prior to making these decisions. Past case studies have investigated the source of sediments at the intra- and inter-storm (e.g., Martínez-Carreras et al. 2010) and seasonal (e.g., Collins et al. 1997) scales. However, at any of those

temporal scales it can be difficult to interpret the results as it is difficult to attribute changes in sediment sources to specific events or seasons as it is challenging to separate the remobilization of previously stored in-stream sediment and new contributions directly from a sediment source. This is an example of how short-lived fallout radionuclides (e.g.,  $^7\text{Be}$ ; half-life of 53.2 days) can provide insight in to both the source of the sediment and geomorphic connectivity of a watershed. Issues of temporal variability become especially important with time-integrated samplers as the relative contributions from any given hydrological event are unknown.

Sample preparation, specifically sieving, prior to analysis and its subsequent effect on the sediment fingerprinting approach has not received much attention in the literature. Source and sediment are commonly sieved to limit differences in the particle size distribution between the two sample types. Sieving to  $< 63 \mu\text{m}$  is the most common approach, but studies have also limited their analysis to finer fractions (e.g.,  $< 10 \mu\text{m}$ ; Wilkinson et al. 2013) and consideration needs to be given as whether the size fraction is representative of sediment transported within the watershed. However, results from the rainfall simulation study (Chapters 3 and 4) demonstrated that despite sieving there were still significant differences in both the particle size distribution and organic matter content between source soil and the eroded sediment which need to be accounted for if a direct comparison is to be made between the two sample types (Section 8.5.2). Furthermore, different grain-size fractions will have different patterns of erosion, transport and deposition within the watershed. Fingerprinting each grain-size fraction individually is one approach that can limit the issues of grain-size difference and the representativeness of collected sediment (e.g., Haddadchi et al. 2015). In addition, sieving source and sediment samples also assumes there are negligible changes in

grain-size due to breakage or abrasion of sediment as it is transported downstream which may not be the case in watersheds with low-strength (i.e., friable) material (e.g., shale sources in the South Tobacco Creek watershed; Chapter 7). In many case studies, the rationale behind the sampling design and methods, as well as sample preparation steps, are typically not well documented. Providing appropriate documentation would provide more context for, and confidence in, the results presented.

### **8.5.2 Data manipulation**

The use of particle size and organic matter correction factors is a contentious practice; while particle selectivity does occur and differences in particle size and organic matter do have an effect on many sediment fingerprints, there is increasing evidence that the commonly used correction factors have unpredictable impacts on the data. As demonstrated in Chapters 3 and 4, this is because the direction, magnitude and linearity of the relation between fingerprint concentration and both particle size and organic matter content can vary considerably between fingerprint properties. The use of correction factors then influence the tracer selection process and, ultimately, the conclusions drawn for the apportionment results. For example, the results from Chapter 4 demonstrated that applying a particle size correction factor for Sn in the eroded sediment resulted in an over-correction of the concentration by 94 % and 15 % as compared to the source soil for the Beaver Valley (BC) and South Tobacco Creek (MB) watersheds, respectively. Applying an organic matter correction factor in addition to the particle size correction factor increased the percent difference to 136 % and 26 % for the Beaver Valley and South Tobacco Creek watersheds, respectively. In many case studies, the correction factor values used are not reported, which makes the assessment of

uncertainty difficult to make.

Other approaches for accounting for differences in particle size and organic matter content have included: linear regression (e.g., Gellis and Noe 2013), rainfall simulations (e.g., Motha et al. 2003), particle size fractionation of source material (e.g., Russell et al. 2001), and expression on a minerogenic basis (e.g., Smith and Dragovich 2008), but many of these approaches remain untested or are laborious and cost prohibitive. Other data manipulation approaches include fingerprint-specific weightings to account for discriminatory power, variability, and analytical precision (e.g., Collins et al. 2010). These weightings are used to give greater importance within the apportionment model to fingerprint properties that have large differences between sources, low variability within a source and high analytical precision. However, research by Lacey and Olley (2015) using artificial sediment mixtures demonstrated that these weightings did not improve mixing model accuracy. Justification of data manipulation approaches needs to be properly documented and results need to be presented in a manner that acknowledges the limitations and uncertainty associated with such manipulations.

### **8.5.3 Fingerprint selection**

Little consideration is given to the results of multi-step statistical procedures that are commonly used to select a set of fingerprints that provide good discrimination between potential sediment sources. Recent work by Palazón et al. (2015) showed that the subset of tracers selected was dependent on the procedure used and that each subset of selected tracers resulted in different apportionment results. Furthermore, a purely statistical approach may not be the most appropriate method, as the conservative behaviour of sediment fingerprints

during transport through the watershed or the underlying processes that lead to their ability to discriminate between sources are not considered (Lacey et al. 2015; Sherriff et al. 2015). A hybrid approach, using a combined statistical- and process-based selection process, was used in selecting appropriate fingerprint properties for the sediment fingerprinting case study in the South Tobacco Creek watershed presented in Chapter 7. Incorporating information on the physical or biogeochemical development of sediment fingerprints have developed and how they behave within the environment into the fingerprint selection process will improve the reliability and robustness of the sediment fingerprinting approach.

