Rare Earth Elements as a Tracer to Understand Sediment Fate and Transport in Small Streams

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Abstract

Sediment is a major source of water quality impairment in streams, rivers and lakes in the US. However, sediment fate and transport in small streams is poorly understood. Previous attempts to characterize sediment transport often insufficiently represented the physical and chemical sediment properties and lacked spatial and/or temporal resolution. Therefore, there is a need to develop better sediment tracers, for which rare earth element (REE)-labeled sediment is examined as an alternative. The objectives of this study were to: 1) assess the adsorption of REEs to natural soils and ensure their reliability as a tracer in a fluvial environment; and 2) evaluate the efficacy of utilizing REE-labeled sediment to quantify fate and transport in a second-order stream during a series of storm events.

Two natural stream bank soils from Stroubles Creek in Virginia were labeled with the REEs lanthanum and ytterbium. The REEs adsorbed equally to both soils and had minimal desorption after several washes with stream water. This suggests that REEs form a dependable natural sediment tracer and sufficiently label natural soils for use in a sediment tracing study.

During two storm events, two unique REE tracers were injected into Stroubles Creek. These tracers were detected at varying discharges and sediment loads in bed and suspended sediment samples up to 875 m downstream. REE tracers proved to be an ideal tracer for detecting sediment fate and transport in a small stream during a series of storm events and hold great potential for evaluating best management practices and sediment transport models.

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1.0 Background

1.1 Introduction and Problem Description

There are more than 170,000 km of rivers and streams that are either threatened or impaired by sediment, making it the second largest impairment of water quality in the U.S. (USEPA, 2012). Not only is sediment an issue in obtaining clean drinking water for cities across the U.S., some of the most productive topsoil from agricultural fields is lost each year due to erosion. The total cost of sediment to the U.S. economy has been estimated at over $16 billion, based on the 1992 U.S. dollar, due to land lost to erosion, the need to dredge streams and rivers, the sedimentation of lakes and reservoirs, the loss of sediment-associated nutrients from the landscape and the mobilization of heavy metals and other pollutants (Osterkamp *et al.*, 1998). Some soil erosion can be attributed directly to anthropogenic activities (Ricker *et al.*, 2008), which may prove even more problematic as global populations continue to increase.

The realization that sediment loading of our nation's water bodies is not sustainable has brought about significant efforts to restore the streams and rivers of the United States for the purposes of improving water quality and minimizing soil losses due to erosion. Since the 1990s there has been an exponential increase in the number of stream and river restoration projects implemented each year, with the total restoration expenditures reaching more than $1 billion per year (Bernhardt *et al.*, 2005). The most commonly stated goal of these river restoration projects is to enhance water quality, which is often due in part to excess sediment entering the stream or river.

The scientific community recognizes that the interactions of sediment with the freshwater ecosystems is poorly understood, which will only become more important as the earth experiences global environmental change (Owens and Xu, 2011). Efforts have been made to understand sediment transport in fluvial systems; however, sediment, especially the suspended sediment, is difficult to label and track as it moves through a fluvial system.

Previous tracers have included fluorescent particles, painted rocks, radioactive isotopes, lycopodium spores and Baker's yeast, to name a few (Leopold *et al.*, 1966; Atkinson *et al.*, 1973; Wood and Ehrlich, 1978; Matisoff *et al.*, 2002; Granger *et al.*, 2011). However, these tracers inadequately represent the sediment they are trying to track in that they have low densities, come in a single size/shape or have different adsorption chemistries. In addition, many of the tracers are difficult to detect and/or require manual counting to determine the recovery rate. An ideal tracer would be one that adequately represents the physical and chemical properties of sediment, while remaining easy to detect at very low concentrations and ideally would have multiple signatures that would all behave the same when used as a tracer (Mahler *et al.*, 1998b).

Given the large impact of sediment on water quality within the United States and the current lack of knowledge regarding sediment fate and transport, there is a need for an increased understanding of the source, transport and fate of sediment in fluvial systems. An improvement in the water quality management of the nation's rivers and streams can be brought about by improved modeling and monitoring efforts, which could be supported by information from an ideal tracer that adequately represents all natural stream sediments.

1.2 Research Objectives

The focus of this research is to evaluate the use of rare earth elements (REEs) as potential tracers of sediment mobility in fluvial systems, such that they can be used to inform sediment lag times and transport models. Previous uses of REEs have focused primarily on the terrestrial application of REE-labeled soils, with limited attention paid to the fate of the sediment once it was eroded. This research sought to create a tracer that can bridge the gap. By developing adsorption isotherms for two natural stream bank soils from Stroubles Creek in southwest Virginia, it was possible to create a sediment tracer that accurately represented the natural soil and provided insight into the fate and transport of sediment in a fluvial setting. This tracer was deployed during storm events in order to determine the transport distance of the labeled soil, the dispersion of the tracer during transport and the extent of deposition that occurred downstream of the injection site. In summary, the specific objectives of this research were:

1. To determine an effective maximum adsorption of REEs to two natural soils from a stream bank along Stroubles Creek;
2. To examine the desorption of REEs from these two soils in Stroubles Creek stream water; and
3. To evaluate the use of REE tracers as a means to detect and quantify sediment transport and deposition under varying discharge rates.

1.3 Organization of Thesis

This document is organized around two journal articles that will be submitted for publication in two different peer-reviewed journals. A comprehensive literature review precedes these two articles, providing a review of erosion processes, methods used to detect erosion from both the landscape and stream banks and highlights previous work involving rare earth elements. The two articles form the core of the thesis, although they can serve as stand-alone documents with a full abstract, introduction, methods, results, discussion, conclusions and references. The article in Section 2, on the adsorption of REEs to a natural soil, will be submitted for publication in *The Journal of Soils and Sediment*. The article on the injection of the REE-labeled tracer during a series of storm events (Section 3) will be submitted for publication in *River Research and Application*. When viewed jointly, these documents provide a more complete picture of the value and use of REE-labeled soils as a tracer of sediment fate and transport. Section 4 provides a summary of this research and highlights areas for future research. All supporting documents for this research, including tables, figures and procedures, are located in Section 5.

Section 2

Kreider, T.A., K.J. McGuire, B.D. Strahm, W.C. Hession, A.R. Buda. 2012. Rare Earth Elements as Tracers of Fluvial Processes. To be submitted to *Journal of Soils and Sediment.*

Section 3

Kreider, T.A., W.C. Hession, K.J. McGuire, D.L. Welsch. 2012. Rare Earth Elements as a Tracer to Understand Sediment Fate and Transport in Small Streams. To be submitted to *River Research and Application.*

1.4 Literature Review

1.4.1 Introduction

Sediment is the second largest threat to river and stream water quality in the US (USEPA, 2012). The nation has over 170,000 km of rivers and streams that are threatened or impaired by sediment, which is more than 20% of all threatened and impaired stream reaches in the US (USEPA, 2012). Not only is the loss of sediment an issue for agricultural fields that rely on high-quality soil to grow crops, this sediment has off-site secondary effects on the entire economy. For instance, Osterkamp *et al.* (1998) estimated that the annual physical, chemical and biological impact of sediment in North America was over $16 billion, based on the 1992 US dollar. The physical impact includes removing sediment at water treatment facilities, the loss of land due to erosion, sediment clogging drainage ditches and the filling of lakes and reservoirs (Morris and Fan, 1997). Other chemical and biological impacts include the degradation of aquatic ecosystems due to sedimentation, the loss of nutrients attached to sediment and the deposition of nutrients and heavy metals in undesirable locations (Osterkamp *et al.*, 1998).

Regionally, the Chesapeake Bay Watershed suffers extensively from an influx, and subsequent deposition, of excess nutrients and sediment. The US Environmental Protection Agency (USEPA) intends to achieve 60% of the necessary reductions in water pollution of the Chesapeake Bay by 2017, of which sediment is a major contributor. However, there are still significant gaps in our understanding of how quickly the system will recover and how effective erosion mitigation programs may be (USEPA, 2009). Erosion can be caused by anthropogenic activities, so as populations grow, there is a potential for greater impacts on stream sedimentation, further impairing the nation's waterways (Ricker *et al.*, 2008). Given the impact of sediment on the water quality and broader economy, it is imperative that we understand how sediment reaches streams and rivers and perhaps even more important is that we understand how this sediment is transported within these fluvial systems. Therefore, this research focused on creating a rare earth element-labeled sediment that can be used to detect and quantify sediment fate and transport in small streams, which can be used to improve best management practices regarding soil erosion.

1.4.2 Sediment and Pollutant Loading

Sediment has been defined as "transported and deposited particles or aggregates derived from rocks, soils or biological material"(SSSA, 2008), which in this study was considered to be any soil that has been labeled specifically for injection into the stream, in addition to the previous definition. A watershed's sediment flux (including rock, soil and biological material) is often less than the total amount of erosion in the watershed, with the ratio of exported to eroded soil known as the sediment delivery ratio. This delivery ratio varies from 2-98% across watersheds of various sizes (Porto *et al.*, 2011), while also varying with individual events in the same watershed (Piest *et al.*, 1975). The sediment delivery ratio, while a simple concept, relies on many assumptions regarding particle size, selective erosion and deposition within the channel, as well as time constraints on the sediment delivery process (Walling *et al.*, 2003). Depending on the channel geomorphology and geology, a stream can be more or less efficient at delivering the supplied sediment. The extreme variability in the fate of sediment after it reaches the channel makes it challenging to predict sedimentation rates in the watershed. Porto et al. (2011) concluded that “there is a need to obtain more direct and spatially distributed evidence of the erosion rates occurring within a catchment and to characterize the links between sediment mobilization, transfer, storage and output.”

Although sediment usually originates from within the watershed, the physical and chemical characteristics do not always match those of the source soil. Walling et al. (1983) found that in the literature, enrichment ratios (ratio of eroded sediment to that of the parent material) for the clay fraction of the soil ranged from 1.47 to 2.29. Therefore, up to twice as much clay exists in the transported sediment, as compared to the parent material. However, Young and Onstad (1978) found that for inter-rill erosion, the enrichment ratio fell to 0.79, indicating less clay in the transported sediment than in the surface soil. Five small watersheds in Ohio had an average enrichment ratio of 1.2 in the runoff sediments, which also caused an increase in the cation exchange capacity (CEC) of 12% (Rhoton *et al.*, 1979). This change in clay content and CEC has important implications for pollutant loads in the watershed.

Nutrients, heavy metals and/or pesticides adsorb to soils on the landscape, with clay soils having the capacity to adsorb more of these pollutants due to their higher CEC. The contaminant concentration on these fine-grained sediments are controlled by the magnitude and variability of the contamination across the landscape (Walling *et al.*, 2003). If the concentration of a pollutant in the water column is reduced, or the pH changes, a previously deposited sediment that is enriched with a pollutant, such as soluble reactive phosphorus (SRP), can serve as a source of contamination (Jarvie *et al.*, 2005; Jarvie *et al.*, 2006; Hamilton, 2011). However, sediment that is relatively low in SRP can serve as a pollutant sink when the concentration in the water is high (Jarvie *et al.*, 2005). Similarly, Spooner et al. (2010) found that the suspended sediment phosphorus concentration was an order of magnitude higher than that of the bed load sediment. Phosphorus and clay have been strongly correlated in stream sediment, such that enrichment of the clay-sized sediment can imply an enrichment of the phosphorus content as well (Quinton *et al.*, 2001). Hamilton (2011) found that the fine silt and clay fraction of the soils serve as a reservoir for much of the soil phosphorus in a fluvial system. In some cases, the pesticide, phosphorus and metal concentrations on the sediment are high enough to impair the stream habitat (Walling *et al.*, 2003). Considering these potentially large sources of pollutants in the suspended and bed sediments, it is important to understand how this soil enters and moves through the fluvial system.

1.4.3 Soil Erosion and Stream Bank Retreat

Sediment can have many sources in the watershed, originating from cultivated fields, pastures, sewage treatment facilities, forested land, road dust, construction sites, stream crossings and the channel bank (Walling *et al.*, 1999; Carter *et al.*, 2003; Ricker *et al.*, 2008; Devereux *et al.*, 2010). Although sediment originates from many unique locations within a watershed, there are two general sources: soil from overland erosion and that from stream bank retreat.

Both erosion processes contribute to the sediment load in a channel; however, the channel processes can often be decoupled from the hillslope processes (Kirkby, 2010). Therefore, this paper will focus on erosion and transport related to stream bank retreat, as it tends to occur in more episodic events and is poorly understood, when compared with overland erosion. While it is recognized that both overland and channel erosion can threaten productivity and critical infrastructure, structures near streams are often built with the assumption that the stream will not move much, if at all, and therefore progressive stream bank retreat can prove costly.

Stream bank retreat can be caused by mass failure and seepage erosion due to positive pore water pressure (Casagli *et al.*, 1999; Fox *et al.*, 2007; Wilson *et al.*, 2007), both of which can result in large sediment inputs over a very short time period. This is in addition to the erosion due to excess shear stress that provides a more consistent sediment supply.. Spooner et al. (2010) found that although single-day discharge events only consisted of 6 – 8% percent of the annual discharge, 25 -37% of the annual suspended sediment load occurred during these events for two incised channels in Iowa, which confirms earlier studies that found similar results (Wolman and Miller, 1960; Knighton, 1998). Once the soil is eroded, either from overland or the stream bank, it may not reach the outlet of the watershed for centuries, as a substantial amount of this soil can be deposited within the catchment.

The stream bank retreat processes that contribute to the sediment load can be broken down into five distinct processes: fluvial erosion of bed material, mass failure, undercutting followed by mass failure, seepage erosion and erosion due to macropore drainage. Fluvial erosion, as defined here, is erosion that is caused by the shear forces created by water flowing down the channel, on both the stream bed and bank. Fluvial erosion dominates total bank erosion at the peak of a minor flow event due to the lack of high shear stresses as the water level is below bank full. However, during larger events, fluvial erosion contributes the most to the sediment load during the rising and falling limbs, when the stream has not quite overtopped its banks (Luppi *et al.*, 2009). Bank retreat due frequent fluvial erosion is comparable that of mass failure, despite differing frequencies and processes (Casagli *et al.*, 1999).

Erosion by mass failure occurs when the soil loses its cohesive strength and slumps into the stream. It is not necessary for the bank to be undercut prior to this failure, as pore water pressure, soil densities and soil liquefaction can combine to cause bank failure without any prior undercutting of the bank (Rinaldi *et al.*, 2004; Chu-Agor *et al.*, 2008).Unlike fluvial erosion or mass failure, macropore and seepage erosion tend to be more localized. Macropore erosion can be attributed to internal erosion as water flows through the soil matrix, as well as erosion of the bank face by water draining from the macropore network (Beven and Germann, 1982; Fox *et al.*, 2007). Seepage erosion often occurs at the boundary of two soil layers, as water begins to move laterally due to a decrease in the hydraulic conductivity in the underlying soil (Fox *et al.*, 2007). Macropore and seepage erosion, which initiate within the soil matrix, are difficult to predict and evaluate without deconstructing the bank.

One or more erosion processes may be occurring simultaneously across a stream bank, increasing the difficulty in separating out individual processes. The natural heterogeneity of the soil, changes in soil moisture and fluctuating water levels all combine to create a very complex system. Bank erosion is simply the end result of a combination of erosion processes and soil properties that eventually cause the bank to fail (Crosta and di Prisco, 1999).

1.4.3.1 Measuring Stream Bank Retreat

Although stream bank erosion models are still being developed, sediment fingerprinting, erosion pins and other methods of detecting bank retreat are often used to partition the sediment load between upland erosion and stream bank retreat. The percentage of the total sediment load attributed to stream bank retreat is highly variable, as it is dependent on the soil type, stream geomorphology and the characteristics of the watershed. Prior to the development of sediment fingerprinting by Walling and Kane (1984), most methods relied on a direct measurement of the loss of stream bank to determine annual stream bank sediment contributions. Table 1 shows a large variability (1.5 – 96%) in the percentage of the sediment load that is attributed to stream bank retreat across the globe using several methods to determine the stream bank proportion of the sediment load.

Table 1. Proportion of sediment load attributable to stream bank erosion for various global watersheds. **A:** Modified from DeWolfe (*2004*) **B**: Added by author.

	River and Location	Drainage Area (km^2)	Sediment Load Attributed to Stream Bank Erosion	Method of Measurement	Source
A	East Nishnabotna (Iowa)	2500	30-40% of suspended sediment	Interpreted from flow model	Odgaard (1987)
	Des Moines (Iowa)	37500	30-40% of suspended sediment	Interpreted from flow model	Odgaard (1987)
	River Culm (England)	276	1.5-23.5% of suspended sediment	Sediment fingerprinting	Walling and Woodward (1995)
	Murrumbidgee River (Australia)	84000	90-96% of sediment fines from stream bank and gully erosion	^{137}Cs and ^{210}Pb mixing model	Olley (1996)
	River Severn	380	17% of suspended sediment	Erosion pins and PEEPs	Bull (1997)
	Lower Gelbaek Stream (Denmark)	11.6	92-93% of suspended sediment	Mass balance	Kronvang et al. (1997)
	Monachyle Glen (Scotland)	7.7	1.5% of the sediment yield	Erosion pins	Stott (1997)
	Kirkton Glen (Scotland)	6.85	7.3% of the sediment yield	Erosion pins	Stott (1997)
	San Diego Creek (California)	228	70% of sediment yield due to channel erosion	Cross section profiles	Trimble (1997)
	River Wharfe (England)	818	23% of suspended sediment	Sediment fingerprinting	Walling et al. (1999)
	River Ouse (England)	3315	37% of suspended sediment	Sediment fingerprinting	Walling et al. (1999)
	Issaquah Creek (Washington)	144	20% of suspended sediment	Sediment budget modeling	Nelson and Booth (2002)
	Blue Earth River (Minnesota)	4050	31-44% of suspended sediment	Total station cross-section profile	Sekely et al. (2002)
B	River Severn, River Dart (UK)	46	3.5% of suspended sediment load	Sediment fingerprinting	Collins et al. (1997)
	River Severn, River Dart (UK)	8.7	25.5% of suspended sediment load	Sediment fingerprinting	Collins et al. (1997)
	Murrumbidgee River (Australia)	13500	86% of sediment load	^{137}Cs and ^{210}Pb mixing model	Wallbrink et al. (1998)
	NE Branch Anacostia River (Maryland)	188	58% of suspended sediment load	Sediment fingerprinting	Devereux (2010)

Most of the higher stream bank contributions (>60%) are from methods that use a direct measurement of stream bank retreat , such as a mass balance (Kronvang *et al.*, 1997) or cross section profile (Trimble, 1997). However, the mixing model (similar to sediment fingerprinting) used by Wallbrink *et al*. (1998), also found a stream bank contribution of 86% of the total sediment load. Based on field mapping and cross section surveys, Spooner *et al.* (2010) and Newson (2007) found that stream bank erosion contributed between 14 – 50% of the total sediment load in their 30-35 km reaches in Iowa and Idaho, respectively. In the case of the direct measurements, soil removed from the stream bank does not necessarily reaches the outlet of the channel, as the delivery ratio is likely less than 1. It should be noted that Kronvang *et al*. (1997) found minimal surface runoff and no rill erosion, in a highly culverted watershed in the Upper Gelbaek catchment, which helps to explain the abnormally high (92-93%) stream bank contribution to the total sediment load.

Given the variability in the sediment load and the natural variation in stream geomorphology and scale, no single method can be used under all conditions to detect bank retreat. Current methods used to monitor bank retreat include erosion pins (Bull, 1997; Stott, 1997; Evans *et al.*, 2006), photo-electronic erosion pins (PEEPs) (Lawler, 2003), ground-based LiDAR (Resop and Hession, 2010), photo-based interpretation (Vandaele *et al.*, 1996), repeated cross-section measurements (Trimble, 1997; Springer *et al.*, 2001) and profilometers (Lam, 1977; Shakesby, 1993).

Reach-Scale Bank Retreat Monitoring

Erosion pins and PEEPS, although very prevalent in the literature, primarily account for fluvial erosion processes. Further, Couper *et al.* (2002) found that there can be a significant portion of erosion pin readings that are negative (aggradation), most of which are not well documented in the literature. In addition, erosion pins can destabilize the bank and promote erosion around the pin; introducing unnatural erosion forces to the bank (Thorne, 1981; Couper *et al.*, 2002). For a photogrammetric analysis, the lack of historical high-resolution images of the entire study site can limit the applicability of this method (Bartley *et al.*, 2008).

Terrestrial laser scanning, while capable of providing disturbance free, high spatial-resolution data, requires complex post-processing and cannot accurately characterize heavily vegetated banks or any portion of the bank that is underwater (Resop and Hession, 2010). Repeated cross sections can provide accurate assessments of changes in the banks at the survey location, but suffer from a need to conduct extremely time-intensive high-resolution surveys or extrapolate between cross-sections (Springer *et al.*, 2001). Profilometers, which do not disturb the bank as much as erosion pins, require a permanent benchmark location and fail to accurately measure stony banks or those with a deep litter layer (Shakesby, 1993). Most methods for monitoring bank erosion also have a coarse temporal resolution, although photo-electronic erosion pins (PEEPs) have drastically improved the temporal resolution (Collins and Walling, 2004).

Watershed-Scale Bank Retreat Monitoring

The use of the radionuclides ^{137}Cs and ^{210}Pb as part of a mixing model suffers from the same lack of temporal resolution as erosion pins, but on a much larger scale. The deposition of ^{137}Cs has generally declined since the mid-1970s when most aboveground nuclear testing ceased, due in part to the Test Ban Treaty of 1963 (Ritchie and McHenry, 1990). The half-lives of the cesium and lead radionuclides (30 and 22 years, respectively) allow them to persist in the soil, and since they are deposited from the atmosphere, the concentrations are much lower in soils that have not been exposed over the last five decades. These differences in half-lives and distribution through the soil profile can be used to partition the gully and channel bank contributions from the total sediment load (Wallbrink *et al.*, 1998). While ^{137}Cs is strongly adsorbed to the soil, there is a need to correct for grain size selectivity during the soil erosion and sediment transportation processes, as clay particles have higher concentrations of ^{137}Cs than larger grain sizes (Walling *et al.*, 1999).

1.4.3.2 Modeling Stream Bank Retreat

By understanding bank erosion processes and factors affecting erosion, it is possible to more accurately model bank erosion and failure, which can be significant contributors to a stream's sediment load. Early erosion models recognized that failure only occurred when the forces on the soil mass overcame the resisting forces. However, they failed to account for the many smaller, but no less important processes that also affect the sediment contribution. Beven (1982) and Thorne (1990) recognized the difficulty in understanding and modeling a system as complex as stream bank erosion, especially when many of the erosion processes are poorly understood.

The current models for predicting bank failure also have their limitations. One widely used method (Casagli *et al.*, 1999; Rinaldi *et al.*, 2004; Luppi *et al.*, 2009) involves calculating a factor of safety (FS) based on an adaption of earlier work by Fredlund et al. (1978). The factor of safety model for a multi-layer soil profile, developed by Simon et al. (2000), is based on the soil weight, hydrostatic uplift forces on the saturated zone, suction forces in the unsaturated zone, confining pressure due to the stream stage, length of the failure plane and the failure plane inclination in a multi-layer soil profile. This model has been used with varying degrees of success in stratified multi-layer soils (Rinaldi *et al.*, 2004) and loamy sands (Lindow *et al.*, 2009), although such factors as vegetation and seepage erosion caused poor model performance. Caution should be used when applying this model to non-uniform banks, as other processes not accounted for in the model may influence the bank stability.

Although laboratory field trials are much more controlled, some qualities of natural bank erosion cannot be reproduced ex situ. Several studies noted that soil heterogeneity (Fox *et al.*, 2006; Wilson *et al.*, 2007), seepage flow rates (Wilson *et al.*, 2007) and pore water pressure (Sultan *et al.*, 2004) are not accurately represented in lysimeter studies, when compared to field measurements. There are also issues of scaling that must be addressed, as most lysimeter studies occur in a laboratory setting, thereby limiting the hydraulic gradient that can be created and depth of bank that can be simulated. The presence of vegetation is also poorly addressed, possibly due to the high variability of vegetation density and difficulty in replicating it in a lysimeter study. Therefore, the area of bank erosion detection and modeling has significant room for improvement in future research.

1.4.4 Sediment Storage and Lag Times

Channel storage of contaminants has been found to represent less than 3% of the annual contaminant flux in two rivers in the United Kingdom (Walling *et al.*, 2003), leading to the conclusion that the storage component was of limited importance in regulating the contaminant flux. However, Marutani *et al.* (1999) found that in two New Zealand tributaries, the channels aggrade during extreme storms, and then erode this soil during periods of lower flow. Fox *et al.* (2010) found similar results for a lowland bedrock stream with pronounced fluvial storage. Depending on when the sediment storage is measured, the channel network can store substantial amounts of sediment.

In addition to the variability in the volume of sediment stored in the channel network, the lag time between reductions in sediment (and associated nutrients) in the watershed and detectable improvements at the watershed outlet can vary on the order of decades. There can be a substantial lag time between reductions in the phosphorus loading (often associated with sediment) within the watershed and measureable reductions at the outlet (Meals *et al.*, 2010). The Chesapeake Bay is expected to suffer from substantial a lag time before a reduction in nitrogen is measureable, due to slow transportation of groundwater through the system (Korcak *et al.*, 2005). The geology in the surrounding area can also limit the response time for improvements in water quality by increasing the residence time of water in the system (Ballantine *et al.*, 2009).

In a survey of the current literature, Hamilton (2011) found that the response times varied from less than a year in stream water, to decades in larger catchments and surficial soils, with the response times of aquatic sediments and deep percolation pathways requiring at least a century. Additionally, Hamilton stated that the lack of long-term data hinders the evaluation of response times across for more sites. Given the potential for long response times and the large sums of money being invested in restoration efforts, there is a need for an improved understanding of sediment and nutrient transport dynamics, in order to make the most informed decision possible (Meals *et al.*, 2010; Hamilton, 2011).

1.4.5 Tracking Sediment Mobilization and Transport

The mobilization and transport of fine particles in terrestrial and fluvial settings has been an area of active research for several decades. Methods used to monitor the movement of these fine particles include: fluorescent particles (Carey, 1989; Granger *et al.*, 2011), fluorescent sand (Kennedy and Kouba, 1970), lycopodium spores (Atkinson *et al.*, 1973), glass beads (Wheatcroft, 1992), painted pebbles (Leopold *et al.*, 1966), gold/silver infused soil (Olmez *et al.*, 1994), Baker's yeast (Wood and Ehrlich, 1978), DNA-labeled clay (Mahler *et al.*, 1998b), magnetic properties of soil (Caitcheon, 1993,1998; Hatfield and Maher, 2009), natural elemental composition of the soil (Papanicolaou *et al.*, 2003; Zhang *et al.*, 2012) and clay labeled with radioactive isotopes including ^{137}Cs (Ritchie and McHenry, 1990; Zhang *et al.*, 1998), ^{210}Pb (Wallbrink and Murray, 1993) and ^{7}Be (Matisoff *et al.*, 2002).

Each of these techniques has advantages and disadvantages as a method to track fine particle mobility. Some of the limitations with these tracers are an inability to differentiate between the soils in the watershed (magnetic and basic properties), a low spatial resolution, inability to address short-term transport and/or erosion, preferential sorption to fines, uneven deposition on floodplains, and a tracer that does not accurately represent the soil under investigation. Problems with previously used tracers are outlined by Mahler *et al.* (1998a) and presented below in Table 2.

When the outlet sediment is used to determine the source of the erosion, a key requirement is that the sources can be differentiated (Walling, 2005; Devereux *et al.*, 2010). Although a single soil characteristic was initially sought to differentiate the soils in a watershed, no such characteristic could be found, requiring multiple characteristics to be combined to uniquely identify the source soils (Ballantine *et al.*, 2009). One multi-parameter method of determining sediment sources is sediment fingerprinting, which uses a combination of inorganic metal and stable isotope (^{13}C, ^{15}N, etc.) concentrations, as well as soil magnetic properties or water geochemical characteristics, to partition the sediment load into its potential source areas

Table 2. A summary of previously used particle tracers and their advantages and disadvantages; modified from Mahler *et al.* (1998a).

