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Multi-year tracking of sediment sources in a small agricultural watershed using rare earth elements

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Abstract

Rare earth elements (REEs) have been successfully used as a sediment tracer, but the REE technique has never been used for studying sediment sources for a multi-year period. A nearly four-year field experiment was conducted on a small agricultural watershed near Coshocton, OH, USA, to assess the applicability of the REE technique for a multi-year period and to evaluate the relative contributions of sediment sources in the watershed. Tracer depletion and tracer enrichment ratio (ratio of the tracer concentrations in sediment to the concentrations in the soil in the areas of application) were evaluated to examine the applicability and accuracy of the technique. A minimum of 91 per cent of the mass of the applied elements was still available on any individual morphological element at the end of the experimental period. The tracer enrichment ratio varied from 0·4 to 2·3, and it was not significantly related to time. The relative contributions of six morphological elements within the watershed were evaluated as proportions to total sediment yield. The relative contribution of the lower channel was significantly increased as a function of the amount of sediment yield, while that of the lower backslope was significantly decreased. The relative contribution of the lower channel significantly decreased as a function of cumulative sediment yield, while the contributions of the shoulder and the upper backslope significantly increased. Our results showed that the REE technique can be used to track sediment sources for a relatively long period with two limitations or potential sources of error associated with a selective depletion of tracers and a contamination of downslope areas with tagged sediments from upslope areas.

Keywords: rare earth element; sediment source areas; soil erosion; hillslope hydrology; tracer depletion; tracer enrichment

Introduction

There has been an increasing interest in identifying sediment sources in watersheds. The information on sediment sources is needed for controlling soil loss and its associated nutrient and pollutant transport, and for developing appropriate watershed management tools. Tracing techniques have been developed and applied to identify and quantify sediment sources. Various soil chemical and physical properties, such as mineral magnesium (Caitcheon, 1998; Motha *et al*., 2004; Parsons *et al*., 1993), radionuclides (Murray *et al*., 1993; Ritchie *et al*., 2003, 2005; Walling and He, 1993; Walling and Woodward, 1992), particle shape and color (Krein *et al*., 2003) and overall grain-distribution of sediments (Kurashige and Fusejima, 1997) have been used as sediment tracers. The combination of several physical and chemical properties of sediments, which is called the fingerprinting technique, has been used in many studies (Carter *et al*., 2003; Collins *et al*., 2001; Collins and Walling, 2002; Krause *et al*., 2003; Walling *et al*., 1999), since multiple-tracer techniques can improve the reliability of estimates of sediment source areas (Walling *et al*., 1993).

Rare earth elements (REEs), which are elements of atomic number 57 through 71, with similar chemical properties, have been successfully used as a multi-sediment tracer (Liu *et al*., 2004; Mahler *et al*., 1998; Matisoff *et al*., 2001; Polyakov and Nearing, 2004; Wei *et al*., 2003; Zhang *et al*., 2003). REEs are nearly uniformly incorporated into

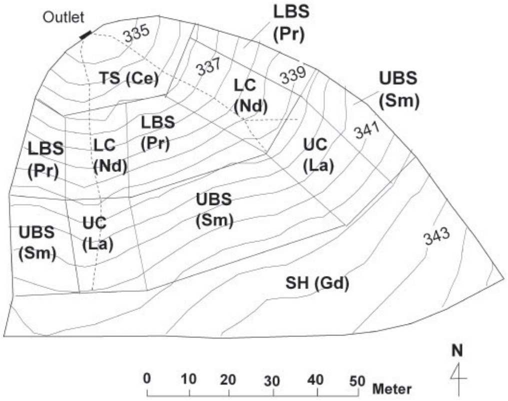

Figure 1. Topography, morphological elements and location of channels on the experimental watershed. The morphological elements were tagged with the following rare earth elements: TS (toeslope), Ce; LBS (lower backslope), Pr; UBS (upper backslope), Sm; LC (lower channel), Nd; UC (upper channel), La; SH (shoulder), Gd. The numbers on the contours show elevation (m). The contour interval is 0·5 m. The broken lines on the lower and upper channel elements show the approximate location of the incised areas with high flow accumulation.

different sizes of soil aggregates for loess-derived silt loam soils, and direct mixing of REEs does not substantially change the physicochemical properties of soil aggregates (Zhang *et al.*, 2001). In addition, REEs are relatively easily and accurately detected with inductively coupled plasma mass spectrometry (ICP-MS). Unlike fingerprinting techniques, the REE technique does not require heterogeneous soil physical and chemical properties within a watershed. The REE technique also allows the estimation of the relative contributions of specific morphological positions to sediment yield from a watershed by appropriate design of the application patterns of the tracers.