Removal of fingerprint properties when one or more samples are below the detection limit is also a common approach, but this may also result in the removal of fingerprints that have good discriminatory power. As an example, a particular fingerprint may provide good discrimination if the concentration within one of the potential sources is at, or near, the detection level while the other sources are well above. There are statistical techniques that can deal with this type of left-censored data (e.g., Helsel 2012), but its integration into the sediment fingerprinting approach remains untested. Fingerprint properties, where the concentration of the sediment falls outside of the range of the potential sediment sources (i.e., the “range test”), are also removed as these properties are deemed to behave in a non-conservative manner. Furthermore, there is a need for better reporting of fingerprint property data for both sources and sediment so the tracer selection process used and its results can be better evaluated.

#### **8.5.4 Interpretation of results**

The previous sections outline some of the issues with the sediment fingerprinting

approach and offer suggestions on how the methodology and application of the approach can be improved (Table 8.1). Two common themes throughout the previous sections that can help address some of the issues presented: i) better reporting of methods, watershed characteristics and fingerprinting data; and ii) a clear assessment of the sources of error and limitations of the sediment fingerprinting study.

Despite the potential short-comings of the sediment fingerprinting approach, it can provide valuable information to help guide watershed management decision-making to reduce non-point source pollution. To obtain reliable conclusions about sediment dynamics within a watershed it is advisable to have multiple independent lines of evidence that come to similar conclusions. Therefore, the inclusion of multiple lines of evidence will help constrain and validate sediment source apportionment estimates. Other lines of evidence that can offer support include sediment budgets, assessment of geomorphic connectivity, small-scale experimentation and observation (e.g., use of  $^{137}\text{Cs}$  to estimate rates of soil erosion), historical records (e.g., aerial photographs time series) and field visits (i.e., visual observations). In cases where the reliability of sediment fingerprinting results are low, due to the limitations described in this dissertation, the value of other lines of evidence becomes a very important and necessary component of drawing meaningful conclusions.

## **8.6 Overall synthesis**

Due to the rapidly increasing global population and the subsequent increased pressures on our soil and water resources to meet the growing demands for food, fibre and fuels, it is critical that resources are managed in a sustainable way (Lal 2006). Sediment and sediment-associated nutrient and contaminant pollution in watersheds are a concern both in

Canada and around the globe as a threat to both human water security and ecological health and biodiversity (Vörösmarty et al. 2010). Successful management of both soil and water resources is often achieved at the watershed scale as it can be considered to be a fundamental unit of the landscape that controls the flux, timing and pathways of water, sediment and chemicals (Owens 2005). Management at the watershed scale also acknowledges that decisions made in one part of the watershed will have impacts on other parts of the watershed. However, designing and implementing long-term management plans that are environmentally, socially and economically acceptable requires information on the locations and relative contributions of sources of sediment (Owens 2005).

Sediment fingerprinting has been identified as a potential tool that can provide this information to watershed managers. However, Mukundan et al. (2012) suggests that the lack of standardization or a well-defined protocol for the sediment fingerprinting approach is a major obstacle in transforming it from a research tool to a management tool. Part of the lack of standardization of the approach stems from the fact that the scientific community is still exploring and assessing different approaches and methods to better link potential sediment sources to collected in-stream sediment. Much of the research focus has been on the tracer selection process (e.g., Palazón et al. 2015), data manipulation (e.g., Smith and Blake 2014) and mixing models (e.g., Haddadchi et al. 2014), but incorporating process-based information has received less attention. Comprehending the physical and biogeochemical processes that link the sediment sources to in-stream sediment, and incorporating these processes into the sediment fingerprinting approach will improve the robustness and reliability of the sediment fingerprinting approach (Fig. 8.1). At this point in time, the confidence surrounding information provided by some sediment source fingerprinting studies

is limited. This is because each watershed presents a unique set of environmental conditions and processes which creates a situation whereby many of the individual steps of the fingerprinting approach (e.g., fingerprint selection) need careful consideration or experimentation to ensure that the approach is sound. However, such considerations and experimentation add a layer of complexity and additional work to the approach which, in turn, makes the sediment fingerprinting approach a less effective tool. This dissertation investigated some of the processes that link potential sediment sources to downstream sediment and was able to provide information on how several key watershed processes affect sediment fingerprint properties. This information can be used to support both the refinement of the sediment fingerprinting approach and the development of standardized protocols.

## **8.7 References**

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