Particle Type	Detection Method	Detection Sensitivity	Size	Specific Gravity	Advantages	Disadvantages
Sand labeled with IR-192 (Sayre and Hubbell 1965)	Scintillation detector	N/A	0.1-1.2 mm	2.65	Radioactively measured in situ	Environmental/ regulatory difficulties
Fluorescent sand (Kennedy and Kouba 1970) (Ingle 1966) (Rathbun et al. 1971)	Manual counting	100 ng/g	0.15-1.3 mm	2.65	Inexpensive Different colors available	Limited to sand-size Paint flakes off Labor-intensive detection
Lycopodium spores (Atkinson et al. 1973)	Manual counting	N/A	30 µm	~1	Six colors available	Single size only Low density
Baker's yeast (Wood and Ehrlich 1978)	Manual counting	N/A	2-3 µm	~1	Appropriate size	Low specific gravity Only one signature available Labor-intensive detection
Fluorescent plastic (Carey 1989)	Filter fluorometry	N/A	3-6 µm	1.4	Different colors available Appropriate size	Low specific gravity
Lanthanide oxides (Krezoski 1989)	Instrumental neutron activation analysis	N/A	N/A	8.35	Sensitive Automated detection	High specific gravity Detection expense
Luminophores (Gerino 1990)	Manual counting	N/A	10-200 µm	N/A		Labor-intensive detection
Plastic microtaggants (Wheatcroft 1991)	Manual counting	N/A	50-180 µm	1.4	Inexpensive	One color Large size Labor intensive detection
Glass beads (Wheatcroft 1992)	Manual counting	N/A	8-420 µm	2.4	Inexpensive Correct density Several size ranges	Labor-intensive detection
Gold/silver doping (Olmex et al. 1994) (Wheatcroft et al. 1994)	Instrumental neutron activation analysis	0.1-1 ng/g	38-125 µm	Same as sediment	Mimics natural sediment Automated Sensitive detection	INAA costs Limited to two tracers Cant use on carbonate sediment
Carboxylate-modified polystyrene latex (Reimus et al. 1996)	Flow cytometry	N/A	0.3-1 µm	~1		Not yet field tested Low density Flow cytometry not readily available

(Walling *et al.*, 1993; Evans *et al.*, 2006; Davis and Fox, 2009; Hatfield and Maher, 2009; Mukundan *et al.*, 2011; Zhang *et al.*, 2012). Source analysis using soil magnetic properties can provide quantitative results, but can be influenced by surface-bound ions (i.e. Fe) that require removal before analyzing (Caitcheon, 1998). Although basic water quality measurements (TSS, turbidity, hydrograph and chemographs of dissolved solids) are easily measured and source identification is possible with these water quality metrics, quantitative results are not easily obtained (Symader and Strunk, 1992; Collins and Walling, 2004).

If an overland vs. stream bank source separation is the final goal, it is reasonable to lump terrestrial land uses together, such as forest, agriculture and pasture. However, this does not address the small scale variations in overland sediment erosion and transport (Nagle *et al.*, 2007). Walling *et al.* (2003) found a preferential transport of PCBs (0-2% of the outlet flux deposited on the floodplains), as compared to lead (36-95% of outlet flux deposited on the floodplain), indicating unequal transport of these metals within the system. Even among assumed conservative tracers there is variability. Mahler *et al.* (1998a) found that a labeled soil tracer arrived before the simultaneously injected NaCl tracer, which was thought to be a conservative tracer, indicating a further need for investigations of sediment tracer mobility.

In addition to the tracer not representing the suspended sediment, the recovery of the tracer can also be problematic. Methods of sampling deposited and previously-suspended sediment include: feldspar clay pads (Schenk and Hupp, 2009; Schenk *et al.*, 2011), artificial turf mats (Walling *et al.*, 2003), time-integrated isokinetic traps (Phillips *et al.*, 2000; Fox and Papanicolaou, 2007; Collins *et al.*, 2010a), bulk water sampling (Carter *et al.*, 2003; Walling, 2005) and filtering (Bonniwell *et al.*, 1999; Ricker *et al.*, 2008). The prominent issue with filtering and centrifuging is the large volumes (25-900 liter) of water needed to obtain the necessary amount of sediment for analysis (Bonniwell *et al.*, 1999; Carter *et al.*, 2003). These large volumes of water can be difficult to transport or require in-field processing; in addition to sufficient stream flow, especially if multiple samples are required. The first three methods are time integrated, thereby providing no temporal resolution, but they also do not require a technician's presence or any automated equipment that can fail during the event.

While sediment sourcing is generally well understood, sediment transport distances and lag times are often less clear. Historically, there has been a lack of knowledge regarding sediment storage, lag times and transport distances (Walling, 1983; Marutani *et al.*, 1999); however, through the use of radioactive isotope detection and better models, these processes are beginning to be unraveled. The transport distance tends to increase with both discharge volume and watershed size (Minshall *et al.*, 2000; Whiting *et al.*, 2005). Although significant differences exist in watersheds worldwide (climate, size, stream power, geology, sediment supply, mean sediment size and anthropogenic influence to name a few), it is necessary to determine how quickly sediment passes through a system if any modeling is to be done within the watershed. In a snowmelt dominated system the fine suspended sediment transport distances can vary from 12 - 60 km (Bonniwell *et al.*, 1999).

Given the variability in the transport distances, the lag time for sediment to exit the system can vary just as much. Lag time can be on the order of months or years in a steep headwater catchment (Caine and Swanson, 1989), while in larger systems, it can be on the order of decades (Newson, 2007). Depending on the tracer used, the lag time may also vary, as Wallbrink *et al.* (1998) found lag times of weeks/months and 10+/-5 years when using ^{137}Cs/^{7}Be and ^{210}Pb, respectively, in the same stream. Often, the lack of long-term data prohibits historical lag time calculations, requiring an inference to be made based on the currently available sediment (Hamilton, 2011). Lag time can also be altered by extreme natural events such as landslides which effectively dam up the channel, giving two nearby watersheds sediment retention rates that differ by more than 20% (Springer *et al.*, 2001).

Considering the variance in watershed topography, geology, sediment supply and anthropogenic influence, it is difficult to summarize the many factors that contribute to sediment erosion, storage and delivery. There are also issues with the currently available methods for detecting erosion, ranging from low spatial resolution (photogrammetry) to low temporal resolution (surveying, erosion pins, radioactive isotope dating, photogrammetry) and high costs/time requirements (surveying, photogrammetry), not to mention the challenges associated with sampling the suspended sediment in the water column. Perhaps the only way to address these issues and improve our understanding of sediment processes is through further empirical studies that examine soil erosion, transport, deposition and re-suspension under many field conditions (Walling, 1983).

This process could be made easier if an “ideal tracer” could be developed with the following characteristics (Mahler *et al.*, 1998b; Zhang *et al.*, 2001). First, the tracer should have similar physical properties to the sediment of interest. Second, an ideal tracer should have multiple unique labels, while still maintaining similar chemical and physical properties, which would allow multiple trials to be completed in the same reach, or for multiple size classes to be labeled and evaluated simultaneously. Third, a low background level is ideal, as this will aid in positive tracer identification. Fourth, a low detection limit allows for recovery of the tracer, even if it is extremely diluted in the system. It should also be environmentally safe for both the user and the environment it will be used in, including minimal plant uptake. Finally, an ideal tracer should be easily and cheaply produced and analyzed with standard lab equipment.

1.4.6 REEs as an Ideal Tracer

In addition to the previously mentioned tracers, rare earth elements (REEs) have been used extensively to label soils for terrestrial erosion monitoring (Tian *et al.*, 1994; Matisoff *et al.*, 2001; Liu *et al.*, 2004; Polyakov, 2004; Kimoto *et al.*, 2006b; Stevens and Quinton, 2008; Laveuf and Cornu, 2009; Polyakov *et al.*, 2009; Michaelides *et al.*, 2010), in addition to a lacustrine (Krezoski, 1989), marsh (Knaus and Van Gent, 1989), groundwater (Johannesson *et al.*, 1997) and karst applications (Mahler *et al.*, 1998a). The outlook for using REEs as a soil particle tracer is good, given the success with multiple soil types and applications (Zhang *et al.*, 2001; Zhang *et al.*, 2003; Lei *et al.*, 2006; Laveuf and Cornu, 2009; Michaelides *et al.*, 2010).

The rare earth elements consist of scandium, yttrium and the lanthanide elements with atomic numbers of 57 – 71, although promethium is not naturally occurring. Thus, this group comprises fourteen unique tracers in the lanthanide series. Each of these REEs is primarily trivalent due to the strong binding energy of the remaining electrons, however some REEs can occasionally also be found as quadrivalent or divalent forms in chemical compounds (Laufer *et al.*, 1984; Tyler, 2004). Although the REEs can be divided into light (LREEs: lanthanum, cerium, praseodymium, neodymium, promethium, samarium and europium) and heavy REEs (HREEs: gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium), it is generally accepted that they form a geochemically coherent group and the natural abundances of individual REEs are positively correlated (Markert, 1987; Tyler, 2004). However, the LREEs tend to be preferentially adsorbed over the HREEs in some cases (Koeppenkastrop and De Carlo, 1992). Previous work has shown that multiple REEs can be used in the same setting while maintaining the ability to differentiate the tracers (Matisoff *et al.*, 2001; Liu *et al.*, 2004; Polyakov *et al.*, 2009), including the use of up to ten individual REEs to determine a sediment's source area (Michaelides *et al.*, 2010).

Although the REEs are called "rare" they are not actually that scarce, making up 0.015% of the earth's crust, and as a whole and are as abundant as copper, lead and zinc (Wang *et al.*, 1989). The rarest REEs have abundances in the earth's crust that are greater than cadmium and selenium (Tyler, 2004). REEs also enter the soil environment in fertilizers, phosphogypsum, sewage sludge, incinerator bottom ashes and atmospheric deposition, which will alter the naturally occurring abundance (Hu *et al.*, 2006). Most REEs are concentrated in the soil (avg. 165 ppm) or the soil parent material (avg. 178 ppm), with minimal contributions from groundwater (avg. 57.2 ppt), river water (avg. 78.3 ppt) and global rainwater inputs (avg. range: 9.8 – 690 ppt) (Laveuf and Cornu, 2009) and references therein. The total abundance of REEs in soils is less than 150 ppm, with no single REE having a concentration greater than 66 ppm (Hu *et al.*, 2006). In the United States, individual REE concentrations in the soil were found to be less than 26 ppm (Wutscher and Perkins, 1993; Zhang *et al.*, 2003; Kimoto *et al.*, 2006a). Given the ability to label soil with an REE on the order of 10,000 ppm, there is minimal concern of diluting the tracer, as long as the applied tracer is applied proportional to the enriched area (Spencer *et al.*, 2007; Polyakov *et al.*, 2009).

While REEs are not an "ideal tracer" in every aspect of the definition provided previously, they satisfy many of the criteria. Since REEs are strongly bound to the soil particles via inner sphere surface complexation (Aja, 1998) and the physiochemical properties of the soil particles and aggregates are not significantly changed when REEs bind to them (Zhang *et al.*, 2001), the labeled particles should behave identically to unlabeled soil particles. REEs can be used to label all particle size classes by mixing with the soil as a solution or powder, although some preferential adsorption to the silt and clay particles does occur (Kimoto *et al.*, 2006a; Michaelides *et al.*, 2010). The REE-labeled soil also persists in the environment for multiple years, providing a method to evaluate longer term erosion processes (Kimoto *et al.*, 2006b). Further, there are three forms of REEs that can be applied to the soil, depending on the application: REE oxides are used primarily in terrestrial soil erosion detection (Zhang *et al.*, 2003; Polyakov, 2004; Kimoto *et al.*, 2006b; Lei *et al.*, 2006; Stevens and Quinton, 2008; Polyakov *et al.*, 2009; Michaelides *et al.*, 2010), while the REE nitrate and REE chloride forms are most often used in studies where the soil remains inundated with water (Laufer *et al.*, 1984; Chegrouche *et al.*, 1997; Aja, 1998; Mahler *et al.*, 1998a; Spencer *et al.*, 2011b).

Most REE samples are analyzed with one of three methods: instrument neutron activation analysis (INAA) (Knaus and Van Gent, 1989; Abdel-Haleem *et al.*, 2001; Liang *et al.*, 2005), high-performance liquid chromatography (HPLC) (Mahler *et al.*, 1998a) or inductively coupled plasma mass spectrometry (ICP-MS) (Hu *et al.*, 1998; Matisoff *et al.*, 2001; Liang *et al.*, 2005; Leybourne and Johannesson, 2008; Collins *et al.*, 2010b) . The minimum detection limit for REEs can be as low as the parts per trillion level (ppt) for INAA (Loveland, 1989), less than 10 parts per billion for HPLC (Mahler *et al.*, 1998a) and less than 10 ppt in a liquid solution for an ICP-MS (Hu *et al.*, 1998; Coppin *et al.*, 2002; Leybourne and Johannesson, 2008). These low detection limits allow for the REE-labeled soil to be recovered even after the sample is highly diluted, although high background concentrations may obscure the results. Further, the ICP-MS provides a quick and easy means of analyzing a large quantity of samples (Jarvis, 1988).

An ideal tracer should not be toxic to the environment that it is used in, so REEs, with their generally low toxicity, fit this criterion (Haley, 1979). In fact, the Chinese often use a spray fertilizer containing REEs at a rate up to 0.23 kg of REE /ha on more than 15 million hectares, with concentrations in plant tissue found to be relatively low (Tyler, 2004). The few plants known to bio-accumulate REEs include two subspecies of ferns (*Dicranopteris dichotoma* and

Athyrium yokoscence - up to 313 ppm of total REEs for dried leaves) and pokeweed (*Phyrolacca americana* - up to 280 ppm of total REEs for dried leaves) (Ichihashi *et al.*, 1992), in addition to hickory trees (*Carya sp.* - up to 2,300 ppm of total REEs for dried leaves) (Robinson *et al.*, 1958). These plants reflect the REE concentrations of the soil they are growing in, showing no preferential uptake of light or heavy REEs (Robinson *et al.*, 1958; Ichihashi *et al.*, 1992).

The detection methods mentioned above can identify all of the REEs, such that a full spectrum of REEs can be analyzed with a single run of an INAA (Loveland, 1989), the ICP-MS (Jarvis, 1988) or HPLC (Mahler *et al.*, 1998a). This reduces the number of times a sample will have to be run, as well as the time required to process samples in the lab. Further, given the low cost of producing REE-labeled soil, REEs have potential as sediment tracers (Stevens and Quinton, 2008). Despite the possibility of marginally high background levels and some plant bioaccumulation, rare earth elements appear to meet most of the criteria for an ideal sediment tracer.

1.4.7 REE Adsorption to Soil

Prior to using any tracer in a field study, it is often evaluated in a lab, to ensure that the tracer is well incorporated into the soil and can be detected on the analytical instrument. In the case of REEs, many studies have examined the sorption of REEs to various soils under unique conditions, but the method is generally the same. A solution of one or more REEs is created in a pH-stabilized environment, to which the soil of interest is added. This mixture is then placed on a shaker and/or allowed to settle, until the chosen equilibration time period is reached. The soil is then recovered via centrifuging (Zhenghua *et al.*, 2001; Coppin *et al.*, 2002) and/or filtration ((Koeppenkastrop and De Carlo, 1992; Chegrouche *et al.*, 1997). Then a sample of the initial REE solution and the final REE solution are analyzed to determine the amount of REE adsorbed to the soil. If necessary, the REEs are stripped from the soil using an Aqua Regia digestion (Koeppenkastrop and De Carlo, 1992; Hu *et al.*, 1998; Stevens and Quinton, 2008). There are many variations of this method that can influence the results, some of which will be discussed in the following paragraphs.

Perhaps the most obvious influence on REE adsorption is the choice of soil. Many types of soil have been labeled, including silt loam, clay, gravelly sandy loam (Table 3), in addition to natural soil from the field site and pure minerals such as kaolinite, montmorillonite, smectite and (Mahler *et al.*, 1998a; Matisoff *et al.*, 2001; Coppin *et al.*, 2002). Given the natural variability of soil (pH, CEC, particle size distribution, mineralogy, clay content, and organic matter content), there is variability in the adsorption rate. The higher the CEC, the higher the REE adsorption,

Table 3. Summary of several laboratory and field trials using REEs to label soil. Adsorption indicates the adsorption of REEs onto the soil from the applied REEs, listed as REE ppm per mass of soil.

Soil Type	REE (s)	Adsorption (ppm)	Reference
Silt loam	Ce	612	(Michaelides *et al.*, 2010)
	Dy	775	
	Er	540	
	Gd	884	
	Ho	999	
	La	2162	
	Nd	2369	
	Pr	561	
	Sm	1204	
Silt loam	Ce	758	(Lei *et al.*, 2006)
	Dy	323	
	Eu	100	
	Ho	47	
	La	782	
	Nd	128	
	Sm	200	
	Tb	67	
	Tm	47	
	Yb	224	
Clay	Gd	~38	(Stevens and Quinton, 2008)
	Nd	~245	
	Pr	~60	
	Sm	~51	
Kaolinite	Nd	1.2	(Aja, 1998)
Kaolinite	Ce	11200	(Laufer *et al.*, 1984)
Gravelly sandy loam	Gd	61097	(Polyakov *et al.*, 2009)
	La	95670	
	Nd	106224	
	Pr	91386	
	Sm	72033	
Gravelly sandy loam	Gd	119; 880 on particles 0.02 - 0.04 mm	(Kimoto *et al.*, 2006a)
	La	204; 2231 on particles 0.01 - 0.02 mm	
	Nd	288; 1727 on particles 0.01 - 0.02 mm	
	Pr	62.7; 612 on particles 0.01 - 0.02 mm	
	Sm	55; 424 on particles 0.02 - 0.04 mm	
Goethite	La	2560	(Zhenghua *et al.*, 2001)
Kaolinite	La	2070	(Zhenghua *et al.*, 2001)

especially at low pH values, as the CEC masks the pH-dependent REE sorption (Coppin *et al.*, 2002; Spencer *et al.*, 2007) The CEC and REE adsorption have proven extremely well correlated (R^2>0.96) for both a deionized water and a saline background electrolyte (Spencer *et al.*, 2007). Generally, as the pH increases, the total adsorption increases as well (Wenming *et al.*, 2001; Zhenghua *et al.*, 2001; Hu *et al.*, 2006) and hence there is less desorption of the REEs (Wen *et al.*, 2002). For montmorillonite at lower pH values, the sorption is mostly to interlayer sites, but switches to primarily edge-binding in the upper pH range, increasing the adsorption capacity (Coppin *et al.*, 2002).

Smaller particle size classes (silt and clay) preferentially adsorb REEs, as compared to the sand and gravel fraction of a well-graded soil, potentially creating problems if the labeled soil is eroded unequally (Matisoff *et al.*, 2001; Kimoto *et al.*, 2006a; Michaelides *et al.*, 2010). The clay content and type of clay are known to strongly influence the REE adsorption, as they often dictate some of the other soil properties, as can be seen in Table 4 (Yong and Zheng, 1993; Wenming *et al.*, 2001; Michaelides *et al.*, 2010). Finally, if there is a significant amount of organic matter (OM) in the soil, the REE adsorption is generally higher than the same soil without organic matter (Beckwith and Butler, 1993; Wen *et al.*, 2002). In a review article on REE sorption, Hu *et al.* found that OM can contain between 0.1 and 35% of the total mass of REEs in a soil, with a mean of 15%, making it a major variable in REE sorption rates (2006).

A less-deterministic variable, even across soil types, is the individual REEs used to label the soil, as they are known to have similar adsorption properties (Beall *et al.*, 1979; Coppin *et al.*, 2002). However, the preferential adsorption of LREEs is found to occur in environments containing carbonate ions, as the HREEs complex more readily with these ions and precipitate out of the solution (Koeppenkastrop and De Carlo, 1992). The uniform adsorption of REEs occurs primarily at lower ionic strengths, while for high ionic strength background electrolytes, the heavy-REEs are preferentially adsorbed by up to a factor of ten (Coppin *et al.*, 2002). Due to the salt effect, the REE adsorption decreases with an increase in the ionic strength of the solution, most noticeably at pH values below 7 (Beall *et al.*, 1979; Coppin *et al.*, 2002).

Very few studies have examined the effect of temperature on REE adsorption. However, Chegrouche *et al.* (1997) found that for lanthanum concentrations below 100 ppm in the solution water, the temperature has a minimal effect on REE adsorption to bentonite. At temperatures above 40° C and REE solution concentrations greater than 100 ppm, the adsorption decreases due to the excess temperatures inhibiting further adsorption, while some of the previously adsorbed REEs desorb (Chegrouche *et al.*, 1997). Desorption is also an area of concern when

Table 4. Lanthanum retention on pure mineral and natural soils, showing the impact of CEC and washing with deionized water (FW) and saline water (SW) for an applied 10 mmol L^{-1} lanthanum solution concentration. DW indicates dry weight. This table is modified from Spencer *et al.* (2007).

	La mg $kgDW^{-1}$*	**La** mg $kgDW^{-1}$ (FW)	**La** mg $kgDW^{-1}$ (SW)	**CEC** meq $100g^{-1}$	**La** as % of total CEC (FW)	**La** as % of total CEC (SW)
Bentonite	57	43200	36000	121	75	64
Illite	49	NA	9600	30	NA	70
Kaolinite	7	1900	5100	22	19	51
Smectite	28	20600	16000	58	76	59
Phlogopite	4	8500	4300	27	68	34
Natural sediment 1 (low organic content)	36	16900	13200	44	77	60
Natural sediment 2 (low organic content)	39	19200	13600	65	64	46

* Natural La concentration in sediments. NA: data not available.

the REE-labeled soil is applied in the field, as the tracer is useless if it immediately desorbs under natural conditions.

Normally there is a minimal amount of desorption from the REE-labeled soil (Matisoff *et al.*, 2001; Kimoto *et al.*, 2006a; Michaelides *et al.*, 2010), although lower pH values (Hu *et al.*, 2006) and the presence of a saline wash (Table 4, Spencer *et al.*, 2007) can increase the desorption. Even after a year of saturation in stream water, a neodymium-labeled montmorillonite soil showed no signs of desorption, indicating that the REE is well-complexed with the soil (Mahler *et al.*, 1998a). In cases where the dry REE oxide was simply mixed into the soil, there was a pulse of REEs in the runoff water at the beginning of the first runoff event (indicating incomplete REE sorption by the soil), suggesting that a REE-solution is a better means of applying the REE to the soil (Polyakov, 2004). Zhang *et al.* (2001) found that a REE-labeled soil column, when leached with deionized water, yielded leachate with REE concentrations in the 0.20 ppt range; however, this is less than 0.001% of the REE applied to the soil.

Another consideration when applying the REEs to the soil is the equilibration time required for the REEs to bind to the soil from the REE-enriched solution. While time periods as short as 30 seconds (Li *et al.*, 2001) and 20 min (Bruque *et al.*, 1980; Aja, 1998) have been suggested as sufficient to reach near-maximum REE sorption to the soil in solution, most studies recommend 24 hours (Koeppenkastrop and De Carlo, 1992; Zhenghua *et al.*, 2001;

Coppin *et al.*, 2002; Spencer *et al.*, 2007) or more (Laufer *et al.*, 1984) to reach an equilibrium between the soil and solution. Equilibration times of more than two weeks have been evaluated; however, there was minimal REE adsorption after the initial REE adsorption uptake (Koeppenkastrop and De Carlo, 1992; Aja, 1998).

If the longer equilibration periods were used, there was concern regarding the sorption of the REE to the walls of the container used to store the solution. This proved to be unfounded for Teflon (Koeppenkastrop and De Carlo, 1992), LDPE bottles (Aja, 1998), polycarbonate containers (Coppin *et al.*, 2002) and polyethylene test tubes (Wenming *et al.*, 2001; Spencer *et al.*, 2011a). Other studies have used centrifuge tubes to carry out a batch equilibration experiments without reporting any complications due to REE sorption to the container (Zhenghua *et al.*, 2001).

Finally, attempts have been made to model the adsorption rate of REEs for several soils, including kaolinite, bentonite and an engineered soil. Both the Freundlich (Aja, 1998) and Langmuir (Zhenghua *et al.*, 2001; Yantasee *et al.*, 2009) adsorption isotherms provide R^2 values of 0.94 or better for kaolinite, an engineered silica-based soil and goethite. For temperatures above 30°C, Chegrouche *et al.* (1997) found that neither isotherm model accurately described the data due to a decrease in total REE adsorption. Yantasee *et al.* (2009) found that both H and L-type isotherms represented the data, but it is unclear if the variation was due to differences between individual REEs, the engineered soil or the background electrolyte concentration. The H-type isotherm is best represented by a Freundlich-type isotherm and the L-type isotherm is best represented by a Langmuir-type isotherm (Hinz, 2001).

1.4.8 Previous Work using REEs as an Applied Tracer

Although background REE concentrations and natural variability in sediments can be used to track sediment mobility and source (Collins *et al.*, 2010b; Devereux *et al.*, 2010), they can also serve as an applied tracer of soil mobilization in the laboratory and field. One of the first uses of REE-labeled soil was to monitor sediment deposition rates in a marsh. Dysprosium and samarium were sprayed on the surface water in the marsh, where they bound to sediment and provided a REE-enriched layer that was used to quantify accretion rates one year later, with good results (Knaus and Van Gent, 1989). A decade prior, chelated dysprosium was injected into a sewage outfall in order to track the fate of the treated sewage water as it moved downstream. Despite finding the tracer 3 miles downstream, this tracer did not actually track the sewage, but rather the water flowing with it (Loveland, 1978).

In studies using REE-labeled soil, there has been a mix of laboratory slope-erosion plots with rainfall simulators (Tian *et al.*, 1994; Zhang *et al.*, 2003; Liu *et al.*, 2004; Polyakov, 2004;

Michaelides *et al.*, 2010) and field-based erosion plots on agricultural watersheds (Matisoff *et al.*, 2001; Polyakov *et al.*, 2004; Kimoto *et al.*, 2006b), a semi-arid watershed (Polyakov *et al.*, 2009) and a farm roadway (Stevens and Quinton, 2008). The laboratory scale plots ranged in size from a 2.5 x 6 m (Tian *et al.*, 1994; Liu *et al.*, 2004; Michaelides *et al.*, 2010) to a 4 x 4 m plot (Zhang *et al.*, 2003; Polyakov, 2004) and used between five (Polyakov, 2004) and ten (Michaelides *et al.*, 2010) unique REEs to label the soil on the experimental plots. In the field studies, the REE-application area ranged from only 0.25m^2 and three REEs (Matisoff *et al.*, 2001) to over 0.30 hectares and six REEs (Liu *et al.*, 2004; Polyakov *et al.*, 2004; Kimoto *et al.*, 2006b; Polyakov *et al.*, 2009). These field studies ranged in duration from a few storm events (Matisoff *et al.*, 2001; Stevens and Quinton, 2008), to over three years of monitoring REE-labeled soil erosion (Liu *et al.*, 2004; Kimoto *et al.*, 2006b). All of the laboratory and field studies found that REEs were capable of estimating erosion rates and re-deposition rates, in addition to allowing the erosion to be traced back to a specific location on the plot.

Another application of REE-labeled sediment includes the use of REE-labeled sediment to monitor sediment reworking on the bed of Lake Superior, where only 1% of the applied samarium could be accounted for after 3 weeks of exposure to transport processes (Krezoski, 1989). Mahler *et al.* (1998a) used lanthanum, cerium, neodymium and two conservative solute tracers (NaCl and rhodamine) to understand the transport of montmorillonite through a small urban creek and a karst spring network in Texas. In the creek, 21% and 3% of the labeled soil was accounted for at the stations 15 and 65 m downstream, respectively, under normal flow (6.3 L s^{-1}). The high-flow (27 L s^{-1}) karst tracer test yielded only 0.93% and 2.5% recovery of the REE-tracer and rhodamine dye respectively, with no REE recovery at low flow (14 L s^{-1}) due to settling out of the labeled sediment.

Most recently, REEs have been used to track sediment deposition in urban storm water management systems (Spencer *et al.*, 2011b). Using a holmium-labeled montmorillonite, Spencer *et al*. examined the sediment deposition areas in a water detention pond under a simulated flood and compared their results to a sediment routing model with good results, indicating that REEs may provide a viable sediment tracer.

1.4.9 Conclusion

Sediment causes significant water quality impairments across the globe due to associated pollutants and the impact of sediment deposition. These impairments require large sums of money to address this problem, for which the processes at work are not yet well defined. There are many contributors to stream bank erosion, limiting our ability to predict these sediment contributions and create sediment budgets. Current attempts to predict stream bank contributions to the sediment load are complicated by vegetated banks, which prohibit the accurate representation of most natural systems. Further, the processes that are understood are based on lysimeter experiments and suffer from scaling issues when the same processes are modeled in the field.

Even the field based erosion monitoring approaches (erosion pins, cross-section profiles and photogrammetry) lack the spatial and temporal resolution necessary to improve our understanding of erosion processes. These methods begin to quantify stream bank retreat, but do not provide good indicators of the sediment delivery ratio. Ideal tracers are needed that can accurately track sediment transport distances, lag time, deposition and re-suspension, and REEs may have that potential. REEs sorb strongly to soils and have provided good results for terrestrial erosion studies and the few instances where they are used in a fluvial setting. If we are to address the problems with associated with sediment in the future, there will be a need to increase our understanding of erosion processes, sediment lag times and single-event transport distances, and tracers may help quantify those processes.