Six rare earth compounds (La_2O_3, Pr_6O_{11}, Sm_2O_3, Gd_2O_3, and CeO_2) were applied to a small, field-sized agricultural watershed (North Appalachian Experimental Watershed 127; WS 127), near Coshocton, OH, USA (Polyakov, 2002; Polyakov *et al.*, 2004). The watershed was subdivided into six different morphological elements (toeslope, upper and lower backslopes, upper and lower channels and shoulder; Figure 1), and each morphological element was tagged with a different element. Sediment translocation was examined by collecting sediment that left the watershed with surface runoff and by spatial sampling of the soil surface. The previous works (Polyakov, 2002; Polyakov *et al.*, 2004) reported that the channel elements had a higher sediment delivery ratio than did the backslope and shoulder elements, due to high sediment transport efficiency in the channel compared to the slopes.

Although the previous works (Polyakov, 2002; Polyakov *et al.*, 2004) have revealed the feasibility of using the REEs as a sediment tracer under field conditions, the applicability of REEs for successive storms for a multi-year period has never been tested. The sediment yield from WS 127 was collected for nearly four years after the original application of the tracers, and the REE concentrations in the sediment were measured to evaluate the relative contribution of each morphological element to sediment yield from the watershed. The total mass of depletion of the elements and the tracer enrichment ratio, which was defined as the ratio of the tracer concentrations in sediment to the concentrations in the soil in the areas of application, were evaluated to examine the applicability and accuracy of the technique during the experimental period. We also discussed the potential sources of error related to using the REE technique for a long period.

The aims of this study were (1) to examine the applicability of the REE technique for successive storm events for a period of nearly four years, (2) to evaluate the relative contribution of each morphological element to sediment yield from the watershed and (3) to examine the potential sources of error related to using the REE technique for a multi-year of period to study sediment sources.

Materials and Methods

Experimental site and procedures

The field-sized watershed (WS 127) was located at the USDA-ARS North Appalachian Experimental Watershed, Coshocton County, OH (40°22′ N and 81°48′ W). The details of the experimental site and the properties of applied

Table I. Tracer application, background concentrations and measured concentrations: UC, upper channel; TS, toeslope; LBS, lower backslope; LC, lower channel; UBS, upper backslope; SH, shoulder. The data was based on Polyakov (2002) and Polyakov *et al.* (2004)

		REE tracer					
	Unit	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Gd**
Application section		UC	TS	LBS	LC	UBS	SH
Area	m^2	741	550	904	717	1545	2300
Fraction of area	%	11·0	8·2	13·4	10·6	22·9	34·0
Background concentration	mg kg^{-1}	13·7	33·4	3·6	14·9	2·8	2·5
Coefficient of variation	%	7·4	8·5	7·3	8·0	4·5	9·8
Confidence of interval	mg kg^{-1}	0·21	0·43	0·05	0·20	0·09	0·13
Number of samples		91	166	102	131	11	17
Mass of elements applied	kg	12·6	28·3	5·0	10·4	4·8	9·5
Measured concentration[a]	mg kg^{-1}	239	773	81	223	49	48
Coefficient of variation	%	27·0	29·0	37·0	21·0	43·0	21·0
Confidence of interval	mg kg^{-1}	23·0	10·5	14·7	18·1	5·6	6·7
Number of samples		29	24	18	29	56	11

[a] The measured concentration is the average of 11–56 samples, depending on the size of the application area, taken after tracer application.

REEs were described by Polyakov (2002) and Polyakov *et al*. (2004). Briefly, the watershed is 0·68 ha in area with a maximum length of 125 m and slopes ranging between 1 and 12°. The primary geomorphic components of the watershed are a toeslope with a gradient ranging from 1 to 3°, a backslope with a gradient ranging from 5 to 12° and a shoulder with a gradient less than 5° (Figure 1).