1.5 References

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2.0 Rare Earth Elements as Tracers of Fluvial Processes

Abstract

Sediment is a major pollutant of streams, rivers and lakes; however, the erosion, fate and transport of sediment in streams are poorly understood. This is due in part to the lack of a sediment tracer which has the same physical and chemical properties as the sediment of interest and yet remains detectable after significant dilution. Therefore, the purpose of this study is to create a viable sediment tracer using rare earth elements (REEs) to label a natural soil and examine its stability under field conditions. Two natural soils from a stream bank on Stroubles Creek in Virginia, USA were dried, sieved and then equilibrated with REE solutions of differing concentrations to create a series of adsorption isotherms to compare the adsorption of lanthanum (La) and ytterbium (Yb) onto both soils. A desorption isotherm was also created using stream water from Stroubles Creek to assess the degree to which REEs desorb under natural conditions.

Both REEs were found to have a similar maximum adsorption on each soil, while the two soils had different adsorption maxima, which can be attributed the different clay content of the two soils. A Freundlich isotherm best fit all four H-type isotherms, which were characterized by a complete adsorption of REEs at low initial solution concentrations, achieving adsorption maxima of 55 -72 μmol REE g^{-1} soil. The desorption isotherm showed retention of more than 99.97% and 99.71% of the initially adsorbed REEs after 5 washes with stream water for La and Yb, respectively. Given the similarities for La and Yb between the fitted Freundlich parameters, the adsorption maxima and the minimal desorption, it is suggested that any of the 14 REEs could be used interchangeably to label natural soils for use as a sediment tracer. Therefore, REEs hold great potential for use as a sediment tracer and further exploration of the link between soil erosion and downstream sediment fate and transport is encouraged.

Keywords: rare earth elements, sediment tracer, sediment transport, Freundlich adsorption isotherm

2.1 Introduction

Sediment is known to severely degrade surface water quality (USEPA, 2012), carrying along with it an excess of pesticides, phosphorus and heavy metals (Walling *et al.*, 2003). This sediment can be traced to erosion processes occurring across the landscape and within stream channels. Sediment from stream channel erosion can make up over 70% of the sediment load in a watershed (Kronvang *et al.*, 1997; Trimble, 1997; Wallbrink *et al.*, 1998; Ward and Trimble, 2004) and also carry other pollutants adsorbed to the sediment (Pitt and Amy, 1973). Further, fine sediment is more difficult to remove from the water column (Li *et al.*, 2007), as it tends to remain suspended and is often transported long distances in the stream network (Bonniwell *et al.*, 1999). Although sediment is currently recognized as a vital link to human health and global environmental change, transport distances for fine sediment and the associated pollutants remains poorly understood (Owens and Xu, 2011). Thus, by understanding the mobility of sediment in a fluvial system, we can also begin to understand the fate and transport of other pollutants as well.

With minimal success, numerous studies have attempted to track sediment transport through the use of fluorescent particles (Carey, 1989; Granger *et al.*, 2011), painted pebbles (Leopold *et al.*, 1966), baker's yeast (Wood and Ehrlich, 1978), lycopodium spores (Atkinson *et al.*, 1973) and DNA-labeled clay (Mahler *et al.*, 1998b). Each of these tracers has its faults, mostly related to an inability to physically represent the sediment of interest, although some recent studies have found that a new method using rare earth element (REE) labeled soil to be close to an ideal tracer in detecting sediment fate and transport (Mahler *et al.*, 1998a; Zhang *et al.*, 2001; Spencer *et al.*, 2011a).

REE-labeled soil has chemical and physical properties that are nearly identical to the sediment it is meant to trace and has experienced success in laboratory flume-scale studies (Polyakov, 2004; Lei *et al.*, 2006; Michaelides *et al.*, 2010), small watershed/plot-scale field studies (Matisoff *et al.*, 2001; Kimoto *et al.*, 2006b; Stevens and Quinton, 2008; Polyakov *et al.*, 2009) and sediment tracking in a storm water detention pond (Spencer *et al.*, 2011b). Most of this work on labeling soil with REEs has been done on pure minerals, including kaolinite (Laufer *et al.*, 1984; Aja, 1998), smectite (Coppin *et al.*, 2002), bentonite (Chegrouche *et al.*, 1997), montmorillonite (Beall *et al.*, 1979), goethite and other iron oxides (Koeppenkastrop and De Carlo, 1992). For these pure minerals, the effects of cation exchange capacity (CEC; (Spencer *et al.*, 2007), ionic strength (Coppin *et al.*, 2002), organic matter content (Wen *et al.*, 2002), pH (Hu *et al.*, 2006) and temperature (Chegrouche *et al.*, 1997) have been explored, leading to the creation of adsorption isotherms for each soil type. Yet, none mimic the heterogeneous, mixed mineralogy and chemistry of natural soils and sediment

Adsorption isotherms, often fit by a Langmuir (Zhenghua *et al.*, 2001; Yantasee *et al.*, 2009) or Freundlich equations (Chegrouche *et al.*, 1997; Aja, 1998), allow for estimates of sorption parameters, sorption capacity, or retardation coefficients for transport modeling. For reliability in tracing the labeled soil, it is important to ensure that the REEs are strongly adsorbed to the soil. Mahler *et al.* (1998a) found cerium (Ce) and neodymium (Nd) chlorides to be strongly bound to montmorillonite, such that neither seawater nor deionized water desorbed significant amounts of either REE. Other studies found minimal desorption of REE oxides and REE nitrates from a silty loam (Michaelides *et al.*, 2010), a gravelly sandy loam (Kimoto *et al.*, 2006a), natural prairie soil and an agricultural field soil (Matisoff *et al.*, 2001). The low desorption of REEs from these soils indicates that they can serve as an useful sediment tracer, especially in soils with a higher clay content (Stokes *et al.*, 1999).

Despite the success that REEs have achieved in tracing soil erosion on the landscape in previous studies, there is still great potential for exploring the maximum adsorption of REEs to natural soil and using these labeled soils in a fluvial setting. The ultimate goal of this REE adsorption study is to show the uniformity and stability among REE-labeled soils, such that approaches for *in-situ* REE labeling of stream bank and landscape soils can be developed to monitor sediment fate and transport during storm events.

This study examines the adsorption isotherms and effective maxima, under a minimally controlled environment, of two natural stream bank soils from Stroubles Creek in southwestern Virginia, USA. This research will increase our understanding of REE adsorption to natural soils, while also improving our ability to utilize REEs to track the fate and transport of fine grained sediments and their associated pollutants during storm events. Such an understanding can inform management practices and improve sediment transport modeling.

2.2 Materials and Methods

2.2.1 Soils

The soils used in this experiment were sourced from a stream bank along Stroubles Creek in southwestern Virginia, USA (37°12’36.38” N, 80°26’42.35” W). Soils adjacent to the stream are mapped as the McGary (Fine, mixed, active, mesic Aeric Epiaqualfs) and Purdy (Fine, mixed, active, mesic Typic Endoaquults) series and form in two distinct alluvial parent material deposits that rise approximately 1 m above base flow stage and limestone bedrock.

There is an abrupt and smooth transition between the two predominant parent materials at approximately 40 cm below the soil surface. Above the transition, the upper portion of the soil profile has a silt loam texture throughout with evidence of some gleying immediately above the transitional boundary. Below the transition, the lower portion of the soil profile is a finer textured silty clay with higher water holding capacity and evidence of gleization throughout. Despite the fact that a stream bank failure would likely result in the contribution of the entire profile to the stream, the two distinct parent materials were treated separately in this sorption study due to the likelihood of their different physicochemical characteristics. Thus, the soil above and below the transition will be referred to as Soil 1 and Soil 2, respectively.

Bulk soil samples from a 1.8 m x 1.5 m section of stream bank of both Soil 1 and 2 were air-dried for seven days at 60°C. Air-dried soil aggregates were broken up mechanically and with a ceramic mortar and pestle before sieving to 2 mm to remove coarse fragments. Less than 0.5% (by mass) of either soil was found to be larger than 2 mm. Using the pipet method (Gee and Bauder, 1986), the particle-size distribution was determined (Table 5). All analyses of soil and water REE concentrations were carried out via inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Varian 730-ES Axial ICP Spectrometer at the USDA-ARS Pasture Systems and Watershed Management Research Unit in University Park, PA. Samples of each soil were also analyzed for organic matter content, elemental composition and base saturation at the Virginia Tech Soil Testing Lab (Maguire and Heckendorn, 2010), with pertinent results presented in Table 5.

2.2.2 REE Sorption Isotherms

Lanthanum (La) and ytterbium (Yb) were chosen to represent all REEs, as they are at the extremes of the ionic radii and atomic weights for the lanthanide series. Therefore, if these two REEs behave similarly, it is expected that any of the other trivalent lanthanides could be used as a tracer without an extensive and independent investigation of the sorption and desorption capacities. Previous work by Coppin *et al.* (2002) supports this approach.

Both La chloride ($LaCl_3$ $7H_2O$) and Yb chloride ($YbCl_3$ $6H_2O$) solutions were independently prepared with deionized (DI) water to achieve initial REE concentrations of 20, 10, 5.0, 2.5 and 1.25 mmol L^{-1} by serial dilution. A 10% sediment suspension was then created by adding 5 g of soil and 50 mL of one of the REE solutions to a 100 mL polypropylene centrifuge tube for a batch-type equilibration. The adsorption was carried out with moderately high soil to solution ratios (Chegrouche *et al.*, 1997; Aja, 1998) in deionized water, without controlling the pH or temperature of the solution, and involved less shaking than previous studies, such that the method could be more applicable to future *in-situ* applications of the tracer. Each of the REE soil and solution mixtures, including blanks with only DI water, was prepared in triplicate for each soil. To ensure adequate time for equilibration, this suspension was swiftly vortexed for a few seconds before equilibrating for 48 h at 21° C ± 1°C. Samples were then placed on a reciprocal shaker (180 oscillations min^{-1}) for 30 min, prior to centrifuging for 30 min at 1,050 g. After centrifuging, the pH of the supernatant was recorded using an Orion 3-Star benchtop pH-meter prior to decanting the supernatant for analysis. A 2.7 µm glass fiber filter was used to filter the supernatant prior to analysis by ICP-OES. REE sorption on each sample was calculated from the loss of REE in the supernatant over the equilibration period, relative to the initial REE concentration. Among the triplicates for each soil and REE concentration, the coefficient of variation was less than 6 % and the minimum detection limit for the instrument was 10 ppb (3.6 nmol g^{-1} soil or 0.072 nmol g^{-1} solution).

The adsorption on each soil sample was calculated with the following expression (Sposito, 1989):

$$S = \frac{\Delta m_{REE} * M_{water}}{M_{soil}} \tag{1}$$

where S is the mass of REE adsorbed to the soil (mmol g^{-1} soil), Δm_{REE} is the change in the REE concentration in the solution (mmol g^{-1}), M_{Water} is the mass of water in each sample (g) and M_{soil} is the mass of soil in the sample (g). Three isotherms were fit to each soil and REE pair using the Non-linear Curve Fitting Tool with a Levenberg-Marquardt optimization in MATLAB (MathWorks; Natick, MA, USA.),. A relative weighting factor of 1/S was used, because variances are poorly estimated with only a triplicate sample (Bolster and Hornberger, 2007). These H1- and H2-type isotherms (Giles *et al.*, 1974) were fit with a Freundlich, general Freundlich and general Langmuir-Freundlich isotherm for each set of averaged points, as suggested by Hinz (2001).

2.2.3 REE Desorption

To examine the desorption of the REEs from the soil under simulated natural conditions, 50 mL of water from Stroubles Creek (collected from the same site as the stream bank soil, filtered to 0.45 µm, stored at room temperature) was added to 5 g of the REE-enriched soil (initial REE concentration of 20 mmol L^{-1}) in a 100 mL centrifuge tube. The stream water had a pH of 7.91 and background La and Yb concentrations of 110 ppb (0.79 nmol g^{-1}) and 30 ppb (0.17 nmol g^{-1}), respectively. After re-suspending the soil and then shaking for 30 sec, the samples were equilibrated for 24 h. The desorption samples were processed using the same method as the adsorption samples prior to analysis on the ICP-OES. Each REE-labeled soil was washed five times in total, using new stream water each time to simulate desorption that could occur if the soil was used as a sediment tracer in a fluvial system.

The total amount of each REE adsorbed to the soil was determined based on the loss of REE from solution during the equilibration period. A series of control samples showed no statistically significant loss of REEs to the polypropylene centrifuge tubes or to the glass fiber filter paper. Further, the filter did not contribute any REEs to a deionized water sample that was passed through it. As the polypropylene centrifuge tubes used in this study were not found to adsorb, or release, any REEs, any reduction in REEs in the solution can be attributed to soil adsorption.

2.3 Results

2.3.1 Adsorption

Both REEs had adsorbed similarly to the same soil (Figure 1). However, Soil 2 adsorbed over 30% more of either REE at the highest equilibrium concentration, as compared to Soil 1. Soil 1 had a maximum adsorption of 0.057 mmol g^{-1} soil and 0.056 mmol g^{-1} soil for La and Yb, respectively, which occurred at the 10 mmol L^{-1} initial REE solution concentration. Soil 2 also had the highest adsorption at the 10 mmol L^{-1} initial REE solution concentration, where the concentrations reached 0.074 mmol g^{-1} soil and 0.072 mmol g^{-1} soil for La and Yb, respectively.

The Freundlich isotherm best represented each soil and REE combination, as it had the best combination of a high R^2, the smallest 95% confidence limits on parameter estimates and parameters that were close to previously published values among all fitted isotherms. The fitted Freundlich isotherm was of the following form:

$$S = K_F * {C_e}^b \tag{2}$$

where K_F (mmol^{1-b} g^{-1} L^b)and b are fitted parameters, C_e is the equilibrium REE concentration in solution (mmol L^{-1}) and S is previously defined. All four H-type adsorption isotherms had a R^2 greater than 86%, indicating this model adequately represents the data. The general Freundlich-Langmuir isotherm (Equation 3) had larger 95% confidence limits and multiple parameter ranges that included zero and was of the form:

$$S = S_{max} * \frac{(k*C_e)^b}{1+(k*C_e)^b} \tag{3}$$

where S_{max} is the theoretical maximum adsorption and k is a fitted parameter representing the binding strength and all other parameters are previously defined.

The fitted isotherms (Table 6, Figure 1) indicate that there is a good agreement between either REE adsorbing to the same soil. All of the K_F and b parameters for the Freundlich isotherm of Soil 1 La and Soil 2 Yb are within the 95% confidence bounds of the other three isotherms, except for the K_F parameters of Soil 1 La and Soil 2 Yb, while for the general Langmuir-Freundlich isotherm, all of the k and b parameters include zero in the 95% confidence limit. It has been suggested that K_F correlates to the relative adsorption capacity of the soil (Van Bladel and Moreale, 1977; Chegrouche *et al.*, 1997), although K_F underestimates the adsorption capacity by 35% in this study. The 95% confidence ranges of both Freundlich fitted parameters are all positive, except in the case of the b parameter of Soil 1 Yb, which also had the poorest R^2 and RMSE.

As the purpose of this study was to examine the effective maximum adsorption, the efficient and total uptake of the tracer from solution is desirable. The effective maximum adsorption is defined as the initial REE solution concentration that provides sufficient labeling of the tracer without leaving excess REEs in solution. This occurs where S begins to plateau in the Freundlich isotherm, or when the general Langmuir-Freundlich isotherm approaches its S_{max} value, which is near the 10 mmol initial REE concentration for all isotherms, soils and REEs.

Since this study is intended to inform the field-based labeling of soils with REEs, the pH was not constrained during the equilibration period, which can make it difficult to understand the mechanics of the adsorption (Aja, 1998). As such, the equilibrium solution pH ranged from 5.3 to 7.0, with the lowest pHs occurring at lowest equilibrium REE concentrations.

2.3.2 Desorption

The goal of this work is to develop an ideal tracer for use in detecting sediment fate and transport in terrestrial and fluvial settings. Therefore, minimal desorption of the REEs under natural conditions (pH 7.7) is desirable. During a series of five batch equilibrium desorption washes with stream water (pH 7.9), less than 0.3% of the adsorbed REEs desorbed into the wash solution (Figure 2). The small amount of REEs that did desorb grouped by REE type, with the Yb-labeled soil releasing eight times as much of the initially adsorbed REE as the La-labeled soil, on average. Less than 0.015 $\mu mol\ g^{-1}$ of either REE desorbed from the unlabeled, natural soil in a deionized water wash, which was less than 0.03% of the amount adsorbed to the most enriched soil (10 $mmol\ L^{-1}$ initial REE solution concentration). Although the amount of La desorbed from the unlabeled soil is relatively small, it is enough to account for the slight desorption after each wash. The Yb desorption, on the other hand, appears to be entirely due to the release of the recently adsorbed Yb.

2.4 Discussion

Given that the uptake of REEs from solution is rapid and stable over several washes, REEs appear to be an ideal candidate for use as a tracer of sediment fate and transport during a storm event. The similarity between the fitted Freundlich parameters, as well as near identical maxima of adsorption, for La and Yb further suggests that any of the trivalent REEs may be used interchangeably to label soils and sediments.

All of the adsorptions fell into a H1 or H2 type isotherms (Giles *et al.*, 1974), for which Hinz (2001) suggested that the Freundlich, general Freundlich and the general Langmuir-Freundlich isotherms would give the best fit to the data. While the Langmuir isotherms have a defined maximum adsorption, which seemed like it would fit well for this data set, the Freundlich isotherm provided the best fit.

In each of the adsorptions, the highest equilibrium concentration (~15 mmol L^{-1}) had a lower mean adsorbed REE concentration, as compared to the next lowest equilibrium concentration (~4 mmol L^{-1}). This affect can been attributed to the "salt effect" (Beall *et al.*, 1979; Chegrouche *et al.*, 1997; Coppin *et al.*, 2002), where the higher concentration of the REE in solution inhibits further adsorption to the binding surface. Despite this effect, the results were still most accurately modeled by a Freundlich isotherm.

La and Yb adsorbed to both soils in a similar manner, with both the K_F (adsorption capacity) and b parameters of the fitted Freundlich isotherm falling well within the 95% confidence interval for both REEs. This supports our assumptions that all REEs will behave similarly in their adsorption to natural soils. Further, the K_F and b values found for La and Yb adsorption to these natural soils are of a similar magnitude as previous Freundlich isotherms for La adsorption to bentonite (Chegrouche *et al.*, 1997). These isotherms show that although the ionic potential varies for all REEs, they still adsorb in a similar manner. Therefore, we believe that any of the REEs can be used interchangeably in soil adsorption studies, with minimal differences in the adsorption properties. Previous research (Zhu and Xing, 1992; Matisoff *et al.*, 2001) has shown that the odd numbered REEs tend to have lower background concentrations; however, in this study no difference in the maximum adsorption was evident as a result of the background concentrations. Even with the soil variability and different REEs, the adsorption isotherms had very similar shapes, most notably the concentration at which they reached near-saturation of the soil with either REE.

Both soils reached their effective maximum adsorption at an initial REE solution concentration of 10 mmol L^{-1}, despite the differences in clay percentage, CEC and elemental concentrations (Table 5). Soil 2 had a slightly higher partitioning coefficient (mass of REE adsorbed per g of soil divided by the mass of REE per mL of solution: K_d) value for any given equilibrium concentration, as compared to Soil 1, as soils with higher clay contents are known to have a higher affinity for REEs (Matisoff *et al.*, 2001; Kimoto *et al.*, 2006a; Michaelides *et al.*, 2010) Therefore, an initial REE solution concentration of approximately 10 mmol REE L^{-1} is suggested for labeling these soils with any trivalent REE.

The range of partitioning coefficients for both soils and REEs spanned from 3.1 to 22,900, which is significantly less than Aja (1998) found for neodymium adsorption to pure kaolinite (3,980 to 1,585,000). This lower partitioning coefficient may be due to mixed mineralogy of the natural soils, despite the presence of organic matter (OM) in Soil 1 and 2, as OM is known to strongly adsorb REEs in both terrestrial soils and aquatic sediments (Horowitz, 1985; Leybourne and Johannesson, 2008). Organic matter can influence the adsorption capacity of both an applied tracer and pollutants in a natural soil (Reuter and Perdue, 1977; Weng *et al.*, 2002); therefore consideration of this soil component is recommended in any soil adsorption used to create a sediment tracer.

If REEs are to be used as an ideal tracer, there must be minimal desorption of the tracer from the labeled soil. Soil 2 had less desorption of La or Yb than Soil 1. We suggest that this may be attributed to the higher clay content and CEC in Soil 2 that held the REE more tightly. In the case of La, all desorption from the labeled soil (0.008% of initially adsorbed La per wash) could be accounted for by the small amount of La that desorbs from unlabeled soil. However, for the Yb-enriched soils, the desorption was greater than the amount that desorbed from the unlabeled soil. The Yb desorption after 120 hours of washing and five changes of water was less than 0.27% of the initially adsorbed REE. Koeppenkastrop and De Carlo (1992) found that the lower atomic number REEs were preferentially adsorbed to soils with Ca^{2+} in the soil matrix, due to the similarity in atomic radii. Given the large Ca concentrations in these natural soils, this would account for the greater retention of La. This desorption study shows that either REE, and hence all REEs, should be stable in the stream environment as a sediment tracer, as the retention rate is greater than 99.7% for both REEs.

2.5 Conclusion

In this study, REEs strongly adsorbed to two natural soils under simulated natural conditions and have potential for use as an ideal tracer in sediment fate and transport studies. There was no difference in the adsorption of either La or Yb in the two soils, suggesting that any of the 14 lanthanides can be used interchangeably in tracer studies. The maximum adsorption of La and Yb was 0.074 mmol g^{-1} soil and 0.072 mmol g^{-1} soil, respectively (315 and 6,990 times the background concentrations, respectively). Therefore, REEs can provide a detectable tracer, even after a dilution of several orders of magnitude (e.g. once added to a stream during a storm event), especially if the background REE concentration of the natural soils is low.

The two soils had unique adsorption maxima that can be attributed to the different percentages of clay in the soil, which also influences the CEC. A Freundlich isotherm provided the best fit for each soil and REE pair, with all four isotherms returning parameters in agreement with previous studies and having correlations better than 86%. From these isotherms, it was determined that an equilibrium REE concentration of 7.5 mmol L^{-1} was sufficient to maximize the adsorption onto the soil, while minimizing the wasting of REEs remaining in solution. Desorption experiments carried out with stream water showed that even after five washes, the cumulative desorption was less than 0.27%.

Given the strong adsorption of these REEs to both natural soils and the tracer stability under simulated field conditions, REE-labeled soil has the potential to become an ideal tracer. This tracer is relatively simple to produce, should behave like natural sediment in the stream system and yet remain detectable after significant dilution and exposure time, making it perhaps the closest approximation of an ideal tracer of sediment fate and transport currently available.

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Table 5. Soil properties for both soils from the stream bank along Stroubles Creek in southwest Virginia, USA. Soil 1 is from the upper layer of alluvial floodplain sediment, while Soil 2 is from the lower layer and is visually differentiable. The relative standard deviation (RSD) is based on at least 3 samples

		Soil 1		**Soil 2**		**Stream Water**
		Mean	**RSD**	**Mean**	**RSD**	**Mean**
Sand	(%)	26.5		18.6		
Silt	(%)	54.3		53.7		
Clay	(%)	19.2		27.7		
OM	(%)	3.4	4.8%	2.9	3.3%	
CEC	(meq 100 g^{-1})	15.7	8.2%	17.3	8.6%	
pH		7.6	2.2%	7.63	0.5%	7.91
La	(μmol g^{-1})	0.146	2.4%	0.235	3.2%	<0.001
Yb	(μmol g^{-1})	0.006	2.4%	0.010	3.0%	<0.001
P	(mg kg^{-1})	9.0	15.7%	3.0	23.1%	
Ca	(mg kg^{-1})	2,528	8.5%	2,714	9.4%	
Zn	(mg kg^{-1})	3.2	15.7%	0.7	26.6%	
Mn	(mg kg^{-1})	26.4	4.1%	11.4	7.6%	
Fe	(mg kg^{-1})	6.5	24.4%	1.0	44.6%	
Base saturation	(%)	100	0.0%	100	0.0%	
Ca saturation	(%)	80.2	0.5%	78.4	0.8%	
Mg saturation	(%)	19.3	2.0%	21	2.8%	
K saturation	(%)	0.6	10.5%	0.5	9.5%	

Table 6. The fitted parameters for the Freundlich and general Freundlich-Langmuir models applied to each REE and soil combination. The Soil 1 Yb general Freundlich-Langmuir model failed to converge. The ± range indicates the 95% confidence limits about the fitted parameter. Each average of three samples was weighted by 1/S, where S is the final REE concentration adsorbed on the soil.

Soil	REE	Model	S_{max}		K_F		k		b		R^2	RMSE
1	La	Freundlich			0.0393	± 0.009			0.124	± 0.071	0.93	0.031
1	La	Langmuir-Freundlich	0.0539	± 0.042			0.260	± 3.124	0.149	± 0.204	0.95	0.032
1	Yb	Freundlich			0.0430	± 0.018			0.135	± 0.200	0.86	0.054
2	La	Freundlich			0.0513	± 0.014			0.160	± 0.084	0.94	0.040
2	La	Langmuir-Freundlich	0.0751	± 0.048			0.382	± 2.895	0.203	± 0.213	0.97	0.034
2	Yb	Freundlich			0.0528	± 0.015			0.148	± 0.085	0.93	0.043
2	Yb	Langmuir-Freundlich	0.0763	± 0.073			0.274	± 3.174	0.177	± 0.236	0.95	0.045

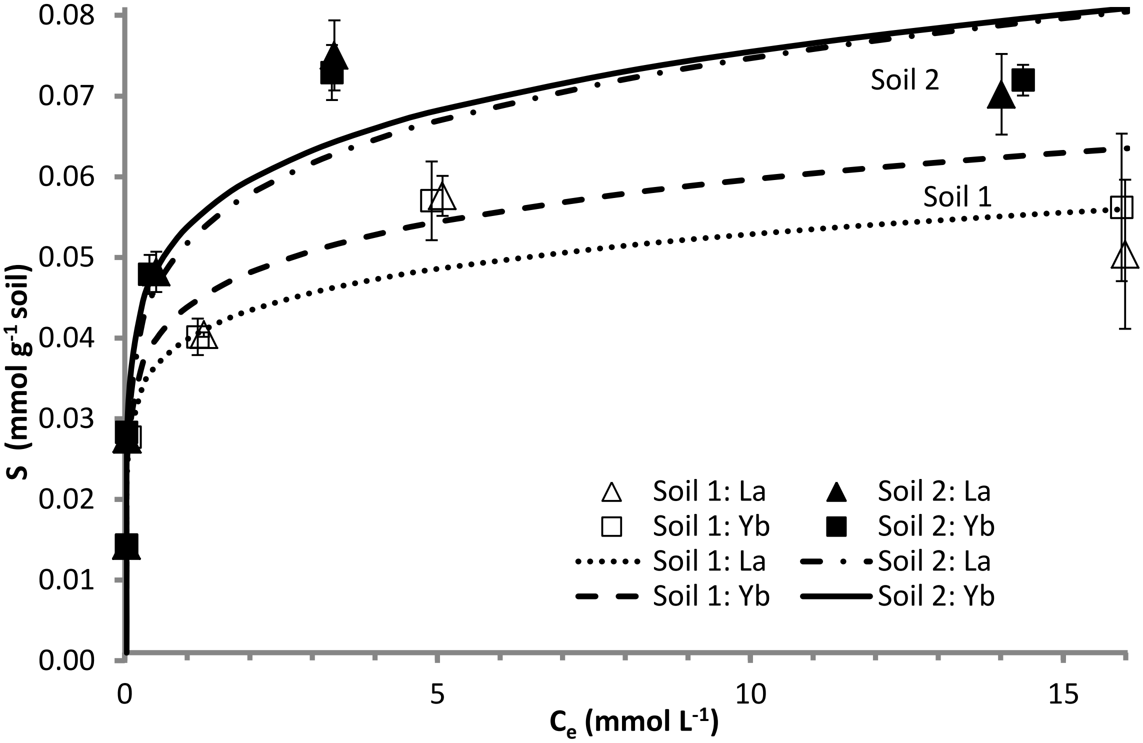

Figure 1. The total amount of La and Yb adsorbed (S) onto each soil plotted as a function of the equilibrium REE concentration in solution (C_e), with the linear plot representing the fitted Freundlich isotherm. The error bars show three standard deviations on either side of the mean of each experiment conducted in triplicate. Some error bars are contained within the symbol.

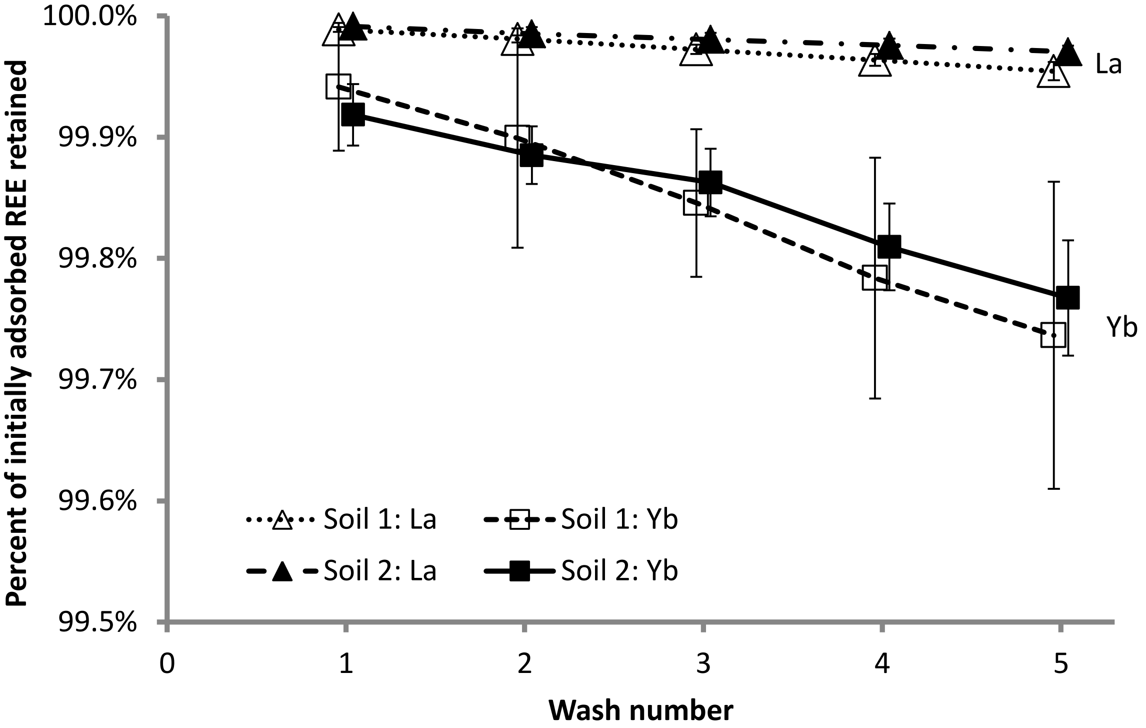

Figure 2. The percent of initially adsorbed REEs that are retained as a function of each wash with Stroubles Creek water. The error bars are for three standard deviations from the mean, based on a triplicate sample, and some of the La error bars are within the symbol

2.7 References

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3.0 Rare Earth Elements as a Tracer to Understand Sediment Fate and Transport in Small Streams

Abstract

Sediment is a major water quality pollutant; however, its fate and transport are poorly understood. This research is believed to be the first to establish rare earth element (REE)-labeled sediment as a viable tracer of sediment fate and transport processes at the reach-scale within a second-order stream. Stream bank soil was labeled with a unique REE for injection during two storm events. Suspended and bed sediment sampling occurred during and after each storm event at intervals along the 875 m reach.

Over 38% of the injected REE was accounted for in the suspended sediment after 250 m. The tracer was also detected in the suspended and bed sediment samples at the maximum sampling distance of 875 m. The injection during the larger discharge event was more quickly diluted and showed less deposition in the bed sediment. Sampling during subsequent storm events showed no resuspension of the previously injected tracers, indicating that the tracer either remained suspended during the first storm or is permanently deposited in the reach. Up to 40% of the tracer was accounted for in the bed sediment, using a simplified approximation.

This tracer could be used to evaluate best management practices on construction sites, agriculture fields and forestry harvest sites where the link between terrestrial erosion and fluvial transport of sediments is poorly understood. REE-labeled sediment exhibits many of the qualities of an ideal tracer and holds great potential for future use in linking soil erosion and sediment fate and transport in both terrestrial and fluvial settings.

Keywords: rare earth elements, suspended sediment transport, tracers, bed sediment deposition

3.1 Introduction

Considerable amounts of sediment are eroded from the landscape and stream channels each year, and re-deposited in downstream systems such as lakes, reservoirs and estuaries. Not only is this a loss of vital soil from arable land, forest land and construction sites (Milliman and Syvitski, 1992), there can be significant nutrient and pollutant loads associated with stream sediments, especially fine sediments. Stream sediment can be a significant source of phosphorus in the water column (Carpenter *et al.*, 1998), and in some cases the phosphorus, pesticide and metal concentrations in sediment can be high enough to degrade the stream habitat (Walling *et al.*, 2003). Unfortunately, these contaminated sediments may take decades to flush from the river system (Hamilton, 2011), for which the sediment-water interactions (Owens and Xu, 2011) and sediment fate and transport are poorly understood (Meals *et al.*, 2010).

Previous studies attempting to track sediment mobility have used applied tracers, including: painted pebbles (Leopold *et al.*, 1966), fluorescent particles (Kennedy and Kouba, 1970; Carey, 1989), glass beads (Wheatcroft, 1992), lycopodium spores (Atkinson *et al.*, 1973), and clay labeled with radioactive isotopes such as: ^{137}Cs (Ritchie and McHenry, 1990; Zhang *et al.*, 1998), ^{210}Pb (Wallbrink and Murray, 1993) and ^{7}Be (Matisoff *et al.*, 2002). In addition to applied tracers, naturally occurring variations in the elemental concentrations of sediments have been used to determine sediment sources on a watershed scale (Papanicolaou *et al.*, 2003; Zhang *et al.*, 2012), although the inability to differentiate sediment sources has proven problematic (Walling, 2005; Devereux *et al.*, 2010). Both the applied and naturally occurring tracers inadequately represent the sediment in the stream with regard to the sediment density, particle size distribution, source area or source soil type. There is still a need for an ideal tracer that adequately represents the physical and chemical properties of natural sediment, while also remaining easy to create, simple to recover, cheap to analyze and have multiple unique labels with very low detection limits (Mahler *et al.*, 1998b; Zhang *et al.*, 2001). In addition, a tracer that can be used to replicate natural erosional processes, such as stream bank failure, would be ideal, given that over $1 billion is spent annually in the United States on stream restoration, which often has a goal of reducing erosion (Bernhardt *et al.*, 2005).

Prior studies of terrestrial soil erosion have indicated that rare earth element (REE)-labeled soil can function as a near-ideal tracer of erosion processes, especially for the silt and clay fraction of soil (Polyakov *et al.*, 2009; Michaelides *et al.*, 2010). REE-labeled soils have been used in laboratory slope erosion plots (Zhang *et al.*, 2003; Liu *et al.*, 2004; Polyakov, 2004), agricultural field erosion plots (Matisoff *et al.*, 2001; Kimoto *et al.*, 2006a) and in a semiarid watershed (Polyakov *et al.*, 2009) with good success in tracking sediment mobility on the landscape. These studies have used up to ten individual REEs on the same site (Michaelides *et al.*, 2010) and been monitored for up to three years after the initial application (Kimoto *et al.*, 2006b). Despite their success in monitoring terrestrial soil erosion, very few studies have used REE-labeled sediment to understand the fate and transport of fine sediments in streams. Spencer *et al.* (*2011*) introduced holmium-labeled montmorillonite into storm water detention ponds to evaluate a sediment transport model. Earlier work by Mahler *et al.* (1998a) used REE-labeled montmorillonite to understand sediment transport rates under multiple flow conditions in a karst spring and a very short (<65 m) reach of a small urban stream with limited success.

Despite decades of research on erosion and sediment processes, there are still significant gaps in our knowledge of the fate and transport of fine sediments in fluvial systems. This is unfortunate, because by understanding sediment mobility, sediment transport models and travel time estimates could be improved, recovery rates for polluted streams could be better estimated and sediment erosion could be assessed on a much more local scale than is currently possible. If a stream restoration site or construction site were to be labeled with REE-enriched soil, a sampling regime downstream could detect if and when soil is eroded and the delivery ratios, which can then be used to evaluate the efficiency of best management practices. Sediment tracers could be used to understand changes in sediment erosion and transport due to disturbance, specifically with regard to global environmental change, which is an area of research that needs more exploration (Owens and Xu, 2011).

Therefore, given the need for increased research on sediment fate and transport in dynamic fluvial systems and the difficulty in assessing best management practices (BMP) effectiveness, our objectives for this study were to:

- Evaluate REE-labeled sediment as a tracer of sediment fate and transport in a second-order urban and agricultural stream reach during a series of storm events,
- Assess the ability of time-integrated suspended sediment samplers and bed sediment sampling to detect an injected REE tracer, and
- Examine the remobilization of any deposited REE-labeled sediment in subsequent storm events.

This research is intended to establish an approach to using REE-labeled sediment as a viable sediment tracer in small streams, while also highlighting some of the issues associated with fine sediment recovery.

3.2 Methods and Materials

We evaluated the use of REE-labeled sediment as a tracer of natural sediment during storm events on Stroubles Creek at the Stream Research, Education And Management (StREAM) Lab in southwestern Virginia. A unique REE was used to evaluate the fate and transport of sediment during each of three storm events in the fall of 2011. The REE sediment transport and deposition was monitored along an 875 m reach of Stroubles Creek to evaluate the recovery of the introduced tracer. During the storm event when the injection occurred and during each of the next two storms, sediment samples were obtained to examine sediment re-suspension during subsequent events.

Stroubles Creek is a second order, pool and riffle stream within the sample reach and drains 1460 hectares at the tracer injection point, including the Virginia Tech campus and most of the town of Blacksburg, VA, which are located in its headwaters. The lower third of the watershed is primarily pasture and agricultural fields under annual row crops. Base flow between storm events fluctuated between 0.037 and 0.107 $m^3 s^{-1}$ and turbidity was also generally low during these times (2-6 NTU). The stream had a mean pH of 7.7 and a bank full discharge of 5.5 $m^3 s^{-1}$. A set of three permanently deployed multi-parameter sondes with optical turbidity sensors were used to help indicate the sediment flux during the storm events. In this study, turbidity is used as a surrogate for total suspended solids, as turbidity and total suspended solids are found to be well-correlated in other mixed-use watersheds (Coulter *et al.*, 2004; Jastram *et al.*, 2010). A Campbell Scientific CS450-L water level logger, located at the injection site, provided stage data throughout the sampling period, from which discharge was calculated from a site-specific stage-discharge curve. The stream bank soils are silt loams and silty clays, composed primarily of well-sorted legacy sediments of differing parent material.

Soil from a stream bank along Stroubles Creek was used as the label matrix with two unique REE chlorides. After obtaining bulk soil samples (30 L) from the full vertical profile of a stream bank, the soil was dried at 60° C for seven days before deaggregating the soil and sieving it to 2 mm. A particle size analysis showed that the soil consisted of 23% sand, 54% silt and 23% clay. As the goal was to simulate a natural soil as closely as possible, neither the pH (7.6) nor the organic matter (3.4% by weight) was adjusted from the in-the-field conditions. To create the REE-labeled sediment, 4.8 kg of soil was mixed with a 10 mmol solution with either lanthanum chloride ($LaCl_3$-$7H_2O$) or ytterbium ($YbCl_3$-$6H_2O$; GFC Chemical, 99.99% purity) at a 1:10 soil to solution ratio. This concentration has previously been shown to provide the maximum adsorption of REE on this soil with minimal excess REE in solution (Kreider *et al.*, in review). The same study found adsorption rates of up to 12,400 ppm for lanthanum (La) and ytterbium (Yb) on this soil and showed minimal (<0.3%) desorption after multiple washes with Stroubles Creek water. La and Yb, elements from the extremes of the REE series, were found to adsorb similarly to this soil. Therefore, we assumed that any REE can be used to label the soil, with no difference in adsorption properties (Kreider *et al.*, in review).

After the initial mixing of the soil and solution, the mixture was agitated three times over a five day period with a stirrer, such that all soil particles were in suspension. The sample was then allowed to settle for at least eight days, upon which all particles had settled out of suspension. Prior to each storm event where sediment was to be injected, the supernatant was siphoned off and a triplicate sample of the REE-labeled sediment was obtained to determine the REE concentration of the injected sediment. The remaining REE-labeled sediment was mixed with stream water 15 min before injection and agitated such that all sediment particles were re-suspended. This slurry was agitated a second time just prior to injection, which occurred by dumping the slurry into a turbulent section of Stroubles Creek.

At a bridge 250 m downstream of the injection site, bulk grab samples (17.5 L) were taken prior to, during and after the injection, in order to detect the REE-sediment slug as it moved down the channel. A small gas-powered pump was used to obtain the bulk samples in less than 30 s at the mean depth of the channel thalwag. Sampling occurred at approximately 2 min intervals when the REE slug was expected to pass by, with the time steps increasing once the plume had moved downstream of the sampling location. If the suspended sediment concentrations were suspected to be low (e.g. Storm 1) duplicate samples were taken at each time step so that enough sediment was obtained for the necessary analyses.

Time-integrated, flow-through suspended sediment samplers (SSS) (Phillips *et al.*, 2000; Russell *et al.*, 2000) were deployed during each storm event to detect the distance that the REE-labeled sediment traveled downstream (Figure 3). These SSS were installed as lateral pairs in riffle sections of the channel, with one pair located 45 m upstream of the injection site, and the remaining pairs located 15, 110, 545 and 875 m downstream of the injection site (Figure 4). Each SSS collected suspended sediment as long as the stage was more than 5 cm above base flow, which provided sampling periods ranging from 8 – 44 h for the seven storm events in this study. These samplers were emptied, thoroughly scrubbed and rinsed with stream water after every storm event.

Within six days of each storm event, bed sediment samples were collected at one site upstream and 12 sites downstream of the injection site, spanning 875 m in length. These samples were obtained by gently scraping the stream bed to collect the layer of unconsolidated sediment that was deposited during the most recent storm event, with samples aggregated over the same 0.16 m^2 area after each storm. Each sample was collected from a slackwater area that remained underwater at base flow.

All sediment samples (bulk, time-integrated and bed sediment samples) were returned to the lab where the sediment was allowed to settle for a minimum of three days prior to decanting the clarified stream water and placing the sediment in a 60° C drying room. The sediment was then de-aggregated and sieved to remove any particles larger than 2 mm. After an aqua-regia digestion following EPA Method 3050b (Kimbrough and Wakakuwa, 1989), each sample was run on a Varian 730-ES Axial ICP Spectrometer at the USDA-ARS Lab in University Park, PA, which had detection limits as low as 0.01 ppm. A minimum of 0.5 g of sediment was needed for analysis on the ICP. Therefore, samples were aggregated until this volume was achieved, which reduced the temporal resolution of the bulk samples in Storm 1.

3.3 Results

The suspended sediment samples collected in the SSS during the four storms prior to any REE tracer injections were used to provide background REE concentrations for the bulk, time-integrated and bed sediment samples. The 95% confidence interval for the background levels of La and Yb was 7.7-20.9 ppm and 1.5-2.5 ppm, respectively. Over the monitoring period, seven storms generated enough flow to mobilize sediment. During storms 1 and 3, a single unique REE-labeled sediment (La for storm 1, Yb for storm 3) was injected at the same location in the stream (Table 7, Figure 4). It was only during these storms that the bulk sampling was performed. Initial results indicated that no excess REEs were detected in the bed sediment samples in subsequent storms after the storm where the REE was injected, so bed sediment samples were not collected for storms 4, 6 and 7. However, bed sediment samples were collected for storm 5, as it was the largest during the monitoring period.

The La and Yb tracers were labeled as expected, with concentrations greater than 13,300 $\mu g\ g^{-1}$ sediment (Table 8). The adsorbed REE concentrations were 500 and 13,800 times the background REE concentration in the soil used as a tracer for La and Yb, respectively. The La and Yb tracers behaved as expected, with adsorption maxima above the 12,400 ppm found by Kreider *et al.* (in review) The distribution coefficient (K_d) is the mass of REE adsorbed onto the sediment divided by the mass of REE in the equilibrium solution, and it was of the same order of magnitude for both tracers. The stream water contained less than 0.1 $\mu g\ (mL)^{-1}$ of each of the REEs used as tracers, limiting any potential for background interference.

The stream discharge varied from 0.20 $m^3 s^{-1}$ (Storm 1) to 1.53 $m^3 s^{-1}$ (Storm 3) at the time of the REE injections, while the turbidity ranged from 14.8 NTU (Storm 1) to 70.1 NTU (Storm 3). The La tracer was injected seven hours after the hydrograph peak, while the Yb tracer was injected 30 min before the hydrograph peak.

Despite different discharges and times of injection during the hydrograph, the breakthrough curve of the Yb tracer for the sampling site 250 m downstream of the injection show that the peak concentration occurred 7 min after the injection. Due to a low discharge and sediment load during the La injection, samples had to be aggregated across 25 min time intervals. Therefore, it is likely that the first bulk sample of La at 10 min after the injection (Figure 5) contained an excess of unlabeled background sediment in addition to the labeled sediment, effectively damping the peak La concentration. Despite this damping, the bulk sampling indicates that the REE concentration in the suspended sediment remained well above background levels for over an hour. During the Yb injection, this REE concentration remained above background concentrations for more than 6 hours after the injection.

Based on the REE breakthrough curves for suspended sediment, 38% and 85% of the La and Yb, respectively, was accounted for at the sampling site 250 m downstream. These percentages are not corrected for particle size, and therefore may be erroneously high due to higher REE concentrations on finer soil particles (Kimoto *et al.*, 2006a), which are more likely to remain in suspension. After 250 m of transport in Stroubles Creek, the REE-labeled tracer was diluted by a factor of 5 and 95 for La and Yb, respectively. This is equivalent to an REE concentration of 102 and 196 times the background La and Yb concentration, respectively, for the suspended sediment samples from the four background storms

The SSS placed upstream of the injection point had REE levels within the 95% confidence interval (CI) for the background REE levels during the Yb injection, while this background CI was exceeded during the La injection (28.4 ppm). The time-integrated SSSs showed elevated concentrations of both the La (36.7 ppm) and Yb (5.1 ppm) tracer at distances of up to 875 m downstream of the injection (Figure 6). The highest REE concentrations occurred within 110 m of the injection site for each injection. During the La injection, the SSS 15 m downstream of the injection was clogged for approximately 10 min, during which the main pulse of the tracer passed by. This may explain why the SSS at 110 m had a higher La concentration than the sampler located 15 m downstream of the injection.

In each of the injections, the tracer concentration increased within the first 110 m, then declined downstream. After 875 m, both the La and Yb concentrations had declined to less than 2.6 times the background concentration. The decrease in REE concentration with distance downstream could indicate either deposition of the tracer within the reach or an increase in the sediment load with distance downstream.

The bed sediment REE concentrations after each tracer injection were very similar to the suspended sediment results, with La and Yb tracer injections having higher concentrations than the background samples (Figure 7). Overall, there is more variability in the bed sediment samples, as compared to the suspended sediment samples, specifically in the Yb samples. The Yb bed sediment samples decrease after initially peaking 5 m downstream of the injection site. By 425 m downstream, the concentrations are no longer distinguishable from the background samples. The La bed sediment samples initially peak 50 m downstream of the injection site. The La sample at 345 m from the injection site barely fell within the 95% CI of the background samples, although all samples further downstream are outside of this range.

3.4 Discussion

The bank soil used in this study adsorbed REEs well above the 12,400 ppm suggested as a maximum adsorption rate by Kreider *et al.* (in review). The La and Yb tracers exceeded this adsorbed concentration by 7.7% and 56.8%, respectively, meeting the goal of creating a highly-enriched tracer. This higher adsorption is attributed the long equilibration time (2-6 weeks) and more frequent mixing than the previous study by Kreider *et al.* (in review).

3.4.1 Suspended Sediment Bulk Samples

At the sampling site 250 m downstream of the injection site, both tracers were detected, regardless of different discharges and sediment concentrations. Due to extremely low suspended sediment concentrations at the time of the La injection, these bulk samples had to be aggregated, which significantly reduced the temporal resolution of this tracer. Despite needing to be aggregated, the La tracer still had the highest REE concentration at the sampling point by an order of magnitude, which can be attributed to the extremely low discharge and lack of sediment in the water column to dilute the tracer. The Yb tracer peaked 7 min after the injection, which was 13 min before the La tracer, which was injected during a much smaller storm event and may be due in part to the aggregation of the bulk samples.

The Yb tracer returned to background levels in about 50 min, while the La tracer was still elevated above background levels after 70 min. Again, this is likely caused by the greater discharge and sediment load during the Yb tracer injection. This suggests that REE tracer mobility is dependent on the discharge, as would be expected for a normal sediment load in a stream, and that this tracer can be used to approximate sediment travel time.

The recovery rates of each tracer (38% and 85% of the La and Yb, respectively) are much greater than previous work by Mahler *et al.* (1998a) on a much shorter reach. They recovered 21% of their Nd-labeled montmorillonite tracer at 15 m and 3% of the tracer at 65 m, whereas we recovered over 38% of each tracer 250 m downstream of the injection site, although our data were not corrected for changes in particle size. For the fine sediments, it has been shown that the enrichment of the fine particles is 2-5.2-fold greater than the coarser particles (Matisoff *et al.*, 2001; Michaelides *et al.*, 2010). If only the clay particles were assumed to be recovered in our study reach, we estimate a minimum recovery of 6.4% 250 m downstream of the injection, although a particle size analysis of the recovered suspended sediment would improve the accuracy of this estimate.

The Yb breakthrough curve had a sharper rising and falling limb than the 65 m experiment by Mahler *et al.* (2010), indicating less mixing within this reach of Stroubles Creek. Unlike Mahler *et al*. (1998a), we did not inject a conservative tracer at the same time as the REE tracer, which proved to be very beneficial for comparison purposes in their short reach. Future REE tracer injections could benefit from the simultaneous injection of a conservative water tracer as a comparative measure regarding tracer dilution and any shifts in the arrival of the tracer.

3.4.2 Time-Integrated Suspended Sediment Samplers

A challenge with using a natural stream and storm events is that the discharge and sediment load varies between injections. Over the course of this study, the seven storm events had discharges ranging from 0.4 to 6.6 $m^3\ s^{-1}$, which resulted in the SSS capturing more sediment during the higher flows, and less for the smaller flows. During the storm events, each SSS collected 0.66-6.67 g of suspended sediment, for which the larger sediment samples can dilute the applied REE tracer. Based on the ability to collect a sample of adequate sample size during large storm events, we recommend installing a plug in the SSS during the larger events to prevent sample collection, until the injection occurs, so that the tracer does not get diluted by a large unlabeled sediment sample. This would also allow for these SSS to be used to examine some of the temporal resolution if multiple samplers were placed at each location and opened/closed at different points during the storm event.

The differences in discharge across each storm event and the varying levels of enrichment above the background REE concentration provide insight to the necessary level of enrichment to achieve a reasonable recovery of the tracers. Considering the REE enrichment ratio on the injected tracer and the sediment load in the stream at the time of injection, the suspended sediment in the stream was labeled at 102 and 196 times the background REE concentration for La and Yb, respectively, at the sampling site 250 m downstream of the injection. The La and Yb tracers, which had in-stream REE concentrations greater than 100 times the background level, provided sufficient labeling to detect the tracer at distances up to 875 m downstream, perhaps suggesting a target tracer concentration of at least 100 times the background REE concentration. Although only based on two injections, we suggest that any REE tracer applied to a stream have an in-stream concentration of at least 100 times the background REE concentration on the suspended sediment, after considering the background REE concentration, the in-stream sediment load, the enrichment ratio on the tracer and the amount of tracer injected.

A satisfactory labeling and recovery of the tracer can be accomplished by selecting REEs that have very low natural background concentrations, such as Yb (1.4 ppm) in our case. Those REEs with higher background concentrations, such as La (26.4 ppm) in our soil, are difficult to label at extremely high enrichment rates due to the maximum adsorption capacity of the soil. This can reduce the amount of labeled sediment or allow for injection during larger storm events without excessive dilution. The challenge remains in estimating the discharge and sediment load before the injection. The suspended sediment concentration (SSC) is much more difficult to quickly determine, as there is not a direct relationship between stage and SSC, so a turbidity-SSC relationship must be established before the tracer injection (Jastram *et al.*, 2010).

Background suspended sediment sampling for almost a year prior to conducting our tracer tests informed us as to what stage was necessary in order to obtain the 0.5 g of sediment required for analysis. However, there were times when the SSS inlets were obstructed by in-stream debris. This was especially problematic after leaf fall, where hourly cleaning of the inlet was required to ensure continued functioning. Stroubles Creek is an urban watershed with a large amount of trash that passes through the stream at the sampling site, some of which covered up the SSS inlet. Thus, it is recommended that these samplers be maintained frequently, especially over critical periods such as during tracer experiments.

Due to the moderately low recovery rates of labeled sediment in the suspended sediment, we thought that we might be able to recover the re-suspended labeled sediments in subsequent storm events. However, the amount of La or Yb tracer detected in either the SSS or the bed samples in subsequent storms was minimal (Figure 6). This leads us to one of two conclusions: 1) The sediment did not leave the system in subsequent storm events and is still located in depositional areas within the reach, or 2) The sediment was transported out of the reach either during the first storm or during subsequent storms and our sampling regime failed to detect it.

3.4.3 Bed Sediment Samplers

The results for the bed sediment samples indicate similar results to the suspended sediment samples, with the La and Yb tracers remaining detectable to a distance of 875 and 525 m downstream of the injection point, respectively. Unlike the SSS samples, the bed samples were much more variable and did not always exhibit the typical dilution with downstream distance. This can be attributed to the sampling method that may have included some bed sediment from the previous storms, although every attempt was made to include only recently-deposited sediment. This problem could be solved by using a feldspar clay pad (Schenk *et al.*, 2011) or artificial turf mat (Carter *et al.*, 2003), as previous work has shown these methods successfully capture deposited sediment in riparian areas (Steiger *et al.*, 2003). Another option is to use a suction device to obtain only the unconsolidated sediment (Turner *et al.*, 2011), although this method still does not ensure that only sediment from the most recent storm event is collected.

For the La and Yb tracers, the bed sediment samples approached the background concentration much more quickly than the suspended sediment samples, which can be attributed to deposition of the coarser tracer particles soon after injection. The Yb injection tended to maintain a higher relative concentration of REE in the bed sediment further downstream, as compared to the La injection, where the discharge was much smaller. The variability in the amount of injected tracer that is deposited or in suspension needs to be accounted for when attempting to reach an overall enrichment of 100 times the background concentration. If unaccounted for, all of the sediment may settle out before the downstream sampling sites (Mahler *et al.*, 1998a).

Despite the variability among the bed sediment samples, a simple calculation suggests that a significant amount of the tracer was deposited on the stream bed during the tracer injection, especially at low flows. Using some simple assumptions such as an average channel depositional width of 2 m, a reach-long average depositional depth of sediment of 0.1 – 1.0 mm from field observations, and a sediment bulk density of 0.5 – 1.42 g cm^{-3} (Williams, 1991; Steiger and Gurnell, 2003; Phillips *et al.*, 2004; Rommens *et al.*, 2006), the amount of bed sediment deposited after the REE injection contained approximately 1.4 - 40.5% and 0.3 - 8.2% of the injected mass of La and Yb, respectively. Although a greater mass of Yb was injected (93 g vs. 63 g for La), the higher discharge during this injection likely carried most of this sediment out of the reach. These ranges are likely low, due to the variability in the bed sediment samples and the fact that sand is less well labeled than clay and preferentially settles out of suspension.

3.4.4 REE Tracer Limitations and Future Applications for Better Understanding Sediment Transport

While the use of REE-enriched sediments as sediment tracers was shown to be successful for two separate events on the same stream, there are some important limitations to consider. Characteristics of the study reach dictate how the method can be used. If there are high background REE concentrations, it will be more difficult to detect the tracer. Second, if the stream has a naturally high sediment load or large discharge, much more tracer will be needed to reach the recommended concentration of 100 times the background concentration in the water column after injection. Also, the length of the stream reach may prohibit the use of this method, as insufficient flows may limit the transport of sediment from the injection site. However, this tracer should not behave any differently than natural sediment and could provide useful information on sediment fate and transport, especially if most of the tracer can be accounted for by the bulk sampling and bed sediment samples

To address the downstream fate and transport of the tracer, we suggest that multiple bulk sampling sites be established along the reach, to inform the downstream transport capacity of the stream. Further, placing SSS at multiple depths at one location in the stream would make it possible to examine sediment transport at varying stages of the storm event. If the reach is small enough to access the SSS at high flow and the sediment load large enough, the samplers could be plugged until the time of the injection, such that there would be minimal dilution of the tracer by background sediment. It may also be of interest to inject a unique REE tracer at various points in the storm hydrograph to track the fate of sediment mobilized at various points in the storm event. A unique REE could be used to label each particle-size class of a natural sediment, which would allow for a better examination of the transport of each size class through the stream reach. Future research might examine different methods of applying REEs to the sediment, whether that be mixing in REE-oxides or spraying a REE-chloride solution on a field or stream bank.

The potential for the use of REE-labeled sediments is quite diverse, as they can serve as both an indicator of terrestrial erosion as well as a tracer of sediment fate and transport once the sediment enters a fluvial system. This tracer provides a link to understand the interactions between terrestrial erosion processes and the many factors that influence sediment transport to the stream. Using REE-labeled sediment, the effectiveness of best management practices could be evaluated in areas of research such as stream restoration design, road closure techniques near stream crossings and construction site erosion management plans. In addition, the use of REE-labeled sediment as a tracer has the potential to improve and validate both terrestrial and fluvial sediment transport models.