The residual soils in the watershed are developed in inter-bedded clay shales and sandstone bedrock, and are represented by two soil series: Coshocton Dystric Luvisol and Haplic Luvisols (FAO classification). Average monthly temperature ranges from –2·6 °C in January to 22·4 °C in July. Average annual precipitation from 1973 to 2002 was 950 mm, and average monthly precipitation ranges from 55 mm in October to 112 mm in July. The watershed was subdivided into six different morphological elements: toeslope, upper and lower backslopes and upper and lower channels (Figure 1). The rare earth element oxide powders were thoroughly mixed with air-dry soil in an approximate proportion of 1:10 (Polyakov, 2002; Polyakov *et al*., 2004). The mixture of rare earth element and soil was wetted and air-dried again to better associate the tracer powder and soil aggregates. The mixture of a rare earth element oxide and soil taken from the watershed was spread on each morphological element on 2 May 2001 by using a calibrated 56 cm wide lawn spreader modified with heavier wheels and weights to improve traction on the loose soil surface. Soil surface samples were collected to determine the REE background concentrations (Polyakov, 2002; Polyakov *et al*., 2004). Locations of the sampling points were determined such that no two were closer than 6 m apart. A total of 94 sample locations were triangulated on the field and marked with flags. Each combined sample consisted of 30 subsamples taken randomly within a distance of 2 m from the flag to a depth of 3 cm using a metal probe 14·5 mm in diameter. The coefficient of variation (CV) of the REE background concentrations ranged from 4·5 per cent for Sm to 9·8 per cent for Gd (Table I). On average, 10 independent random samples are needed to estimate the background level of an REE element in soil with an allowable error of 5 per cent at 95 per cent confidence (Polyakov, 2002; Polyakov *et al*., 2004). The measured REE concentration was the tracer concentration in the soils in the area of application. It was the average of 11–56 samples, depending on the size of the application area, taken after tracer application using a metal probe (14·5 mm in diameter and 3 cm in depth). The CV of the measured concentrations ranged from 21·0 per cent for both Nd and Gd to 43·0 per cent for Sm. The target REE concentrations were 10–17 times the background concentrations of the elements, assuming an incorporation depth 8 cm, but the actual measured concentrations within their respective areas of application were 15–23 times the background levels (Table I). The differences between the target and measured REE concentrations probably resulted from insufficient depth of tracer incorporation (Polyakov *et al*., 2004).

The sequence of cropping and tillage practices conducted during the experimental period is summarized in Table II. Normally the watershed is disked three to four times before planting, but it was disked more intensively in 2001 to smooth the surface for tracer application and also to incorporate the applied tracer. The watershed was planted to soybeans (*Glycine max* L.) in 2001 at a spacing of 76 cm with rows along the contour. It was planted to wheat (*Triticum aestivum* L.) after soybean harvest in 2001. The wheat was undressed to red clover (*Trifolium pratense* L.) in 2002. Corn (*Zea mays* L.) was planted in 2003 and soybean was planted in 2004.

Table II. Cropping and tillage practices on Watershed 127 during the experimental period

Year	Day, Month	Operation
2001	02 May	Disk intensively
	11 May	Soybean planted
	09 October	Soybean harvested, disked once, wheat planted
2002	12 March	Red clover planted
	08 July	Wheat harvested
2003	15 April	Disked once to kill and incorporate the red clover
	23 April	Disked once
	28 April	Disked twice, corn planted
	03 November	Corn harvested
2004	11 May	Disked once
	14 May	Disked twice
	14 June	Disked once, soybean planted
	12 October	Soybean harvested

Runoff and sediment were measured at the watershed outlet on an event basis from May 2001 to September 2004. Runoff volumes were measured using a H flume equipped with an automatic water stage recorder. The sediment consisted of two components, suspended sediment that was sampled using a flow-proportional Coshocton wheel sampler (Brakensiek *et al*., 1979) and sediment that was deposited in the approach to the H flume before reaching the Coshocton wheel sampler. Most events did not deposit sediment on the flume floor. Sediment samples for each fraction (Coshocton wheel sample and flume floor sample) were air-dried, thoroughly mixed and ground prior to the REE analysis.

REE extraction and ICP-MS analysis

A sample preparation procedure modified by Zhang *et al*. (2001) from the USEPA standard method for extractions of metals from environmental samples (USEPA, 1995) was used in this study. The REE concentrations for each fraction (Coshocton wheel sample and flume floor sample) were measured separately.