3.5 Conclusions

The use of REE tracers proved successful in detecting the transport of sediment along an 875 m reach of Stroubles Creek, with an enrichment of both suspended and bed sediment samples along the entire reach. The La and Yb tracers reached the sampling site 250 m downstream of the injection point at about the same time, despite being injected at two different flows and sediment loadings. The SSS effectively captured the REE tracer over the storm event, although there was some dilution of the tracer due to a high background sediment load. Bed sediment samples, although more variable due to the collection technique, showed that the REE-labeled sediment was transported more than 875 m in at least one event, and may contain substantial amounts of the REE tracer. Finally, there was no significant remobilization of the REE-labeled sediment in subsequent storm events, although the small mass of sediment injected may have prohibited this detection.

REEs were effectively used to label a natural soil at up to 13,800 times the background REE concentration, making it an applicable tracer of sediment fate and transport. The success in this preliminary investigation indicates that REEs may become an ideal tracer for evaluating sediment fate and transport in both terrestrial and small-scale fluvial systems. Based on this study, REE tracers can be used to assess the effectiveness of best management practices on construction, agriculture and forest harvesting sites. The information gathered from such studies on sediment transport distances, lag times and re-suspension rates can then be used to validate soil erosion and water quality models which can inform policy on how mitigation and restoration funds are allocated so that the most critical areas can be protected.

3.6 Acknowledgements

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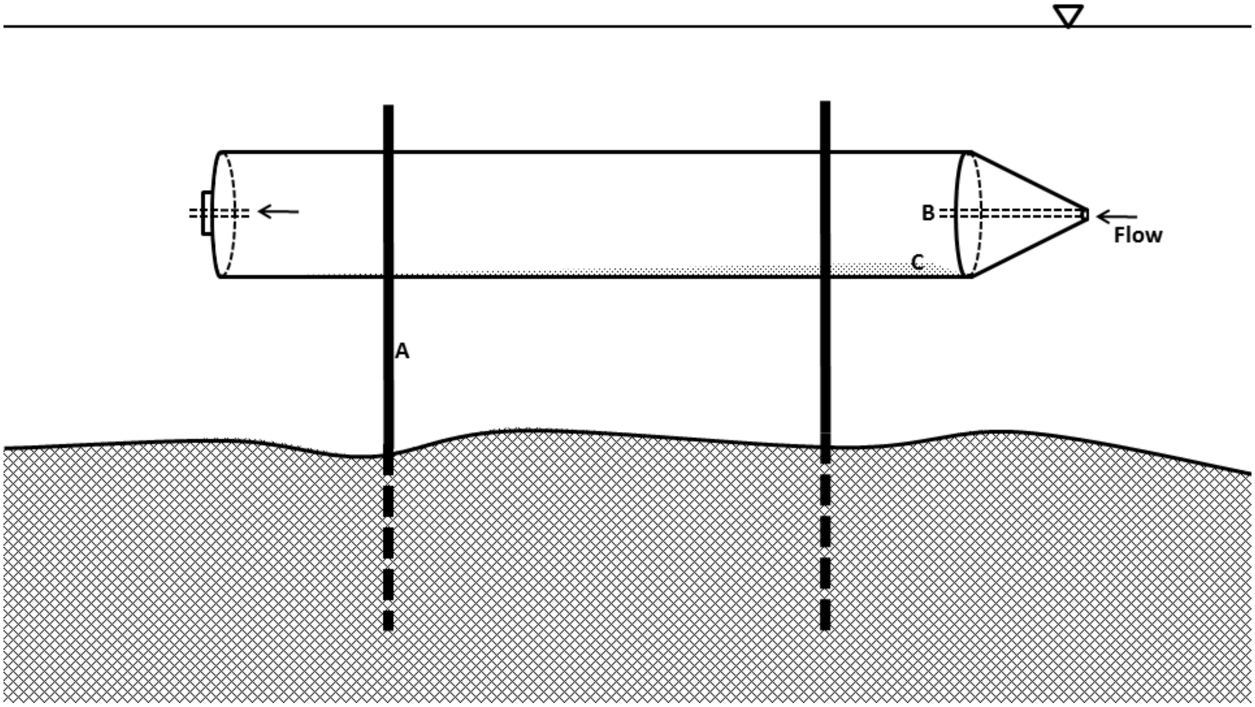

Figure 3. Suspended sediment sampler (SSS) design used in pairs in Stroubles Creek. The 1 m long, 98 mm diameter settling chamber was secured to the rebar supports (A) by hose clamps. A 4 mm inlet hose (B) at the upstream end of the sampler continuously supplied stream water to the settling chamber where sediment was deposited (C) before the sampled water was returned to the stream via a second 4 mm outlet hose. Design modified from Phillips *et al.* (*2000*).

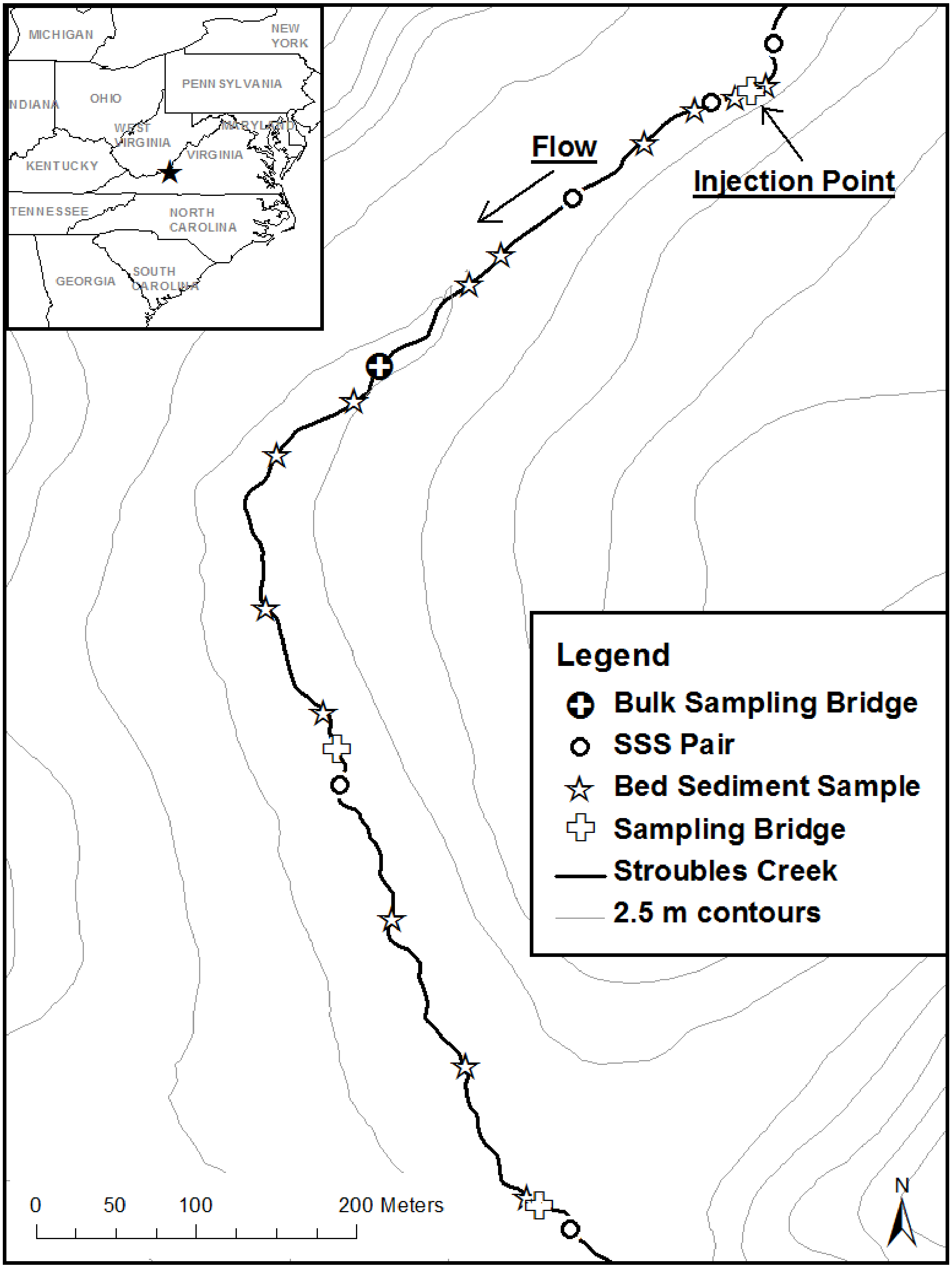

Figure 4. Sampling locations along Stroubles Creek, in Southwest Virginia, USA. There was one bulk sampling location, 5 SSS pairs, 13 bed sediment sampling locations and 4 sampling bridges, including the one used for bulk sampling. Flow is from north to south.

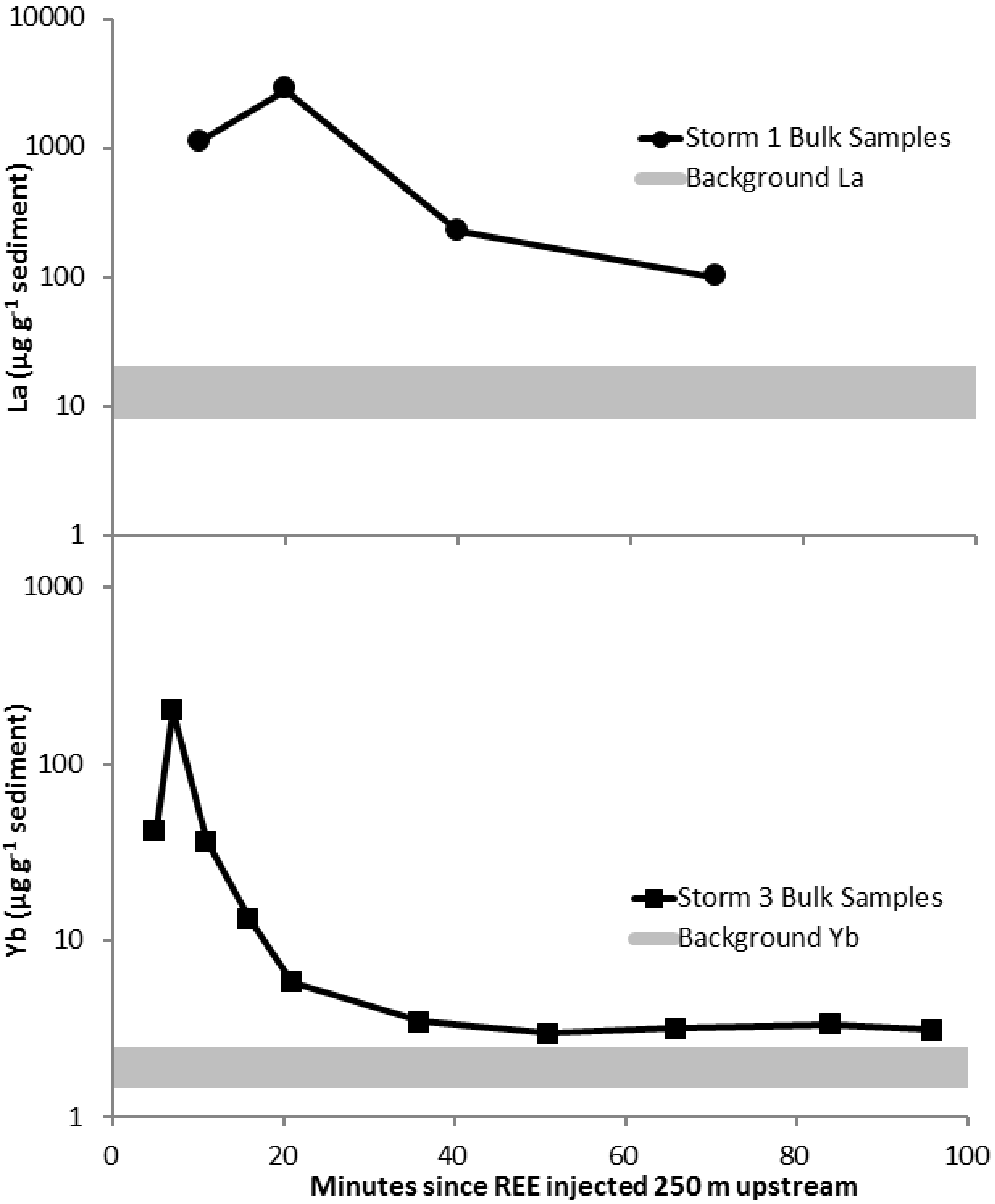

Figure 5. REE tracer breakthrough curves for the bulk samples collected during the La and Yb tracer injections at a sampling site 250 m downstream from the injection. The background levels indicate 95% confidence intervals of the mean background REE concentration, calculated from suspended sediment samples collected prior to any injections.

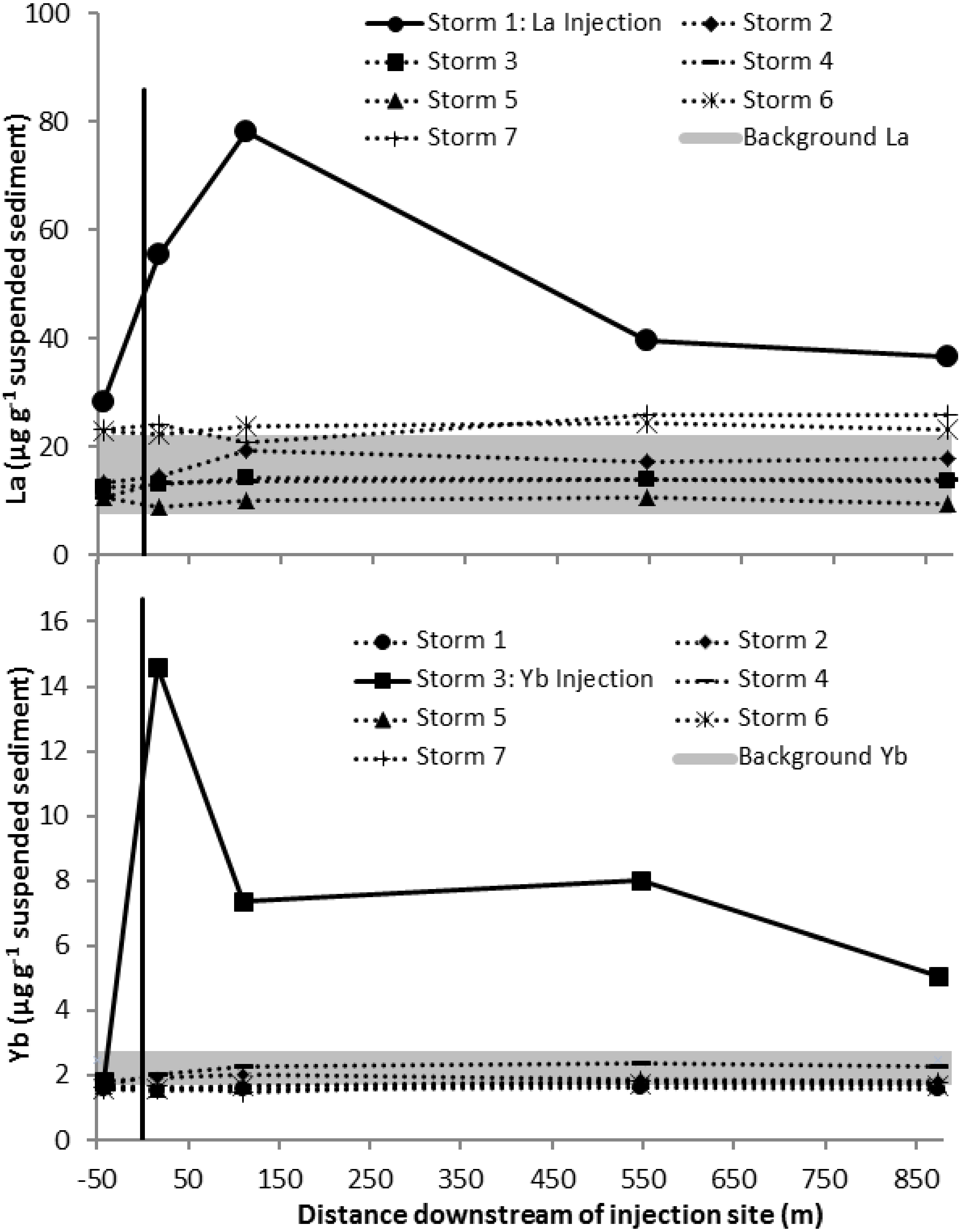

Figure 6. REE concentrations in the time-integrated suspended sediment samples after each REE injection. The background levels indicate 95% confidence intervals of the mean background REE concentration, calculated from suspended sediment samples collected prior to any injections. The vertical line indicates the injection point.

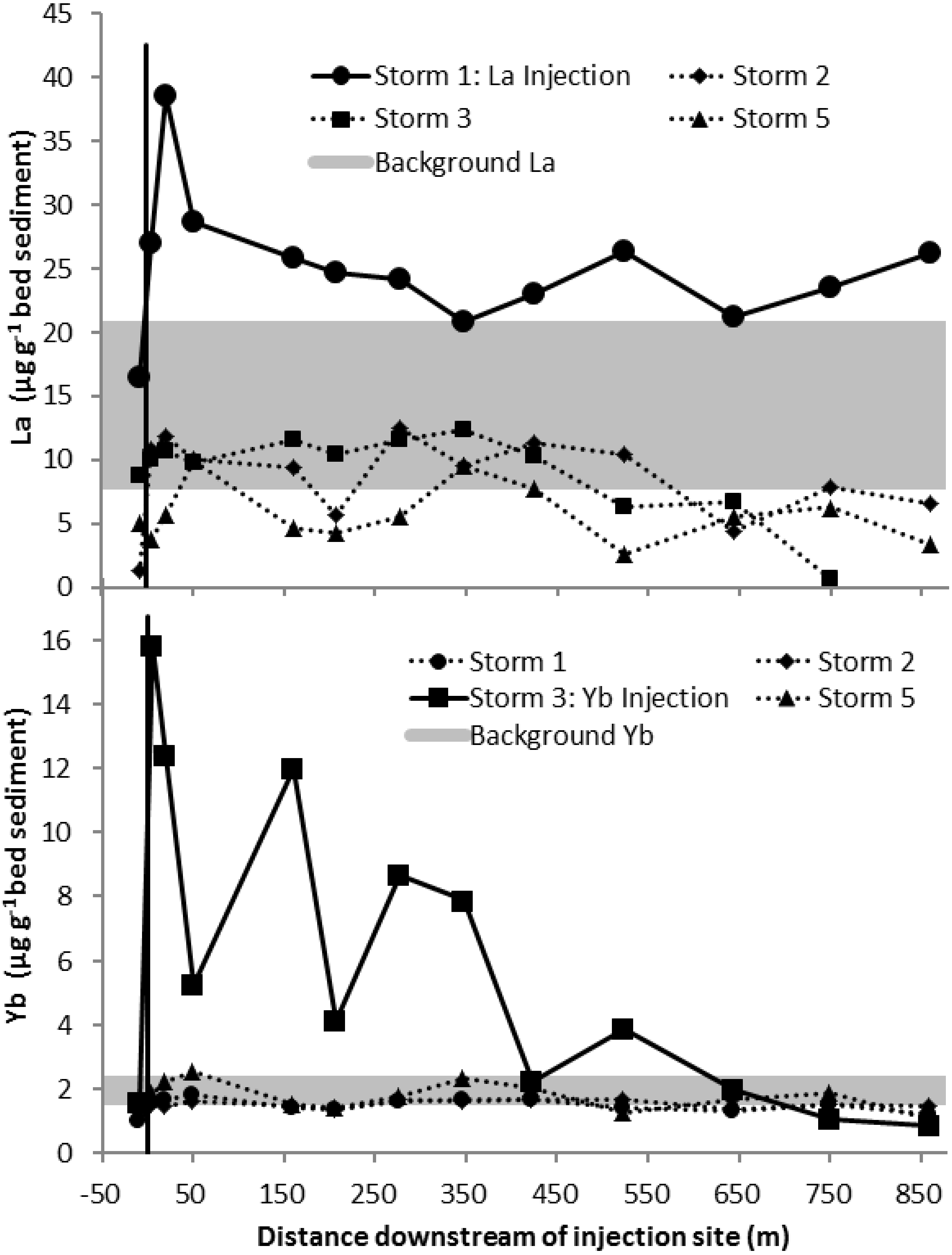

Figure 7. Bed sediment REE concentrations after each REE injection. The background levels indicate 95% confidence intervals of the mean background REE concentration, calculated from suspended sediment samples collected prior to any injections. The vertical line indicates the injection point.

Table 7. Storm events at the injection site in southwest Virginia for the fall of 2011.

Storm	**Date**	**REE Tracer**	**Rain** (cm)	**Max Flow** (m^3 s^{-1})	**Flow at Injection** (m^3 s^{-1})	**Max Turbidity** (NTU)	**Turbidity at Injection** (NTU)	**SSS Sample Period** (h)	**Avg. SSS Sample Mass** (g)
1	Oct. 29	La	1.88	0.37	0.20	25.7	14.8	24	1.38
2	Nov. 3	-	1.65	0.64		48.4		18.2	2.46
3	Nov. 15	Yb	2.36	1.66	1.53	152.9	28.4	32.2	4.25
4	Nov. 22	-	1.47	2.83		194.2		17.3	3.35
5	Nov. 29	-	3.78	6.58		169.4		40.8	6.67
6	Dec. 6	-	4.78	2.51		115.9		85.7	7.56
7	Dec. 16	-	1.14	0.53		59.6		10.2	0.66

Table 8. Mean REE concentrations, from a triplicate sample, for the bank soil, REE tracers and stream water.

	Lanthanum (µg g^{-1} sediment)	**Ytterbium** (µg g^{-1} sediment)	K_d
Unlabeled Bank Soil	26.4	1.4	
La Tracer	13354.8	1.4	33.7
Yb Tracer	20.1	19440.3	56.2
Stream water	0.1	0.0	

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4.0 Conclusions and Future Research

4.1 Conclusions

4.1.1 REE Adsorption to Natural Soils

REEs were shown to strongly adsorb to two natural soils and have great potential for use as a sediment tracer in both terrestrial and fluvial settings. La and Yb, two REEs from opposite ends of the lanthanide series, were shown to bind equally to a natural soil, suggesting that there could be 14 unique tracers available for creating REE tracers. The variance in adsorption maxima for both natural soils indicated that the clay mineralogy and organic matter content influence REE adsorption. However, both soils were labeled in excess of 7,700 ppm which is almost 300 times the background concentration, despite the high background La concentration. Considerations for use of REE-labeled tracers include selecting REEs that have low background concentrations to maximize the likelihood of detection. As there are differences in adsorption between soils, a preliminary investigation of the tracer adsorption is likely necessary prior to creating a larger batch of the tracer.

REE-labeled tracers are an improvement over previous sediment tracers for the following reasons: 1) they are physically the same as the sediment they are attempting to track, thereby minimizing any preferential transport or settling of the particles; 2) Tracer detection is relatively simple and quick through the use of an ICP, which has detection limits of 0.01 ppm or less; and 3) The tracer can be simply, quickly and relatively cheaply produced in bulk, which allows for greater labeling at the site.

4.1.2 REE-labeled Sediment as a Sediment Tracer

Two unique REE-labeled sediments injected during a series of storm events at Stroubles Creek in Virginia proved extremely useful in assessing sediment fate and transport at the reach scale. Although REEs have been used to label soil in a terrestrial setting, this is believed to be the first such application of REEs to an extended stream reach to inform sediment transport. The results of these tracer injections indicate that REE-labeled sediments, when applied at appropriate concentrations, can provide a vital link between terrestrial erosion and fluvial transport processes. One limitation of this method is that it requires a sediment sample size of at least 0.5 g for analysis on the ICP, making the method difficult to use in streams with low sediment loads. Further, all sampling methods should be evaluated prior to the tracer injection, so that any problems with sampler inlet clogging or an inability to sample only recently deposited sediment can be addressed.

These tracers performed as expected during the two storm events when a uniquely labeled tracer was injected, although no significant re-suspension of the tracer in subsequent events was observed. These two tracers showed that REE-labeled sediment can inform both the suspended sediment transport distance and bed sediment deposition on an event basis. Further temporal resolution could be provided if multiple samplers were employed at each site. REE-labeled sediments have a great potential as a terrestrial and fluvial tracer of sediment fate and transport. Future work with this tracer is needed to inform sediment transport models, improve sediment control structures and validate streamside best management practices.

4.2 Future Research

4.2.1 REE Adsorption to Natural Soils

- Expand the soils included in the adsorption isotherms to include those with more coarse fragments so that the use of this tracer on sandy and/or gravel soils is better understood
- Use additional REEs to label the soil to further validate the assumption that all 14 REEs adsorb similarly to any soil
- Assess the impact of equilibration time for creating large volumes of the tracer so that the tracer could be created just prior to use on a field site if necessary
- Evaluate other methods of labeling the soil with REEs (i.e. mixing REE-chlorides and/or REE-oxides with a damp soil, injecting an REE-chloride solution into a stream bank with a syringe and/or spraying a bank with a REE-chloride solution) to expand the applications of REEs to natural soils in field experiments

4.2.2 REE-labeled Sediment as a Sediment Tracer

- Expand the number of bulk sampling sites and SSSs further downstream to evaluate the transport and deposition of the tracer at greater downstream distances
- Extend the sampling reach to 1600 m or greater and try larger doses of REE-labeled sediment to see if the tracer is detectable at even greater distances
- Use REEs to label a stream bank or other near-stream areas *in-situ* so that the link between terrestrial erosion and fluvial transport can be better understood
- Apply REE-tracers to smaller or larger streams to examine feasibility at other scales
- Use REE-tracers to validate best management practices for erosion control on stream restoration projects, forestry road closures and construction sites. Each component of a site could be labeled with a unique REE to define which areas are significant contributors to the stream sediment load

5.0 Appendices

A. Stroubles Stage Discharge Data and Curve Fitting

Table 9. Stage-discharge measurements for Stroubles Creek in southwest Virginia, recorded just downstream of Bridge 1

#	Date & Time	Method of measurement	Mean Q ($m^3 s^{-1}$)	Mean A (m^2)	Avg. Velocity ($m s^{-1}$)	Width (m)	Stage (m)
1	September 5, 2011 1715	ADCP Raft	0.618	0.85	0.725		0.3655
2	September 6, 2011 0800	ADCP Raft	1.146	1.34	0.855		0.4948
3	September 7, 2011 0700	ADCP Raft	0.195	0.64	0.303		0.2045
4	October 12, 2011 0800	ADCP Raft	0.758	1.1	0.481	4.060	0.3517
5	October 12, 2011 1015	ADCP Raft	0.494	0.8	0.457	3.430	0.2718
6	October 12, 2011 1345	ADCP Raft	0.272	0.5	0.445	2.510	0.1919
7	October 13, 2011 1445	Marsh McBirney	0.125	0.556	0.200	3.300	0.1812
8	October 14, 2011 1020	Marsh McBirney	0.086	0.619	0.118	3.450	0.1974
9	October 28, 2011 1110	Marsh McBirney	0.036	0.294	0.114	2.550	0.0792
10	October 29, 2011 0915	Marsh McBirney	0.169	0.8045	0.210	3.950	0.1829
11	November 16, 2011 1850	ADCP Raft	1.560	1.8	0.668	5.380	0.5299
12	November 16, 2011 2000	ADCP Raft	0.970	1.3	0.489	4.070	0.3999
13	November 29, 2011 0540	ADCP Raft	5.703	4.8	1.293	7.370	0.9452
14	November 29, 2011 0630	ADCP Raft	2.983	3.1	0.726	5.610	0.7311

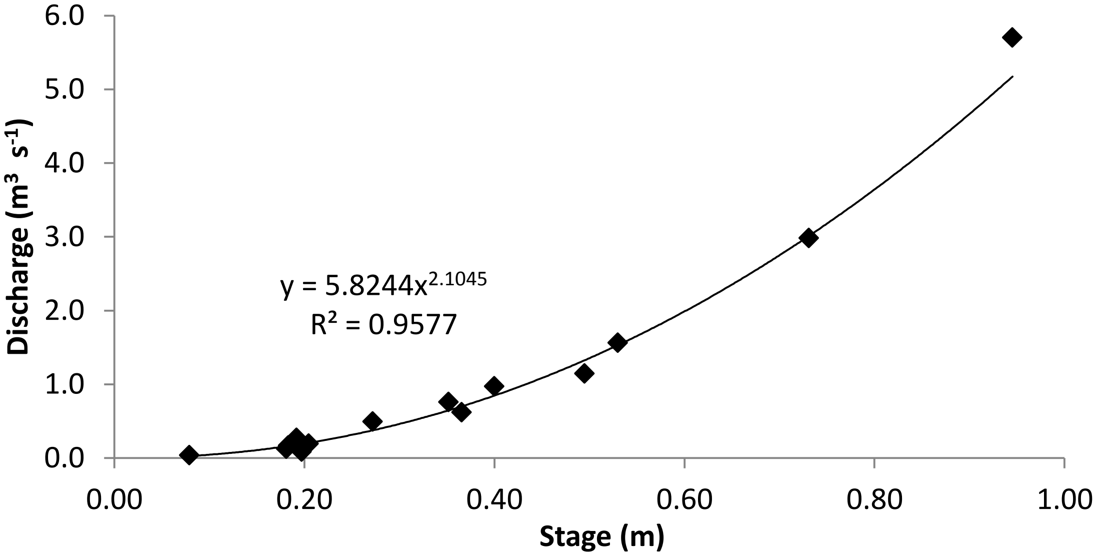

Figure 8. Stage-discharge relationship for Stroubles Creek at Bridge 1

B. Adsorption and Desorption Isotherm Data

B.1 Elemental Concentrations on the Bank Soil and Stroubles Creek water

Table 10. Stream bank soil chemical properties

Sample ID	Description	pH	P (mg/kg)	K (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Zn (mg/kg)	Mn (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	B (mg/kg)	Est. CEC (meq/100g)
A2	Soil 1	7.71	11	34	2326	349	3.1	26.4	0.6	8.8	1.3	14.6
A3	Soil 1	7.78	8	31	2368	343	2.6	25.4	0.5	5.8	1.3	14.7
A7	Soil 1	7.45	8	37	2657	375	3.4	25.9	0.5	6.2	1.4	16.4
A8	Soil 1	7.47	9	33	2760	407	3.8	27.9	0.5	5.2	1.5	17.2
B2	Soil 2	7.65	3	33	2511	416	0.6	11.1	0.2	1.4	0.7	16
B3	Soil 2	7.66	3	35	2489	420	0.5	10.6	0.2	1.2	0.6	16
B7	Soil 2	7.58	2	38	2853	458	0.9	12.6	0.1	0.9	0.7	18.1
B8	Soil 2	7.63	2	37	3001	467	0.6	11.1	0.1	0.4	0.7	18.9
	Soil 1: Average:	7.60	9.0	33.8	2527.8	368.5	3.2	26.4	0.5	6.5	1.4	15.7
	Soil 2: Average:	7.63	2.5	35.8	2713.5	440.3	0.7	11.4	0.2	1.0	0.7	17.3

Table 11. Base saturation and organic matter content of Soils 1 and 2

Sample ID	**Description**	**Base Sat** (%)	**Ca Sat** (%)	**Mg Sat** (%)	**K Sat** (%)	**OM** (%)
A2	Soil 1	100	79.7	19.7	0.6	3.4
A3	Soil 1	100	80.3	19.2	0.5	3.2
A7	Soil 1	100	80.6	18.8	0.6	3.4
A8	Soil 1	100	80	19.5	0.5	3.6
B2	Soil 2	100	78.1	21.4	0.5	2.9
B3	Soil 2	100	77.8	21.6	0.6	2.8
B7	Soil 2	100	78.6	20.8	0.5	3
B8	Soil 2	100	79.2	20.3	0.5	3
	Soil 1: Average:	100	80.2	19.3	0.6	3.4
	Soil 2: Average:	100	78.4	21.0	0.5	2.9

Table 12. REE concentrations in the stream bank soil and Stroubles Creek water

Sample ID	**Description**	**La** (µg g^{-1})	**Nd** (µg g^{-1})	**Yb** (µg g^{-1})
A4	Soil 1	19.7	12.1	1.1
A5	Soil 1	20.7	12.7	1.1
A6	Soil 1	20.4	12.7	1.1
B4	Soil 2	33.7	20.9	1.8
B5	Soil 2	32.2	20.6	1.8
B6	Soil 2	31.8	20.4	1.7
187	Stroubles Creek water	0.07	0.00	0.00
188	Stroubles Creek water	0.07	0.00	0.00
189	Stroubles Creek water	0.08	0.00	0.01

B.2 Particle Size Analysis

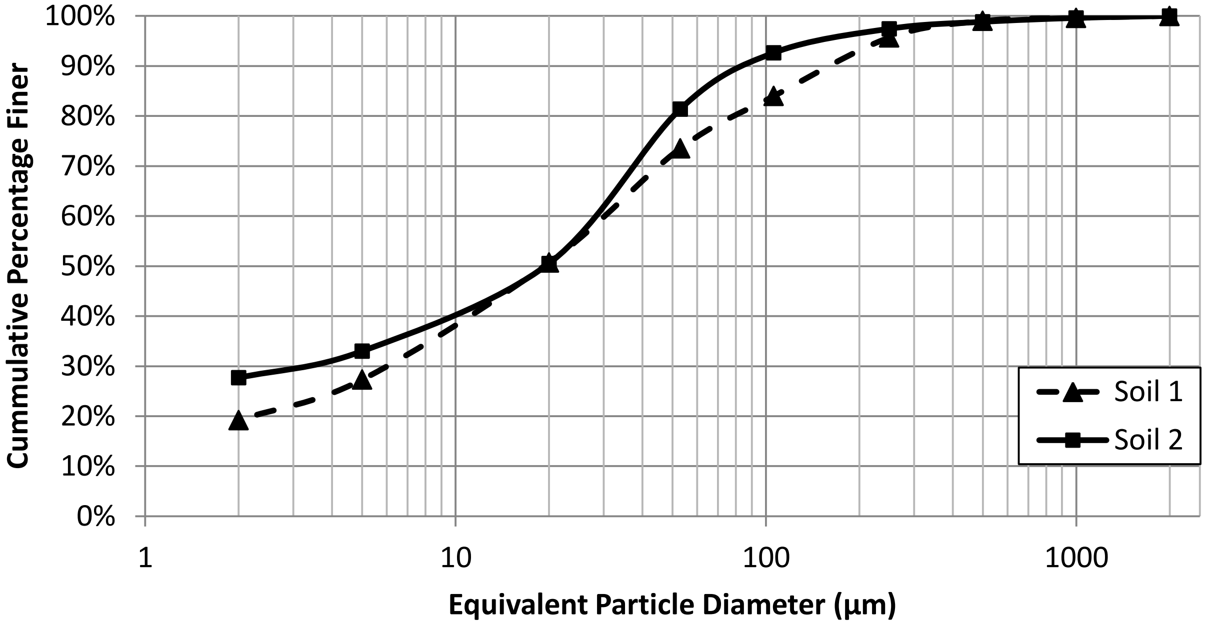

Figure 9. Particle Size distribution for both stream bank soils from the StREAM Lab

B.3 Adsorption Isotherm REE Concentrations

Table 13. REE concentrations for the adsorption isotherm on Soil 1

Soil 1: Sample ID	Target Conc. and REE	Stock Sol. Conc. (mmol/L)	Stock Solution added (mL)	Mass Soil added (g)	Final pH	Equili-brium La conc. (mmol/L)	Equili-brium Yb conc. (mmol/L)	Adsorbed Conc. (mmol REE/g soil)
AL1	0 mmol La	0.00	50.0	5.02	7.25	0.00		0.000
AL2	0 mmol La	0.00	50.0	5.01	7.33	0.00		0.000
AL3	0 mmol La	0.00	50.0	5.00	7.14	0.00		0.000
AL4	1.25 mmol La	1.33	50.0	5.00	6.51	0.00		0.013
AL5	1.25 mmol La	1.33	50.0	5.00	6.44	0.00		0.013
AL6	1.25 mmol La	1.33	50.0	4.98	6.4	0.00		0.013
AL7	2.5 mmol La	2.66	50.0	5.00	6.04	0.01		0.027
AL8	2.5 mmol La	2.66	50.0	4.99	6.3	0.01		0.027
AL9	2.5 mmol La	2.66	50.0	5.00	6.21	0.02		0.026
AL10	5 mmol La	5.18	50.0	4.98	5.83	1.34		0.038
AL11	5 mmol La	5.18	50.0	5.01	5.89	1.17		0.040
AL12	5 mmol La	5.18	50.0	5.00	5.94	1.20		0.040
AL13	10 mmol La	10.72	50.0	5.01	5.73	4.80		0.059
AL14	10 mmol La	10.72	50.0	5.00	5.8	4.97		0.058
AL15	10 mmol La	10.72	50.0	5.02	5.79	5.38		0.053
AL16	20 mmol La	20.90	50.0	5.00	5.76	15.72		0.052
AL17	20 mmol La	20.90	50.0	4.99	5.75	15.92		0.050
AL18	20 mmol La	20.90	50.0	5.02	5.83	16.24		0.046
AY1	0 mmol Yb	0.00	50.0	5.03	7.27	0.00		0.000
AY2	0 mmol Yb	0.00	50.0	4.98	7.21	0.00		0.000
AY3	0 mmol Yb	0.00	50.0	5.00	7.21	0.00		0.000
AY4	1.25 mmol Yb	1.34	50.0	5.02	6.39	0.00	0.00	0.013
AY5	1.25 mmol Yb	1.34	50.0	5.00	6.35	0.00	0.00	0.013
AY6	1.25 mmol Yb	1.34	50.0	5.00	6.44	0.00	0.00	0.013
AY7	2.5 mmol Yb	2.73	50.0	4.99	5.7	0.00	0.06	0.027
AY8	2.5 mmol Yb	2.73	50.0	5.02	5.76	0.00	0.04	0.027
AY9	2.5 mmol Yb	2.73	50.0	5.00	5.81	0.00	0.08	0.027
AY10	5 mmol Yb	5.06	50.0	5.02	5.49		1.21	0.038
AY11	5 mmol Yb	5.06	50.0	5.01	5.57		1.07	0.040
AY12	5 mmol Yb	5.06	50.0	5.00	5.66		1.14	0.039
AY13	10 mmol Yb	10.48	50.0	5.01	5.52		4.89	0.056
AY14	10 mmol Yb	10.48	50.0	5.00	5.47		4.71	0.058
AY15	10 mmol Yb	10.48	50.0	5.00	5.52		5.03	0.055
AY16	20 mmol Yb	21.43	50.0	5.01	5.31		15.66	0.058
AY17	20 mmol Yb	21.43	50.0	5.00	5.43		15.80	0.056
AY18	20 mmol Yb	21.43	50.0	5.00	5.43		16.25	0.052

Table 14. REE concentrations for the adsorption isotherm on Soil 2

Soil 2: Sample ID	Target Conc. and REE	Stock Sol. Conc. (mmol/L)	Stock Solution added (mL)	Mass Soil added (g)	Final pH	Equilibrium La Conc. (mmol/L)	Equilibrium Yb conc. (mmol/L)	Adsorbed Conc. (mmol REE/g soil)
BL1	0 mmol La	0.00	50.0	5.00	7.36	0.00		0.000
BL2	0 mmol La	0.00	50.0	5.02	7.23	0.00		0.000
BL3	0 mmol La	0.00	50.0	5.03	7.42	0.00		0.000
BL4	1.25 mmol La	1.33	50.0	5.02	6.89	0.00		0.013
BL5	1.25 mmol La	1.33	50.0	4.97	6.89	0.00		0.013
BL6	1.25 mmol La	1.33	50.0	5.03	6.97	0.00		0.013
BL7	2.5 mmol La	2.66	50.0	5.01	6.29	0.01		0.026
BL8	2.5 mmol La	2.66	50.0	4.99	6.37	0.00		0.027
BL9	2.5 mmol La	2.66	50.0	4.99	6.28	0.01		0.027
BL10	5 mmol La	5.18	50.0	5.00	5.92	0.55		0.046
BL11	5 mmol La	5.18	50.0	4.97	5.94	0.43		0.048
BL12	5 mmol La	5.18	50.0	4.97	5.95	0.45		0.048
BL13	10 mmol La	10.72	50.0	5.00	5.89	3.18		0.075
BL14	10 mmol La	10.72	50.0	5.00	5.85	3.32		0.074
BL15	10 mmol La	10.72	50.0	5.00	5.86	3.47		0.073
BL16	20 mmol La	20.90	50.0	5.00	5.55	13.93		0.070
BL17	20 mmol La	20.90	50.0	5.01	5.68	14.15		0.067
BL18	20 mmol La	20.90	50.0	4.98	5.71	13.87		0.071
BY1	0 mmol Yb	0.00	50.0	5.02	7.81	0.00	0.00	0.000
BY2	0 mmol Yb	0.00	50.0	4.98	7.55	0.00	0.00	0.000
BY3	0 mmol Yb	0.00	50.0	5.03	7.5	0.00	0.00	0.000
BY4	1.25 mmol Yb	1.34	50.0	5.01	6.58	0.00	0.00	0.013
BY5	1.25 mmol Yb	1.34	50.0	5.00	6.56	0.00	0.00	0.013
BY6	1.25 mmol Yb	1.34	50.0	5.02	6.53	0.00	0.00	0.013
BY7	2.5 mmol Yb	2.73	50.0	5.01	5.8	0.00	0.00	0.027
BY8	2.5 mmol Yb	2.73	50.0	5.00	5.91	0.00	0.00	0.027
BY9	2.5 mmol Yb	2.73	50.0	4.98	5.98	0.00	0.00	0.027
BY10	5 mmol Yb	5.06	50.0	5.01	5.5		0.39	0.047
BY11	5 mmol Yb	5.06	50.0	5.00	5.54		0.44	0.046
BY12	5 mmol Yb	5.06	50.0	5.01	5.62		0.27	0.048
BY13	10 mmol Yb	10.48	50.0	5.00	5.54		3.21	0.073
BY14	10 mmol Yb	10.48	50.0	5.02	5.53		3.21	0.072
BY15	10 mmol Yb	10.48	50.0	5.00	5.5		3.42	0.071
BY16	20 mmol Yb	21.43	50.0	4.99	5.35		14.41	0.070
BY17	20 mmol Yb	21.43	50.0	5.01	5.34		14.26	0.072
BY18	20 mmol Yb	21.43	50.0	5.01	5.38		14.32	0.071

B.4 Desorption Isotherm REE Concentrations

Table 15. Desorption data for Soil 1, lanthanum. Blank cells indicate values below the minimum detection limit

Sample ID	Description	Volume of Solution added (mL)	Initial Mass Soil added (g)	Final pH	Equilibrium La Conc. (mmol/L)	Equilibrium Yb Conc. (mmol/L)	Initial Mass REE sorbed (mmol REE/g soil)	Desorbed Amount (µmol REE/g soil)	Cumulative % Initial REE Retained
AL16	20 mmol La	50.0	5.00	5.76	15.7241		0.05		
AL17	20 mmol La	50.0	4.99	5.75	15.9159		0.05		
AL18	20 mmol La	50.0	5.02	5.83	16.2368		0.05		
AL16.1	20 mmol La, Wash #1	50.0	5.00	6.4	0.0005			0.01	99.990%
AL17.1	20 mmol La, Wash #1	50.0	4.99	6.42	0.0006			0.01	99.989%
AL18.1	20 mmol La, Wash #1	50.0	5.02	6.45	0.0005			0.01	99.988%
AL16.2	20 mmol La, Wash #2	50.0	5.00	6.71	0.0004	0.0011		0.00	99.982%
AL17.2	20 mmol La, Wash #2	50.0	4.99	6.71	0.0004	0.0008		0.00	99.981%
AL18.2	20 mmol La, Wash #2	50.0	5.02	6.72	0.0004	0.0007		0.00	99.980%
AL16.3	20 mmol La, Wash #3	50.0	5.00	6.99	0.0004	0.0007		0.00	99.974%
AL17.3	20 mmol La, Wash #3	50.0	4.99	7.07	0.0004	0.0006		0.00	99.972%
AL18.3	20 mmol La, Wash #3	50.0	5.02	7.09	0.0004	0.0005		0.00	99.971%
AL16.4	20 mmol La, Wash #4	50.0	5.00	7.15	0.0004	0.0020		0.00	99.965%
AL17.4	20 mmol La, Wash #4	50.0	4.99	7.18	0.0004	0.0015		0.00	99.963%
AL18.4	20 mmol La, Wash #4	50.0	5.02	7.17	0.0004	0.0012		0.00	99.962%
AL16.5	20 mmol La, Wash #5	50.0	5.00	7.22	0.0005	0.0014		0.00	99.957%
AL17.5	20 mmol La, Wash #5	50.0	4.99	7.22	0.0004	0.0011		0.00	99.955%
AL18.5	20 mmol La, Wash #5	50.0	5.02	7.17	0.0005	0.0009		0.00	99.952%

Table 16. Desorption data for Soil 1, ytterbium. Blank cells indicate values below the minimum detection limit

Sample ID	Description	Volume of Solution added (mL)	Initial Mass Soil added (g)	Final pH	Equilibrium La Conc. (mmol/L)	Equilibrium Yb Conc. (mmol/L)	Initial Mass REE sorbed (mmol REE/g soil)	Desorbed Amount (μmol REE/g soil)	Cumulative % Initial REE Retained
AY16	20 mmol Yb	50.0	5.01	5.31	0.0022	15.6636	0.06		
AY17	20 mmol Yb	50.0	5.00	5.43	0.0023	15.7962	0.06		
AY18	20 mmol Yb	50.0	5.00	5.43	0.0022	16.2528	0.05		
AY16.1	20 mmol Yb, Wash #1	50.0	5.01	6.44	0.0006	0.0025		0.02	99.957%
AY17.1	20 mmol Yb, Wash #1	50.0	5.00	6.43	0.0006	0.0031		0.03	99.945%
AY18.1	20 mmol Yb, Wash #1	50.0	5.00	6.41	0.0006	0.0040		0.04	99.923%
AY16.2	20 mmol Yb, Wash #2	50.0	5.01	6.77	0.0003	0.0018		0.02	99.927%
AY17.2	20 mmol Yb, Wash #2	50.0	5.00	6.76	0.0004	0.0023		0.02	99.904%
AY18.2	20 mmol Yb, Wash #2	50.0	5.00	6.71	0.0004	0.0029		0.03	99.867%
AY16.3	20 mmol Yb, Wash #3	50.0	5.01	7.08	0.0007	0.0034		0.03	99.868%
AY17.3	20 mmol Yb, Wash #3	50.0	5.00	7.05	0.0004	0.0043		0.04	99.828%
AY18.3	20 mmol Yb, Wash #3	50.0	5.00	7.09	0.0003	0.0013		0.01	99.841%
AY16.4	20 mmol Yb, Wash #4	50.0	5.01	7.18	0.0004	0.0026		0.03	99.822%
AY17.4	20 mmol Yb, Wash #4	50.0	5.00	7.19	0.0004	0.0036		0.04	99.765%
AY18.4	20 mmol Yb, Wash #4	50.0	5.00	7.2	0.0004	0.0040		0.04	99.765%
AY16.5	20 mmol Yb, Wash #5	50.0	5.01	7.31	0.0004	0.0021		0.02	99.785%
AY17.5	20 mmol Yb, Wash #5	50.0	5.00	7.29	0.0004	0.0029		0.03	99.714%
AY18.5	20 mmol Yb, Wash #5	50.0	5.00	7.3	0.0004	0.0028		0.03	99.710%

Table 17. Desorption data for Soil 2, lanthanum. Blank cells indicate values below the minimum detection limit

Sample ID	Description	Volume of Solution added (mL)	Initial Mass Soil added (g)	Final pH	Equilibrium La Conc. (mmol/L)	Equilibrium Yb Conc. (mmol/L)	Initial Mass REE sorbed (mmol REE/g soil)	Desorbed Amount (µmol REE/g soil)	Cumulative % Initial REE Retained
BL16	20 mmol La	50.0	5.00	5.55	13.9344		0.07		
BL17	20 mmol La	50.0	5.01	5.68	14.1493		0.07		
BL18	20 mmol La	50.0	4.98	5.71	13.8668		0.07		
BL16.1	20 mmol La, Wash #1	50.0	5.00	6.24	0.0006			0.01	99.992%
BL17.1	20 mmol La, Wash #1	50.0	5.01	6.14	0.0006			0.01	99.991%
BL18.1	20 mmol La, Wash #1	50.0	4.98	6.2	0.0006			0.01	99.992%
BL16.2	20 mmol La, Wash #2	50.0	5.00	6.63	0.0006	0.0005		0.01	99.983%
BL17.2	20 mmol La, Wash #2	50.0	5.01	6.55	0.0004	0.0004		0.00	99.986%
BL18.2	20 mmol La, Wash #2	50.0	4.98	6.61	0.0003	0.0004		0.00	99.987%
BL16.3	20 mmol La, Wash #3	50.0	5.00	6.93	0.0003	0.0003		0.00	99.979%
BL17.3	20 mmol La, Wash #3	50.0	5.01	6.88	0.0003	0.0003		0.00	99.981%
BL18.3	20 mmol La, Wash #3	50.0	4.98	6.86	0.0003	0.0003		0.00	99.982%
BL16.4	20 mmol La, Wash #4	50.0	5.00	6.97	0.0003	0.0008		0.00	99.974%
BL17.4	20 mmol La, Wash #4	50.0	5.01	6.98	0.0003			0.00	99.976%
BL18.4	20 mmol La, Wash #4	50.0	4.98	6.99	0.0003			0.00	99.977%
BL16.5	20 mmol La, Wash #5	50.0	5.00	7.16	0.0004	0.0006		0.00	99.969%
BL17.5	20 mmol La, Wash #5	50.0	5.01	7.05	0.0004	0.0006		0.00	99.971%
BL18.5	20 mmol La, Wash #5	50.0	4.98	7.09	0.0004	0.0005		0.00	99.972%

Table 18. Desorption data for Soil 2, ytterbium. Blank cells indicate values below the minimum detection limit

Sample ID	Description	Volume of Solution added (mL)	Initial Mass Soil added (g)	Final pH	Equilibrium La Conc. (mmol/L)	Equilibrium Yb Conc. (mmol/L)	Initial Mass REE sorbed (mmol REE/g soil)	Desorbed Amount (µmol REE/g soil)	Cumulative % Initial REE Retained
BY16	20 mmol Yb	50.0	4.99	5.35	0.0045	14.4097	0.07		
BY17	20 mmol Yb	50.0	5.01	5.34	0.0044	14.2552	0.07		
BY18	20 mmol Yb	50.0	5.01	5.38	0.0043	14.3159	0.07		
BY16.1	20 mmol Yb, Wash #1	50.0	4.99	6.25	0.0006	0.0055		0.06	99.922%
BY17.1	20 mmol Yb, Wash #1	50.0	5.01	6.29	0.0005	0.0065		0.07	99.909%
BY18.1	20 mmol Yb, Wash #1	50.0	5.01	6.29	0.0005	0.0053		0.05	99.925%
BY16.2	20 mmol Yb, Wash #2	50.0	4.99	6.64	0.0003	0.0022		0.02	99.891%
BY17.2	20 mmol Yb, Wash #2	50.0	5.01	6.56	0.0003	0.0024		0.02	99.876%
BY18.2	20 mmol Yb, Wash #2	50.0	5.01	6.6	0.0003	0.0026		0.03	99.889%
BY16.3	20 mmol Yb, Wash #3	50.0	4.99	6.91	0.0003	0.0013		0.01	99.873%
BY17.3	20 mmol Yb, Wash #3	50.0	5.01	6.9	0.0003	0.0016		0.02	99.854%
BY18.3	20 mmol Yb, Wash #3	50.0	5.01	6.89	0.0003	0.0020		0.02	99.861%
BY16.4	20 mmol Yb, Wash #4	50.0	4.99	7.04	0.0004	0.0035		0.03	99.823%
BY17.4	20 mmol Yb, Wash #4	50.0	5.01	6.94	0.0004	0.0038		0.04	99.801%
BY18.4	20 mmol Yb, Wash #4	50.0	5.01	6.97	0.0004	0.0040		0.04	99.804%
BY16.5	20 mmol Yb, Wash #5	50.0	4.99	7.16	0.0004	0.0026		0.03	99.786%
BY17.5	20 mmol Yb, Wash #5	50.0	5.01	7.13	0.0004	0.0030		0.03	99.759%
BY18.5	20 mmol Yb, Wash #5	50.0	5.01	7.1	0.0004	0.0033		0.03	99.758%

B.5 REE Concentrations in Stock Solutions

Table 19. REE stock solution concentrations. Blank cells indicate values below the minimum detection limit

Stock Solutions Sample ID	Description (Target Conc. and REE)	pH	La Conc. (mmol/L)	Yb Conc. (mmol/L)
C1	DI water only	-		
C2	DI water only	-		
C3	DI water only	-		
C4	1.25 mmol La	4.02	1.32	
C5	1.25 mmol La	3.91	1.34	
C6	1.25 mmol La	3.92	1.33	
C7	2.5 mmol La	5.02	2.65	
C8	2.5 mmol La	5.03	2.66	
C9	2.5 mmol La	5.1	2.66	
C10	5 mmol La	4.98	5.16	
C11	5 mmol La	4.82	5.29	
C12	5 mmol La	4.89	5.08	
C13	10 mmol La	4.18	10.69	
C14	10 mmol La	5.27	10.75	
C15	10 mmol La	5.32	10.73	
C16	20 mmol La	3.33	20.94	
C17	20 mmol La	2.94	20.79	
C18	20 mmol La	3.03	20.98	
C37	20 mmol La - no soil	4.64	20.98	
C38	20 mmol La - no soil	4.42	21.40	
C39	20 mmol La - no soil	4.58	20.77	
C43	Filtered DI water	-		
C44	Filtered DI water	-		
C45	Filtered DI water	-		
C19	1.25 mmol Yb	5.23		1.33
C20	1.25 mmol Yb	5.3		1.33
C21	1.25 mmol Yb	5.28		1.34
C22	2.5 mmol Yb	5.34		2.73
C23	2.5 mmol Yb	5.28		2.74
C24	2.5 mmol Yb	5.25		2.73
C25	5 mmol Yb	5.2		5.16
C26	5 mmol Yb	5.25		5.00
C27	5 mmol Yb	5.18		5.02
C28	10 mmol Yb	4.18		10.62
C29	10 mmol Yb	4.62		10.37
C30	10 mmol Yb	4.71		10.45
C31	20 mmol Yb	5.1		21.72
C32	20 mmol Yb	5.15		21.23
C33	20 mmol Yb	5.1		21.33
C34	20 mmol Yb - no soil	5.24		21.29
C35	20 mmol Yb - no soil	5.12		21.16
C36	20 mmol Yb - no soil	5.12		21.86
C40	Stroubles Creek water	7.85	0.0015	0.0001
C41	Stroubles Creek water	7.93	0.0005	0.0002
C42	Stroubles Creek water	7.96	0.0005	0.0002
C46	Filtered 5 mmol La	-	5.52	0.00
C47	Filtered 5 mmol La	-	5.42	0.00
C48	Filtered 5 mmol La	-	5.54	0.00

B.6 pH Variability in Relation to REE Adsorption and Desorption

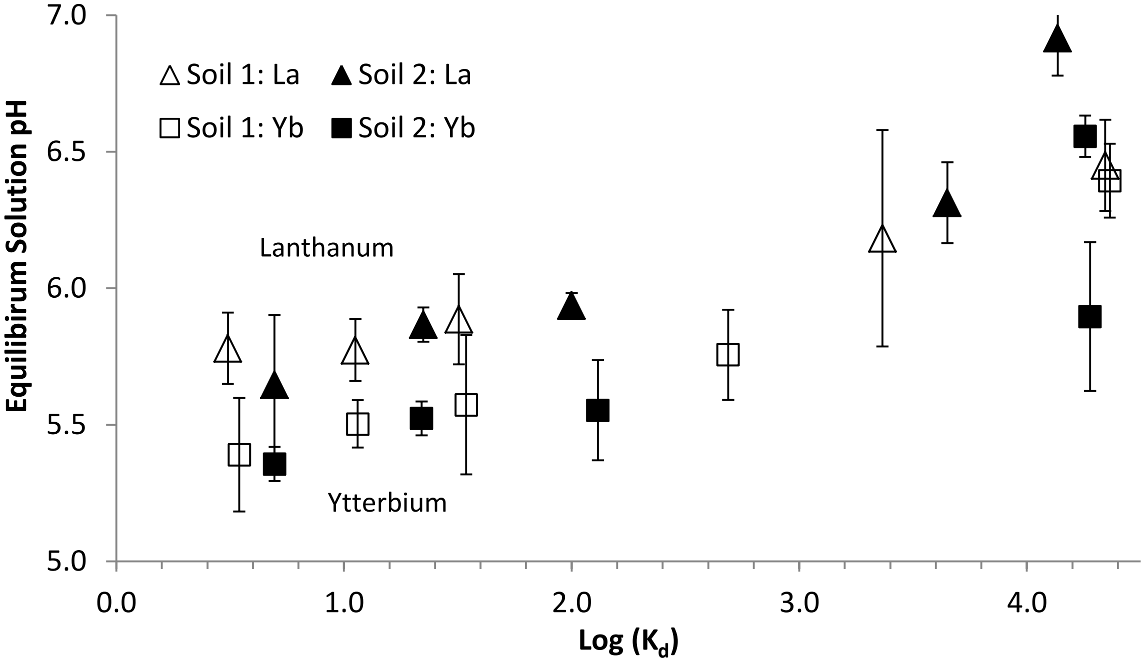

Figure 10. pH as a function of the distribution coefficient, K_d

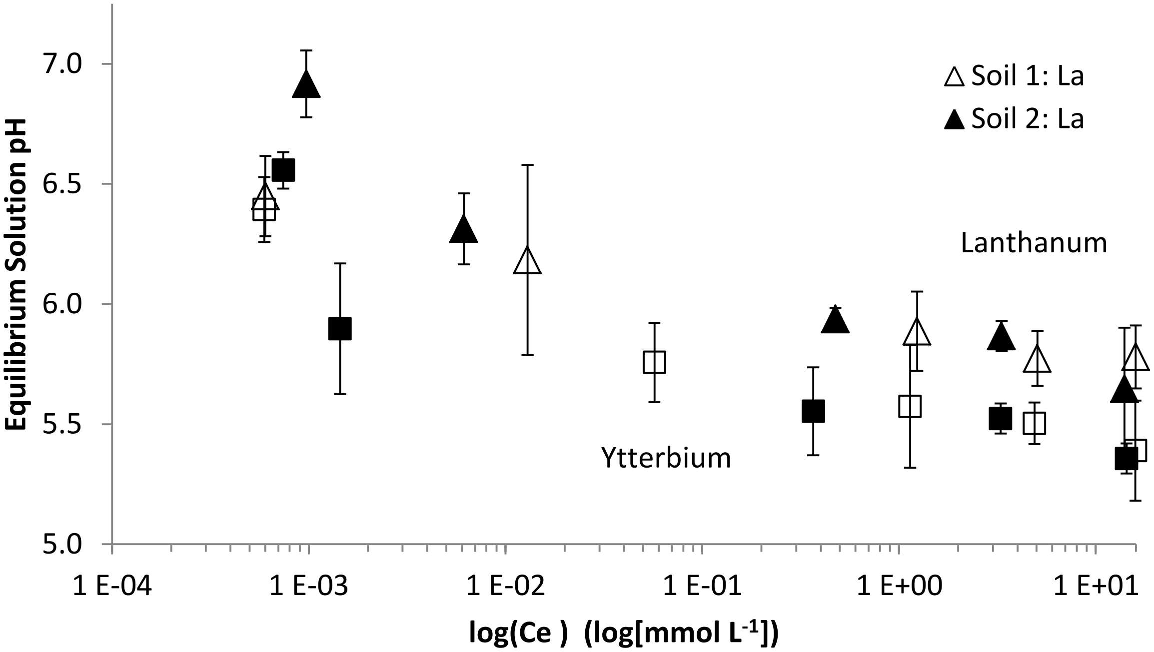

Figure 11. pH as a function of the equilibrium REE concentration

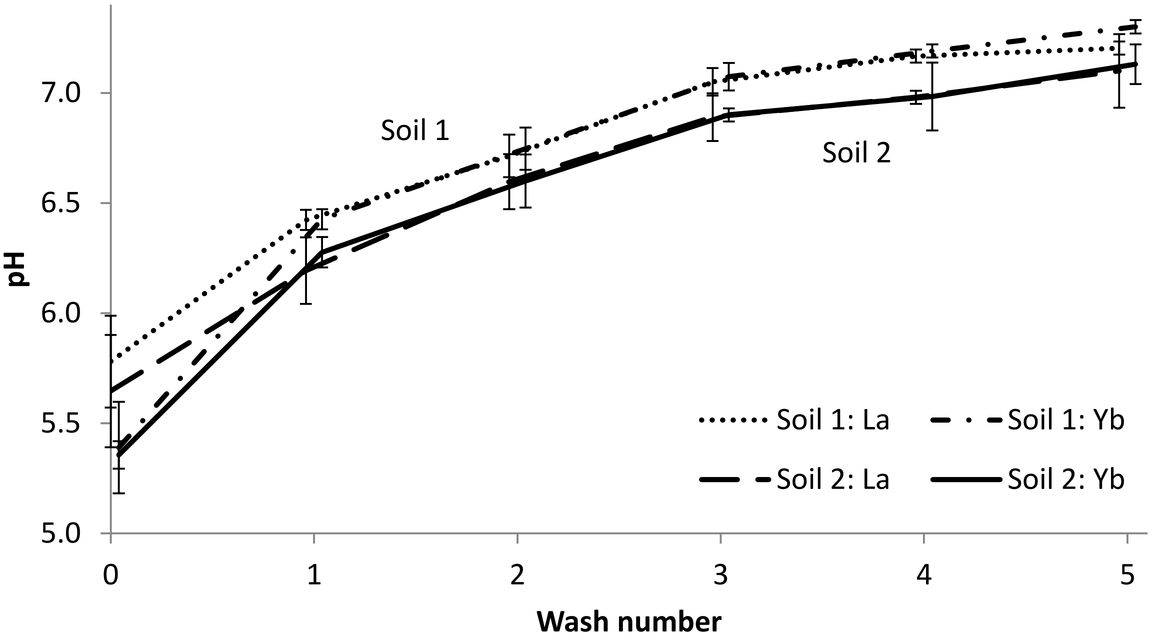

Figure 12. pH as a function of the wash number, during the desorption isotherm

C. REE Tracer Injection Data and Figures

C.1 Background Suspended Sediment Sampler REE Concentrations

Table 20. Background SSS REE concentrations for all five pairs of samplers on Stroubles Creek, averaged over all storms where there was no REE injection

Sampler Location	**Distance Downstream of Injection** (m)	**La** (μg g^{-1})	**Nd** (μg g^{-1})	**Yb** (μg g^{-1})
Bridge 1 UP	-43.0	15.9	14.0	1.8
Bridge 1 DS	16.0	15.2	13.5	1.8
Bridge 1.5	111.0	16.2	13.6	1.9
Bridge 2	547.0	16.8	14.1	1.9
Bridge 3	874.0	16.6	14.0	1.9

C.2 Background Bed Sediment REE Concentrations

Table 21. Background bed sediment REE concentrations for all thirteen sample locations along Stroubles Creek, averaged over all storms where there was no REE injection

Distance downstream from injection (m)	**La** (μg g^{-1})	**Nd** (μg g^{-1})	**Yb** (μg g^{-1})
-8.0	5.0	8.9	1.0
5.0	8.2	11.1	1.6
20.0	9.4	10.4	1.7
51.0	9.9	11.3	1.8
160.0	8.5	10.9	1.4
207.0	6.8	9.0	1.4
277.0	9.9	11.5	1.6
347.0	10.5	12.0	1.7
424.0	9.8	11.2	1.7
524.0	6.4	9.9	1.4
644.0	5.5	9.1	1.3
750.0	4.9	7.8	1.5
860.0	4.9	9.2	1.2

C.3 REE Concentrations in the bulk samples during each injection

Table 22. La concentrations and discharge rates for the bulk samples taken during Storm 1

Sample ID	**Time of Bulk Sample**	**Discharge** (at time of sample) ($m^3 s^{-1}$)	**La Conc.** ($\mu g\ g^{-1}$)	**Bulk Sample Mass** (g)
142	7:12	0.21	44.26	0.62
145	7:30	0.19	1109.67	0.50
149	7:39	0.19	2807.66	0.55
151	7:59	0.18	227.94	0.55
157	8:34	0.17	100.69	0.22

Table 23. Yb concentrations and discharge rates for the bulk samples taken during Storm 3

Sample ID	**Time of Bulk Sample**	**Discharge** (at time of sample) ($m^3 s^{-1}$)	**Yb Conc.** ($\mu g\ g^{-1}$)	**Bulk Sample Mass** (g)
340	16:47	0.48	71.00	2.57
341	17:42	1.11	78.57	5.34
342	17:59	1.50	128.82	6.33
343	18:01	1.53	290.36	5.98
344	18:05	1.55	125.20	5.68
345	18:10	1.58	96.18	6.44
346	18:15	1.61	92.62	5.10
347	18:30	1.63	90.26	3.48
348	18:45	1.58	94.97	2.52
349	19:00	1.43	92.96	2.00
350	19:18	1.30	98.63	1.34
351	19:30	1.14	97.71	1.07
352	19:45	0.96	103.23	0.85
353	20:00	0.85	105.90	0.68
354	20:30	0.60	110.58	0.89
356	21:00	0.47	117.14	0.92
358	21:30	0.39	114.90	0.61
366	22:10	0.31	124.18	0.69
370	22:50	0.26	124.44	0.65
372	23:45	0.21	124.49	0.76

Table 24. Nd concentration and discharge rates for the bulk samples taken during Storm 5

Sample ID	**Time of Bulk Sample**	**Discharge** (at time of sample) ($m^3 s^{-1}$)	**Nd Conc.** ($\mu g\ g^{-1}$)	**Bulk Sample Mass** (g)
540	6:10	3.84	15.03	1.08
541	6:50	2.34	15.80	0.55
542	6:56	2.18	17.01	0.91
543	7:00	2.07	16.71	0.83
544	7:05	1.94	17.14	0.95
545	7:07	1.89	324.31	0.97
546	7:09	1.84	173.11	0.97
547	7:11	1.79	75.25	0.81
548	7:13	1.75	39.86	0.82
549	7:15	1.71	28.49	0.79
550	7:17	1.67	22.87	0.86
551	7:19	1.63	20.84	0.63
552	7:21	1.59	19.89	0.84
553	7:23	1.56	18.94	0.84
554	7:25	1.53	18.91	0.82
555	7:27	1.49	18.51	0.66
556	7:29	1.46	18.00	0.78
557	7:31	1.42	17.25	0.74
558	7:35	1.36	17.40	0.72
559	7:40	1.28	17.82	0.72
566	7:45	1.21	17.81	0.66
567	7:50	1.14	16.65	0.65
568	7:55	1.08	17.00	0.72
569	8:00	1.03	17.12	0.68
570	8:10	0.95	16.93	0.48
571	8:20	0.88	16.94	0.61
572	8:30	0.80	17.14	0.55

C.4 REE Concentrations in the SSS and bed sediment samples from all storm events

Table 25. REE concentrations in all SSS, bed sediment and bulk samples for all storm events

Sample ID	Description	La (μg g^{-1})	Nd (μg g^{-1})	Yb (μg g^{-1})	Distance downstream of injection (m)	Time	Time since injection (min)
Background samples from 4 storms before any REE injections occurred							
166	SSS: Sept 8, 2011: B1 UP	13.5	14.0	2.0	-43.0		
167	SSS: Sept 8, 2011: B1 DS	12.0	13.3	1.8	16.0		
168	SSS: Sept 8, 2011: B1.5	12.5	13.5	1.9	111.0		
169	SSS: Sept 8, 2011: B2	14.3	14.5	2.0	547.0		
170	SSS: Sept 8, 2011: B3	13.4	13.9	2.0	874.0		
171	SSS: Oct. 5, 2011: B1 UP	12.5	13.3	1.9	-43.0		
172	SSS: Oct. 5, 2011: B1 DS	12.7	13.8	1.9	16.0		
173	SSS: Oct. 5, 2011: B1.5	14.7	14.9	2.0	111.0		
174	SSS: Oct. 5, 2011: B2	15.5	15.0	2.1	547.0		
175	SSS: Oct. 5, 2011: B3	15.0	15.3	2.0	874.0		
176	SSS: Oct. 17, 2011: B1 UP	13.1	14.2	1.8	-43.0		
177	SSS: Oct. 17, 2011: B1 DS	12.0	13.4	1.8	16.0		
178	SSS: Oct. 17, 2011: B1.5	13.6	14.3	1.9	111.0		
179	SSS: Oct. 17, 2011: B2	13.7	14.3	1.9	547.0		
180	SSS: Oct. 17, 2011: B3	14.1	14.5	2.0	874.0		
181	SSS: Oct. 21, 2011: B1 UP	28.0	23.5	3.1	-43.0		
182	SSS: Oct. 21, 2011: B1 DS	13.3	14.1	1.8	16.0		
183	SSS: Oct. 21, 2011: B1.5	14.5	15.0	2.0	111.0		
184	SSS: Oct. 21, 2011: B2	13.6	14.4	1.9	547.0		
185	SSS: Oct. 21, 2011: B3	14.3	15.1	1.9	874.0		
Storm 1: October 28/29 storm - La Injection							
109	10 mmol La solution - Initial	2,033.2					
110	10 mmol La solution - Initial	1,948.5					
111	10 mmol La solution - Initial	1,978.2					
121	La sol. Pulled Oct. 18, 2011	404.1					
122	La sol. Pulled Oct. 18, 2011	383.1					
123	La sol. Pulled Oct. 18, 2011	402.5					
124	La Soil	13,793.8		1.6			
125	La Soil	13,014.7		1.3			
126	La Soil	13,255.9		1.3			

Sample ID	Description	La (µg g^{-1})	Nd (µg g^{-1})	Yb (µg g^{-1})	Distance downstream of injection (m)	Time	Time since injection (min)
127	Sed. Sample: Oct. 30, 2011	26.2		1.1			
128	Sed. Sample: Oct. 30, 2011	23.6		1.2			
129	Sed. Sample: Oct. 30, 2011	21.2		0.9			
130	Sed. Sample: Oct. 30, 2011	26.4		1.3			
131	Sed. Sample: Oct. 30, 2011	23.0		1.3			
132	Sed. Sample: Oct. 30, 2011	20.8		1.0			
133	Sed. Sample: Oct. 30, 2011	24.2		1.4			
134	Sed. Sample: Oct. 30, 2011	24.6	5.5	1.3			
135	Sed. Sample: Oct. 30, 2011	25.9		1.3			
136	Sed. Sample: Oct. 30, 2011	28.7		1.4			
137	Sed. Sample: Oct. 30, 2011	38.6		1.3			
138	Sed. Sample: Oct. 30, 2011	27.0		1.3			
139	Sed. Sample: Oct. 30, 2011	16.5		0.8			
						Time	
142	5 gal. sample aggregate	44.3		1.5		7:12	-8.1
145	5 gal. sample aggregate	1,109.7		1.5		7:30	9.9
149	5 gal. sample aggregate	2,807.7	6.9	1.7		7:40	19.9
151	5 gal. sample aggregate	227.9	5.4	1.5		8:00	39.9
157	5 gal. sample aggregate	100.7		1.7		8:30	69.9
160	SSS: Oct. 29, 2011: B1 UP	28.4	8.6	1.6	-43.0		
161	SSS: Oct. 29, 2011: B1 DS	55.4	8.4	1.6	16.0		
162	SSS: Oct. 29, 2011: B1.5	78.1	8.7	1.6	111.0		
163	SSS: Oct. 29, 2011: B2	39.5	8.8	1.7	547.0		
164	SSS: Oct. 29, 2011: B3	36.7	8.5	1.6	874.0		
Storm 2: Nov. 3/4 storm							
227	Sed. Sample: Nov. 10, 2011	6.6	9.2	1.5	860.0		
228	Sed. Sample: Nov. 10, 2011	7.8	9.5	1.5	750.0		
229	Sed. Sample: Nov. 10, 2011	4.4	8.7	1.4	644.0		
230	Sed. Sample: Nov. 10, 2011	10.4	11.1	1.7	524.0		
231	Sed. Sample: Nov. 10, 2011	11.4	10.9	1.7	424.0		
232	Sed. Sample: Nov. 10, 2011	9.6	11.2	1.6	347.0		
233	Sed. Sample: Nov. 10, 2011	12.4	11.3	1.7	277.0		
234	Sed. Sample: Nov. 10, 2011	5.7	9.6	1.4	207.0		
235	Sed. Sample: Nov. 10, 2011	9.3	9.5	1.5	160.0		
236	Sed. Sample: Nov. 10, 2011	10.0	11.3	1.6	51.0		
237	Sed. Sample: Nov. 10, 2011	11.9	9.8	1.5	20.0		
238	Sed. Sample: Nov. 10, 2011	10.8	11.0	1.5	5.0		
239	Sed. Sample: Nov. 10, 2011	1.3	6.6	1.0	-8.0		

Sample ID	Description	La (µg g^{-1})	Nd (µg g^{-1})	Yb (µg g^{-1})	Distance downstream of injection (m)	Time	Time since injection (min)
Storm 2: Nov. 3/4 storm - continued							
260	SSS: Nov. 7, 2011: B1 UP	12.7	13.9	1.8	-43.0		
261	SSS: Nov. 7, 2011: B1 DS	14.0	14.5	1.9	16.0		
262	SSS: Nov. 7, 2011: B1.5	19.2	15.0	2.2	111.0		
263	SSS: Nov. 7, 2011: B2	17.2	13.4	1.9	547.0		
264	SSS: Nov. 7, 2011: B3	17.8	14.2	1.9	874.0		
276	SSS: Nov. 7, 2011: B1 UP	13.8	14.6	1.9	-43.0		
277	SSS: Nov. 7, 2011: B1 DS	15.2	14.4	2.0	16.0		
278	SSS: Nov. 7, 2011: B1.5	19.2	14.7	1.8	111.0		
279	SSS: Nov. 7, 2011: B2	17.4	14.3	1.9	547.0		
280	SSS: Nov. 7, 2011: B3	18.0	14.2	1.8	874.0		
Storm 3: November 15/16 storm - Yb Injection							
112	10 mmol Yb solution - Initial			1,663.1			
113	10 mmol Yb solution - Initial			1,789.3			
114	10 mmol Yb solution - Initial			1,738.1			
321	Yb sol., Pulled Oct. 18, 2011			297.0			
322	Yb sol., Pulled Oct. 18, 2011			387.7			
323	Yb sol., Pulled Oct. 18, 2011			359.4			
324	Yb Soil , pulled Nov 14, 2011	20.0	16.6	19,698.7			
325	Yb Soil , pulled Nov 14, 2011	20.8	17.7	19,244.9			
326	Yb Soil , pulled Nov 14, 2011	19.6	16.5	19,377.2			
327	Sed. Sample: Nov. 17, 2011			0.8	860.0		
328	Sed. Sample: Nov. 17, 2011	0.6	6.1	1.1	750.0		
329	Sed. Sample: Nov. 17, 2011	6.6	9.6	2.0	644.0		
330	Sed. Sample: Nov. 17, 2011	6.2	8.8	3.9	524.0		
331	Sed. Sample: Nov. 17, 2011	10.2	11.6	2.2	424.0		
332	Sed. Sample: Nov. 17, 2011	12.3	12.9	7.9	347.0		
333	Sed. Sample: Nov. 17, 2011	11.5	11.6	8.7	277.0		
334	Sed. Sample: Nov. 17, 2011	10.4	11.9	4.1	207.0		
335	Sed. Sample: Nov. 17, 2011	11.6	12.2	12.0	160.0		
336	Sed. Sample: Nov. 17, 2011	9.8	11.3	5.2	51.0		
337	Sed. Sample: Nov. 17, 2011	10.7	11.0	12.4	20.0		
338	Sed. Sample: Nov. 17, 2011	10.0	11.2	15.8	5.0		
339	Sed. Sample: Nov. 17, 2011	8.7	11.2	1.6	-8.0		

Sample ID	Description	La (µg g^{-1})	Nd (µg g^{-1})	Yb (µg g^{-1})	Distance downstream of injection (m)	Time	Time since injection (min)
340	1647, 5-gallon sample	12.0	12.4	1.6		16:47	-67.0
341	1742, 5-gallon sample	14.8	13.7	2.0		17:42	-12.0
342	1759, 5-gallon sample	24.9	13.4	42.7		17:59	5.0
343	1801, 5-gallon sample	24.8	13.8	204.9		18:01	7.0
344	1805, 5-gallon sample	25.4	14.0	36.9		18:05	11.0
345	1810, 5-gallon sample	27.2	13.3	13.2		18:10	16.0
346	1815, 5-gallon sample	32.5	14.0	5.9		18:15	21.0
347	1830, 5-gallon sample	31.5	14.5	3.5		18:30	36.0
348	1845, 5-gallon sample	26.0	14.4	3.0		18:45	51.0
350	1918, 5-gallon sample	16.7	15.4	3.4		19:18	84.0
352	1945, 5-gallon sample	17.7	15.9	3.3		19:45	111.0
354	2030, 5-gallon sample, aggregate	17.8	16.7	3.2		20:30	156.0
358	2130, 5-gallon sample, aggregate	17.9	17.1	3.2		21:30	216.0
366	2200, 5-gallon sample, aggregate	18.1	17.9	3.0		22:10	256.0
370	2300, 5-gallon sample, aggregate	17.8	17.6	3.1		22:50	296.0
372	2330, 5-gallon sample, aggregate	22.1	18.3	3.3		23:45	351.0
360	SSS: Nov. 19, 2011: B1 UP A	12.0	13.3	1.8	-43.0		
361	SSS: Nov. 19, 2011: B1 DS A	13.0	13.7	14.9	16.0		
362	SSS: Nov. 19, 2011: B1.5 A	14.3	13.9	7.0	111.0		
363	SSS: Nov. 19, 2011: B2 A	14.4	13.4	8.8	547.0		
364	SSS: Nov. 19, 2011: B3 A	14.0	13.4	4.8	874.0		
378	SSS: Nov. 19, 2011: B1.5 B	14.1	14.1	7.8	111.0		
379	SSS: Nov. 19, 2011: B2 B	13.8	13.5	7.3	547.0		
380	SSS: Nov. 19, 2011: B3 B	13.5	13.0	5.4	874.0		
Storm 4: November 22/23 storm							
460	SSS: Nov. 27, 2011: B1 UP A	9.6	11.7	1.6	-43.0		
461	SSS: Nov. 27, 2011: B1 DS A	14.3	14.6	2.0	16.0		
462	SSS: Nov. 27, 2011: B1.5 A	13.6	14.2	2.3	111.0		
463	SSS: Nov. 27, 2011: B2 A	14.4	14.4	2.4	547.0		
464	SSS: Nov. 27, 2011: B3 A	14.5	14.4	2.4	874.0		
476	SSS: Nov. 27, 2011: B1 UP B	11.7	13.0	1.8	-43.0		
477	SSS: Nov. 27, 2011: B1 DS B	12.5	13.5	2.0	16.0		
478	SSS: Nov. 27, 2011: B1.5 B	13.8	14.3	2.3	111.0		
479	SSS: Nov. 27, 2011: B2 B	13.8	14.2	2.4	547.0		
480	SSS: Nov. 27, 2011: B3 B	13.3	13.9	2.2	874.0		

Sample ID	Description	La (µg g^{-1})	Nd (µg g^{-1})	Yb (µg g^{-1})	Distance downstream of injection (m)	Time	Time since injection (min)
Storm 5: November 28/29 Storm - Nd Injection							
115	10 mmol Nd solution - Initial		547.5	29.2			
116	10 mmol Nd solution - Initial		564.3				
117	10 mmol Nd solution - Initial		558.8				
521	Nd sol., Pulled Nov. 22, 2011		111.0	31.3			
522	Nd sol., Pulled Nov. 22, 2011		127.7				
523	Nd sol., Pulled Nov. 22, 2011		118.6				
524	Nd Soil, pulled Nov 22	16.7	4,028.6	76.3			
525	Nd Soil, pulled Nov 22	18.1	4,500.8	67.5			
526	Nd Soil, pulled Nov 22	18.8	4,665.3	76.6			
527	Sed. Sample: Dec. 1, 2011	3.3	7.8	1.1	860.0		
528	Sed. Sample: Dec. 1, 2011	6.2	9.6	1.9	750.0		
529	Sed. Sample: Dec. 1, 2011	5.6	8.9	1.7	644.0		
530	Sed. Sample: Dec. 1, 2011	2.6	7.1	1.3	524.0		
531	Sed. Sample: Dec. 1, 2011	7.7	10.1	2.1	424.0		
532	Sed. Sample: Dec. 1, 2011	9.6	11.4	2.3	347.0		
533	Sed. Sample: Dec. 1, 2011	5.6	9.0	1.8	277.0		
534	Sed. Sample: Dec. 1, 2011	4.3	8.3	1.4	207.0		
535	Sed. Sample: Dec. 1, 2011	4.6	8.7	1.5	160.0		
536	Sed. Sample: Dec. 1, 2011	9.9	12.2	2.5	51.0		
537	Sed. Sample: Dec. 1, 2011	5.6	9.8	2.2	20.0		
538	Sed. Sample: Dec. 1, 2011	3.7	7.9	1.9	5.0		
539	Sed. Sample: Dec. 1, 2011	5.0	8.6	1.2	-8.0		
540	610, 5-gallon sample	13.6	15.0	2.0		6:10	-50.0
541	650, 5-gallon sample	13.9	15.8	2.1		6:50	-10.0
542	656, 5-gallon sample	15.0	17.0	2.0		6:56	-4.0
543	700, 5-gallon sample	15.1	16.7	2.8		7:00	0.0
544	705, 5-gallon sample	25.5	17.1	1.9		7:05	5.0
545	707, 5-gallon sample	26.0	324.3	1.8		7:07	7.0
546	709, 5-gallon sample	26.8	173.1	1.8		7:09	9.0
547	711, 5-gallon sample	25.6	75.2	1.7		7:11	11.0
548	713, 5-gallon sample	25.6	39.9	1.7		7:13	13.0
549	715, 5-gallon sample	26.2	28.5	1.7		7:15	15.0
550	717, 5-gallon sample	25.7	22.9	1.7		7:17	17.0
551	719, 5-gallon sample	25.4	20.8	1.7		7:19	19.0
552	721, 5-gallon sample	15.8	19.9	2.0		7:21	21.0
553	723, 5-gallon sample	15.6	18.9	2.0		7:23	23.0
554	725, 5-gallon sample	16.4	18.9	2.1		7:25	25.0

Sample ID	Description	La (μg g^{-1})	Nd (μg g^{-1})	Yb (μg g^{-1})	Distance downstream of injection (m)	Time	Time since injection (min)
555	727, 5-gallon sample	16.5	18.5	2.1		7:27	27.0
556	729, 5-gallon sample	15.3	18.0	2.0		7:29	29.0
557	731, 5-gallon sample	15.3	17.3	2.0		7:31	31.0
558	735, 5-gallon sample	15.7	17.4	2.0		7:35	35.0
559	740, 5-gallon sample	16.7	17.8	2.1		7:40	40.0
566	745, 5-gallon sample	12.3	17.8	1.7		7:45	45.0
567	750, 5-gallon sample	11.2	16.7	1.6		7:50	50.0
568	755, 5-gallon sample	11.8	17.0	1.7		7:55	55.0
569	800, 5-gallon sample	11.4	17.1	1.7		8:00	60.0
570	810, 5-gallon sample	11.4	16.9	1.7		8:10	70.0
571	820, 5-gallon sample	12.0	16.9	1.7		8:20	80.0
572	830, 5-gallon sample	11.8	17.1	1.7		8:30	90.0
560	SSS: Dec 1, 2011: B1 UP A	12.8	13.6	1.8	-43.0		
561	SSS: Dec 1, 2011: B1 DS A	8.8	14.0	1.6	16.0		
562	SSS: Dec 1, 2011: B1.5 A	10.2	14.8	1.7	111.0		
563	SSS: Dec 1, 2011: B2 A	10.6	14.4	1.8	547.0		
564	SSS: Dec 1, 2011: B3 A	10.6	14.2	1.8	874.0		
576	SSS: Dec 1, 2011: B1 UP B	8.8	13.2	1.5	-43.0		
577	SSS: Dec 1, 2011: B1 DS B	9.3	14.5	1.6	16.0		
578	SSS: Dec 1, 2011: B1.5 B	9.9	15.0	1.7	111.0		
579	SSS: Dec 1, 2011: B2 B	10.7	14.4	1.8	547.0		
580	SSS: Dec 1, 2011: B3 B	8.1	13.3	1.7	874.0		
Storm 6: December 6/7 Storm							
660	SSS: Dec 13, 2011: B1 UP A	22.8	13.6	1.6	-43.0		
661	SSS: Dec 13, 2011: B1 DS A	23.6	14.3	1.6	16.0		
662	SSS: Dec 13, 2011: B1.5 A	23.9	13.9	1.7	111.0		
663	SSS: Dec 13, 2011: B2 A	24.5	14.9	1.8	547.0		
664	SSS: Dec 13, 2011: B3 A	23.4	14.0	1.7	874.0		
676	SSS: Dec 13, 2011: B1 UP B	23.1	13.8	1.6	-43.0		
677	SSS: Dec 13, 2011: B1 DS B	21.3	12.0	1.5	16.0		
678	SSS: Dec 13, 2011: B1.5 B	23.5	14.2	1.7	111.0		
679	SSS: Dec 13, 2011: B2 B	24.2	14.7	1.7	547.0		
680	SSS: Dec 13, 2011: B3 B	23.1	14.1	1.7	874.0		

Sample ID	Description	La (μg g^{-1})	Nd (μg g^{-1})	Yb (μg g^{-1})	Distance downstream of injection (m)	Time	Time since injection (min)
Storm 7: Dec 16 Storm							
860	SSS: Dec 20, 2011: B1 UP A	23.4	14.0	1.7	-43.0		
861	SSS: Dec 20, 2011: B1 DS A	24.4	14.3	1.7	16.0		
862	SSS: Dec 20, 2011: B1.5 A	21.8	12.4	1.5	111.0		
863	SSS: Dec 20, 2011: B2 A	25.8	15.6	1.8	547.0		
864	SSS: Dec 20, 2011: B3 A	25.3	15.1	1.7	874.0		
876	SSS: Dec 20, 2011: B1 UP B	23.3	14.1	1.6	-43.0		
877	SSS: Dec 20, 2011: B1 DS B	23.8	14.6	1.7	16.0		
878	SSS: Dec 20, 2011: B1.5 B	19.7	10.9	1.4	111.0		
879	SSS: Dec 20, 2011: B2 B	25.8	15.6	1.8	547.0		
880	SSS: Dec 20, 2011: B3 B	26.5	16.1	1.9	874.0		

C.5 REE concentration graphs for bulk, suspended and bed sediment samples for the La, Yb and Nd tracer injections

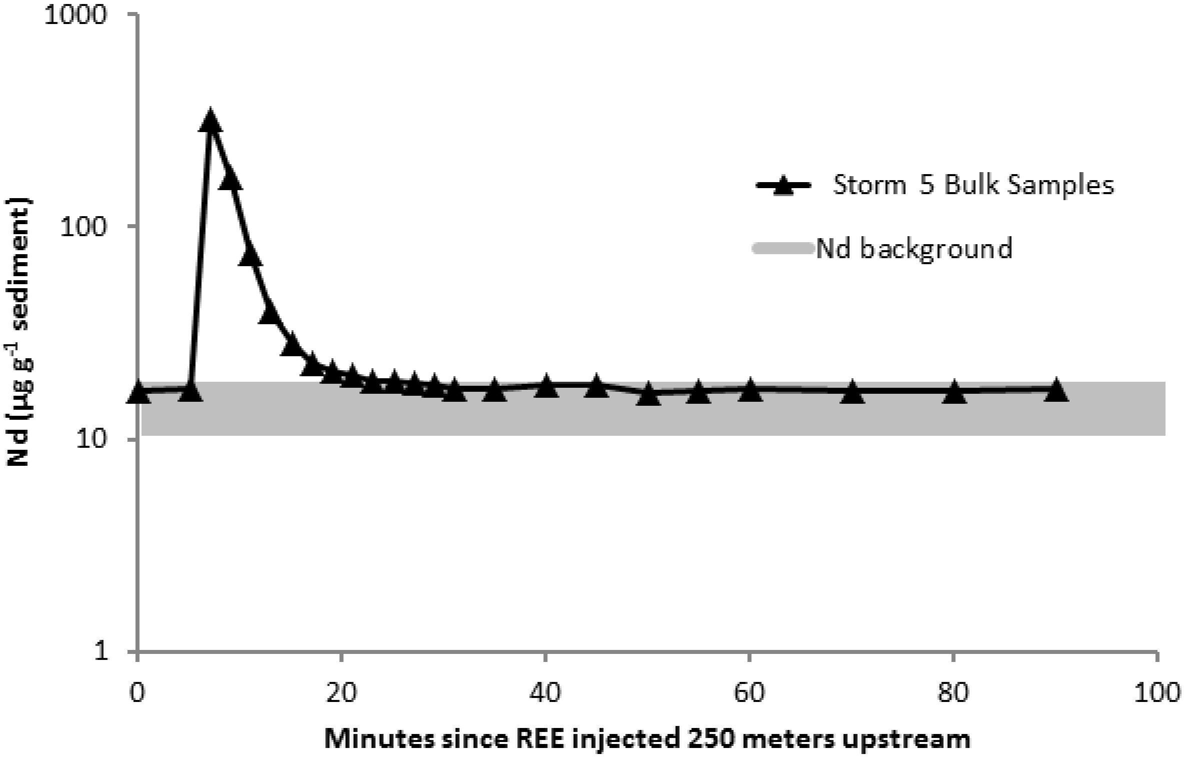

Figure 13. Nd concentration in bulk suspended sediment samples. The background levels indicate 95% confidence intervals of the mean background REE concentration, calculated from suspended sediment samples collected prior to any injections.

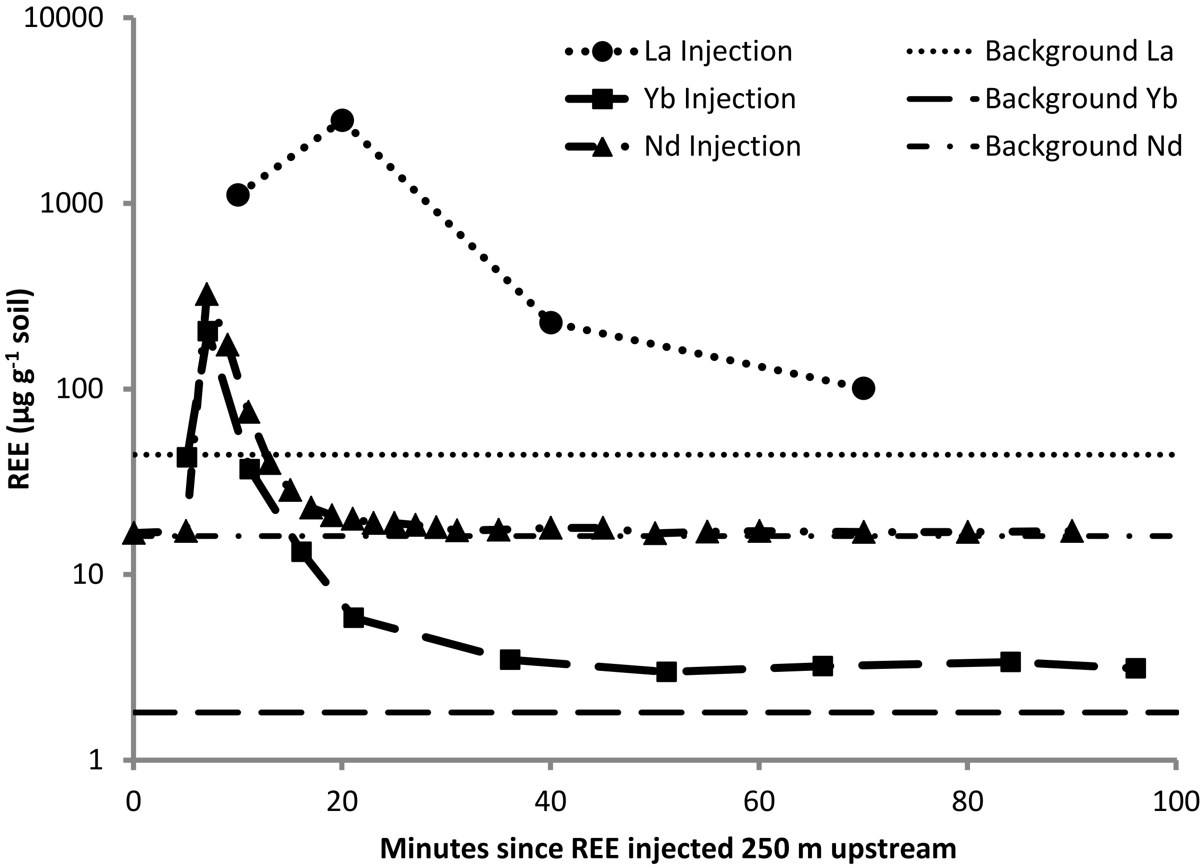

Figure 14. REE concentrations in bulk suspended sediment samples from the La, Yb and Nd tracer injections.

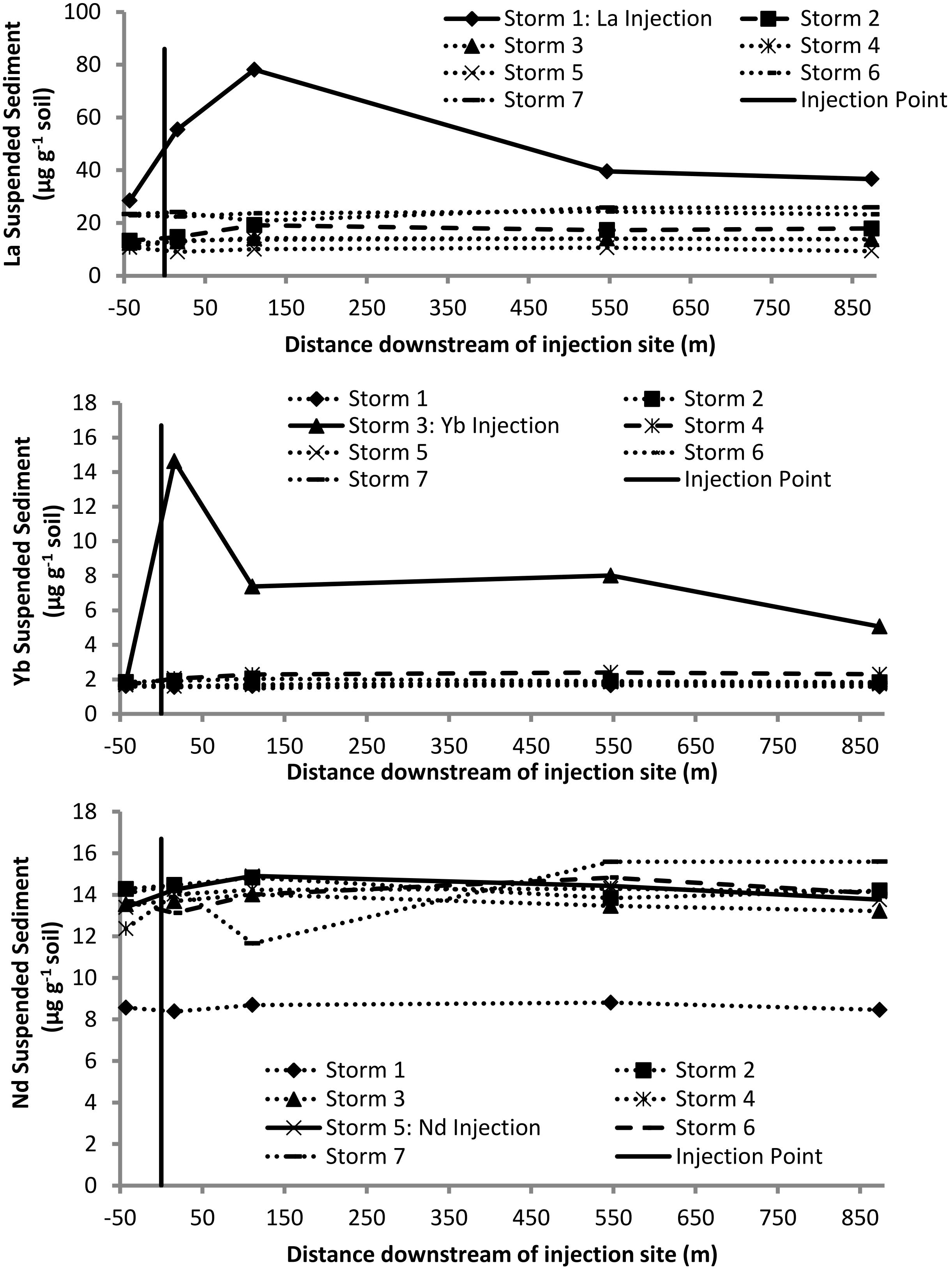

Figure 15. Time-integrated suspended sediment REE concentrations for individual storm events

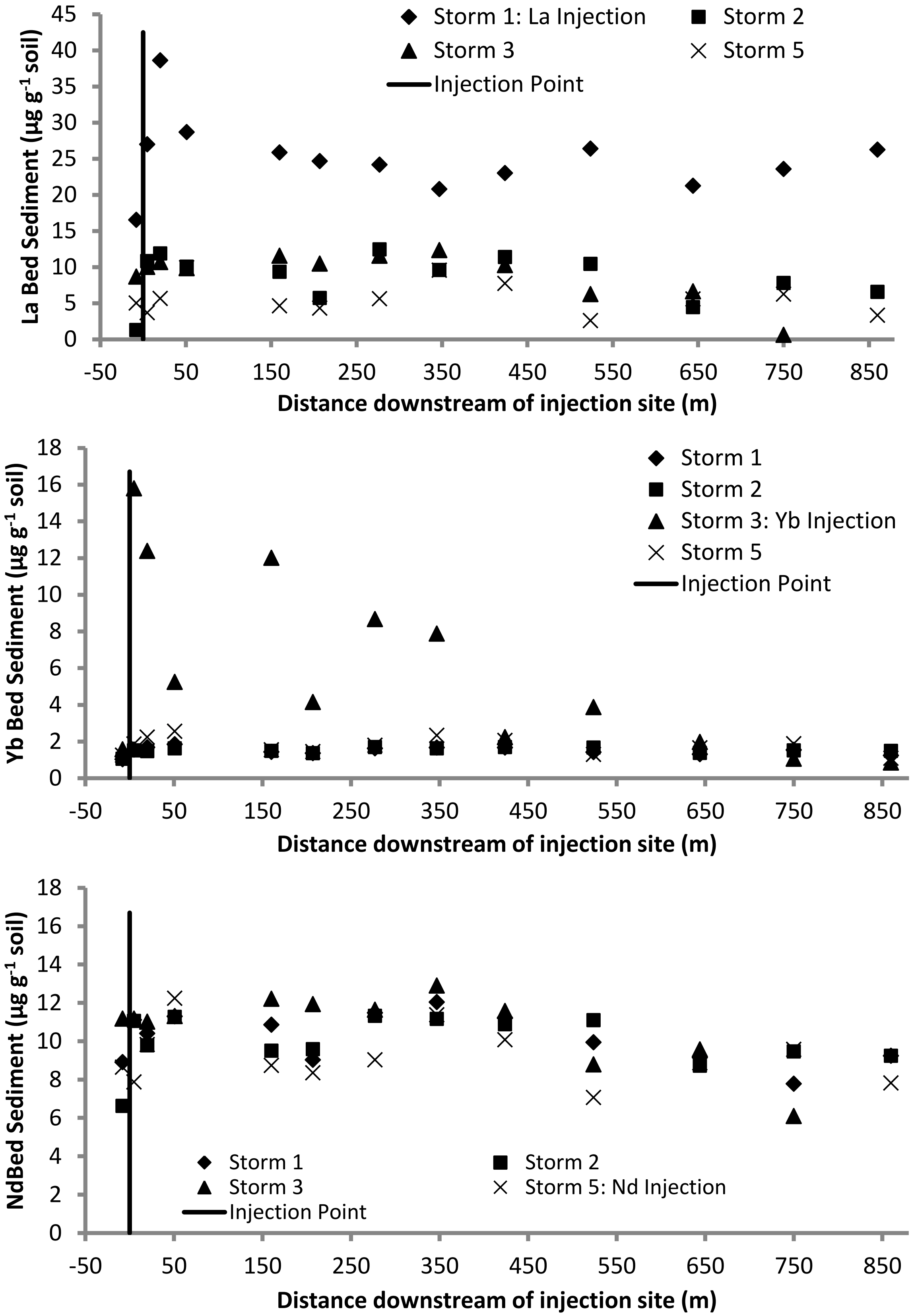

Figure 16. REE concentrations in bed sediment samples for individual storm events

C.6 Mass of sediment collected by the suspended sediment samplers

Table 26. Mass of sediment collected by the suspended sediment samplers from April 2011 – January 2012

Date of collection	Sampler location	Mass of sed. in sampler (g)	Average per time period (g)	Date of collection	Sampler location	Mass of sed. in sampler (g)	Average per time period (g)
4/9/11	Bridge 1 UP	4.26	3.57	7/6/11	Bridge 1 UP	4.28	6.25
4/9/11	Bridge 1 DS	2.83		7/6/11	Bridge 1 DS	8.94	
4/9/11	Bridge 2	2.93		7/6/11	Bridge 2	5.77	
4/9/11	Bridge 3	4.26		7/6/11	Bridge 3	6.00	
4/15/11	Bridge 1 UP	8.46	7.81	7/13/11	Bridge 1 UP	4.22	6.61
4/15/11	Bridge 1 DS	11.14		7/13/11	Bridge 1 DS	12.98	
4/15/11	Bridge 2	7.73		7/13/11	Bridge 2	4.78	
4/15/11	Bridge 3	3.92		7/13/11	Bridge 3	4.46	
4/20/11	Bridge 1 UP	5.74	7.22	8/2/11	Bridge 1 UP	2.75	4.37
4/20/11	Bridge 1 DS	11.26		8/2/11	Bridge 1 DS	7.14	
4/20/11	Bridge 2	6.07		8/2/11	Bridge 2	1.59	
4/20/11	Bridge 3	5.83		8/2/11	Bridge 3	5.99	
5/2/11	Bridge 1 UP	3.92	7.20	8/10/11	Bridge 1 UP	1.48	2.51
5/2/11	Bridge 1 DS	12.75		8/10/11	Bridge 1 DS	5.08	
5/2/11	Bridge 2	5.42		8/10/11	Bridge 2	1.16	
5/2/11	Bridge 3	6.70		8/10/11	Bridge 3	2.34	
5/16/11	Bridge 1 UP	9.61	13.87	9/8/11	Bridge 1 UP	23.74	25.52
5/16/11	Bridge 1 DS	25.26		9/8/11	Bridge 1 DS	43.68	
5/16/11	Bridge 2	7.16		9/8/11	B 1.5	26.05	
5/16/11	Bridge 3	13.44		9/8/11	Bridge 2	12.12	
5/31/11	Bridge 1 UP	15.38	17.16	9/8/11	Bridge 3	22.02	
5/31/11	Bridge 1 DS	26.23		10/5/11	Bridge 1 UP	3.08	4.00
5/31/11	Bridge 2	15.36		10/5/11	Bridge 1 DS	7.47	
5/31/11	Bridge 3	11.67		10/5/11	B 1.5	2.98	
6/14/11	Bridge 1 UP	1.72	3.14	10/5/11	Bridge 2	3.87	
6/14/11	Bridge 1 DS	5.26		10/5/11	Bridge 3	2.62	
6/14/11	Bridge 2	1.63		10/17/11	Bridge 1 UP	3.49	10.55
6/14/11	Bridge 3	3.96		10/17/11	Bridge 1 DS	22.50	
6/22/11	Bridge 1 UP	3.33	5.65	10/17/11	B 1.5	7.10	
6/22/11	Bridge 1 DS	11.73		10/17/11	Bridge 2	13.00	
6/22/11	Bridge 2	4.59		10/17/11	Bridge 3	6.66	
6/22/11	Bridge 3	2.95					

Date of collection	Sampler location	Mass of sed. in sampler (g)	Average per time period (g)	Date of collection	Sampler location	Mass of sed. in sampler (g)	Average per time period (g)
10/21/11	Bridge 1 UP	3.22	3.73	12/1/11	Bridge 1 UP	5.19	6.67
10/21/11	Bridge 1 DS	5.05		12/1/11	Bridge 1 DS	10.53	
10/21/11	B 1.5	2.59		12/1/11	B 1.5	5.08	
10/21/11	Bridge 2	4.13		12/1/11	Bridge 2	7.43	
10/21/11	Bridge 3	3.68		12/1/11	Bridge 3	5.12	
10/30/11	Bridge 1 UP	1.20	1.38	12/13/11	Bridge 1 UP	4.82	7.11
10/30/11	Bridge 1 DS	1.77		12/13/11	Bridge 1 DS	10.80	
10/30/11	B 1.5	1.03		12/13/11	B 1.5	6.49	
10/30/11	Bridge 2	1.87		12/13/11	Bridge 2	8.54	
10/30/11	Bridge 3	1.01		12/13/11	Bridge 3	7.14	
11/7/11	Bridge 1 UP	1.77	2.46	12/20/11	Bridge 1 UP	0.98	0.66
11/7/11	Bridge 1 DS	5.18		12/20/11	Bridge 1 DS	1.02	
11/7/11	B 1.5	1.40		12/20/11	B 1.5	0.21	
11/7/11	Bridge 2	2.36		12/20/11	Bridge 2	0.58	
11/7/11	Bridge 3	1.61		12/20/11	Bridge 3	0.52	
11/19/11	Bridge 1 UP	2.85	4.25	1/17/12	Bridge 1 UP	8.14	10.97
11/19/11	Bridge 1 DS	5.79		1/17/12	Bridge 1 DS	11.85	
11/19/11	B 1.5	3.28		1/17/12	B 1.5	9.91	
11/19/11	Bridge 2	5.02		1/17/12	Bridge 2	13.77	
11/19/11	Bridge 3	4.30		1/17/12	Bridge 3	11.19	
11/27/11	Bridge 1 UP	2.66	3.35				
11/27/11	Bridge 1 DS	3.73					
11/27/11	B 1.5	2.83					
11/27/11	Bridge 2	4.02					
11/27/11	Bridge 3	3.50					

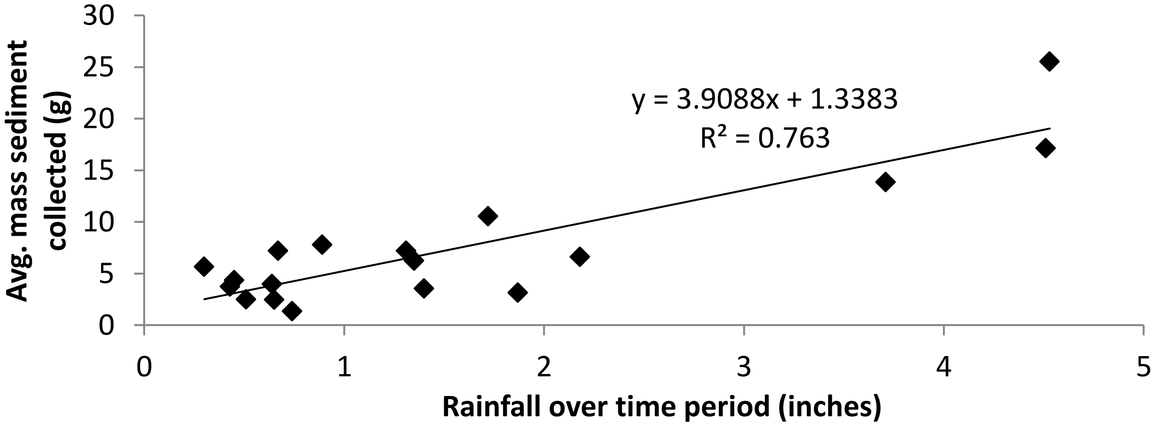

Figure 17. Mass of sediment collected in suspended sediment samplers as a function of rainfall

D. Procedure for Emptying SSS

Procedure for emptying the suspended sediment samplers (SSS, aka white rockets) at Stroubles Creek

By Tyler Kreider, Spring 2012

In general, the samplers require a stage of at least 0.30 meters for a duration of about 4 or more hours to provide an adequate sediment sample, if they are set just above the water surface at a stage of 10-15 cm. However this varies with the sediment load in the stream. It is easiest to wait until the water recedes below the samplers to attempt to empty them (Ideal Emptying Stage in Figure 1), otherwise you have to raise the sampler up on the rebar (without tilting it! – see Step 1.a) before attempting any of the following steps.

Supplies needed for sampling:

- 5/16” nut driver (flathead screwdriver can work as well)
- Sampling bags, (Whirl-Pak 18 oz bags work well)
- Brush to clean out sampler (6” dryer cleaning brush works well)
- Bag/backpack to hold samples

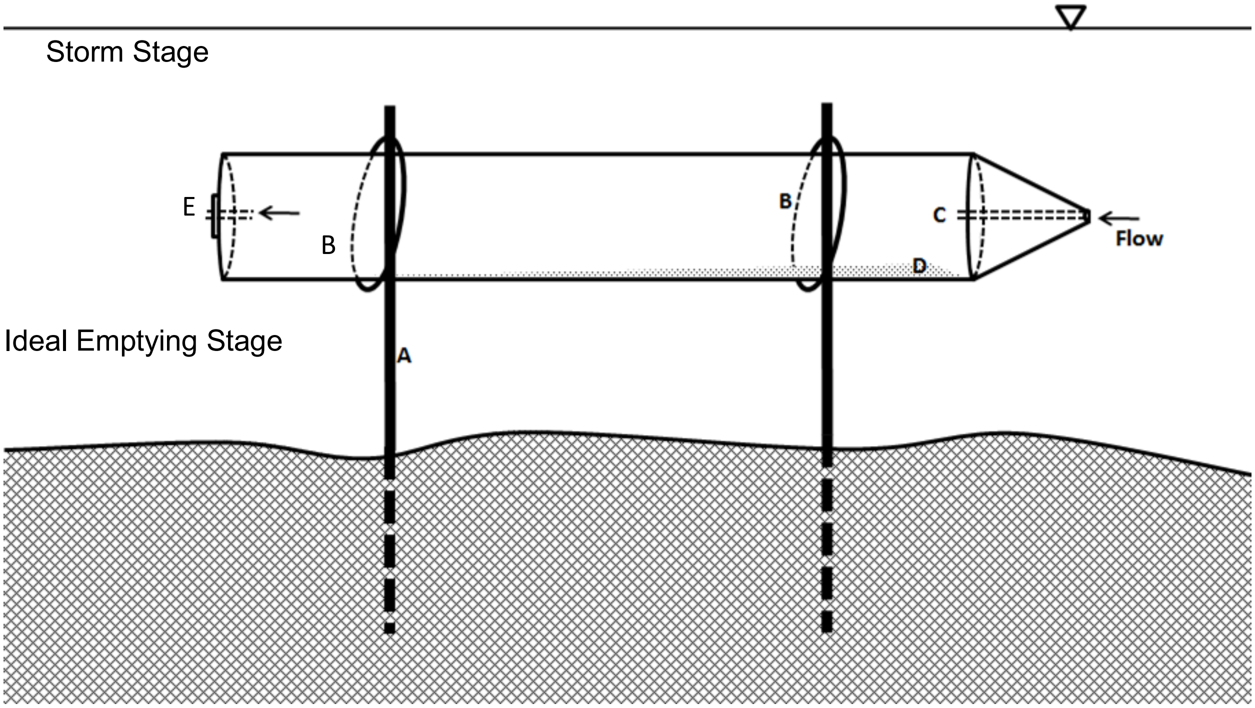

Figure 18. Suspended sediment sampler (SSS) design for installation in pairs in Stroubles Creek. The 1 m long, 98 mm diameter settling chamber was secured to the rebar supports (A) by hose clamps (B). A 4 mm inlet hose (C) at the upstream end of the sampler continuously supplied stream water to the settling chamber where sediment was deposited (D) before the sampled water was returned to the stream via a second 4 mm outlet hose. Design modified from Phillips *et al.* (*2000*).

1. If the sampler is almost entirely out of the water, unscrew the back end cap (E), but ***don't let the water drain out***. Tilt the cap backwards so that some of the water drains out, leaving only ¼ " (0.5 cm) in the bottom of the SSS, provided it is level. Screw the end cap back in.
    a. If there is no water in the SSS, raise the back of the sampler up 4", unscrew the back cap and pour about 6 oz of water into the sampler. Use the brush to scrub the dirt from inside the sampler, taking care not to lose any of the water from the sampler. Extract the brush very carefully, so that minimal water/sediment is lost. Screw the back cap into place again
2. Use the nut driver (or flathead screwdriver) to loosen the hose clamps (B), but do not totally remove them unless necessary. Slide the hose clamps up the rebar to remove the SSS from the rebar posts (it works best to lift on the clamp right below where it is attached to the rebar).
3. Place a finger over the inlet and outlet hose and shake the SSS to loosen any sediment that settled inside. Shake for 45 seconds or so to be sure all sediment is loosened
4. Keep the upstream end pointed down at a 45° angle, while unscrewing the back cap – ***make sure none of the sample is draining out the inlet hose***!
5. Pour the now-suspended sediment sample into your sample bag, taking care not to lose any of the sample. If the sample does not fit, use a second sample bag, or let the first bag settle for 5 minutes, and then pour off the upper half and add the rest of the sample from the SSS. Seal the sample bag and place it in your backpack.
    a. If considerable sediment remains after pouring off the sample, follow Step 1.a to recover the additional sediment, except that a smaller volume of water may be used.
6. Scrub the end cap with your fingers to remove any sediment from the inside of the cap, making sure the outlet hose is still clear.
7. Fill the SSS ¼ full of stream water and use the 6" brush to scrub the inside of the sampler, making sure to rotate the brush as you raise and lower the brush in the now-vertical sampler. ***Make sure to put the inlet of the sampler on the toe of your shoe/boot***, so it does not get clogged with sediment. Pour out the water back into the stream and check to be sure all sediment is removed. Repeat if necessary.
8. Replace the end cap (don't screw it to tight) and then slide hose clamps back over the rebar. Set the sampler at the desired elevation, ***making sure the 3 small air holes are facing UP***! Tighten down the hose clamps and move to the next sampler.
9. Back in the lab: let the samples settle for 3 days, then decant off the water and dry at 60°C until dry. Crush the soil and use as necessary.

Design of the samplers follows (Phillips *et al.*, 2000):

Phillips JM, Russell MA, Walling DE. 2000. Time-integrated sampling of fluvial suspended sediment: A simple methodology for small catchments. *Hydrological Processes* **14**: 14.