One gram of sediment sample was placed into a 50 mL Erlenmeyer flask, except for two cases when the sample mass of the collected sample was insufficient. The suspended sediment sample from the Coshocton wheel sampler on 20 November 2003 and 3 April 2004 weighed only 0·3 and 0·24 g, respectively, but these samples were considered to be sufficient to obtain REE concentration values. Ten milliliters of concentrated HNO_3 (70% by weight) were added to the flask and refluxed at 85 °C for 2 hours in a water bath. After cooling to less than 70 °C, 10 mL of H_2O_2 (30% by weight) were slowly added to remove organically bound REEs. The solution was heated at 85 °C for 2–3 minutes, and then 5 mL of concentrated HCl (36% by weight) were added. The solution was refluxed again at 85 °C for 2 hours in a water bath. After cooling to room temperature, the solution was filtered through No. 5 Whatman filter paper. The solution was eluted with 5 mL of de-ionized water (18 $\mathrm{M\Omega\,cm^{-1}}$), and after a 24 hour waiting period was filtered through a 0·45 μm membrane. It was then transferred to 50 mL centrifuge tubes. The mean of the two sediment sample replicates was used in all analyses, except for the two cases where there was insufficient sample mass to obtain replicates. The extracted samples were diluted around 1000-fold in 1 per cent nitric acid and subjected to ICP-MS analysis at the Soil, Water and Environmental Science Department, University of Arizona, Tucson. Three replicate measurements were made for each extracted sample.

REE data analysis

The REE data were analyzed following the procedures of Zhang *et al*. (2003), Polyakov and Nearing (2004) and Polyakov *et al*. (2004).

Tracer depletion was evaluated as a percentage of the total mass of depletion of an element to the mass of the applied element on a morphological element:

$$D_i = \Sigma(\mathrm{MSC}_n\ \mathrm{CC}_{in} + \mathrm{MSF}_n\ \mathrm{CF}_{in})/T_i \times 100 \tag{1}$$

where D_i (%) is the ith tracer depletion, MSC_n (kg) and MSF_n (kg) are the measured sediments from the Coshocton wheel sampler and the flume floor for the nth storm, CC_{in} (mg kg^{-1}) and CF_{in} (mg kg^{-1}) are measured ith tracer concentrations in sediments from the Coshocton wheel sampler and the flume floor for the nth storm and T_i (kg) is the applied amount of the ith tracer.

The tracer enrichment ratio was defined as the ratio of the tracer concentrations in sediment to the concentrations in the soil in the areas of application. A ratio different from 1·0 is the result of preferential transport of either sediment or tracer (Polyakov and Nearing, 2004). The tracer enrichment ratio was calculated to assess the accuracy of the technique.

$$\mathrm{ER} = \Sigma[(C_{\mathrm{w}i} - C_{\mathrm{b}i})/(C_{\mathrm{a}i} - C_{\mathrm{b}i})] \tag{2}$$

where ER is a tracer enrichment ratio, $C\mathrm{w}_i$ (mg kg^{-1}) is the weighted average of the measured ith tracer concentration in sediments from the Coshocton wheel sampler and the flume floor, $C_{\mathrm{b}i}$ (mg kg^{-1}) is the measured background concentration and $C_{\mathrm{a}i}$ (mg kg^{-1}) is the measured tracer concentration in the soils in the area tagged with the ith tracer.

The relative contribution of each morphological element to sediment yield from a watershed was calculated as

$$P_i = \mathrm{CS}_i / \Sigma\mathrm{CS}_j \tag{3}$$

where P_i is the relative contribution of the ith morphological element to sediment from a watershed, CS_i (kg) is the calculated sediment from the ith morphological element and $\Sigma\mathrm{CS}_j$ (kg) is the calculated sediment from a watershed.

The sediment from the ith morphological element, CS_i, consisted of suspended sediment from the Coshocton wheel sampler and sediment from the flume floor. The sediment for each fraction was computed by the proportional method, assuming that the concentration of the tracer in bulk soil was equal to the concentration in the eroding soil. The REE concentrations in a sediment sample were compared to the background and application levels for the whole soil (Table I). Increased tracer concentration in the sediment sample indicated that the area labeled with the corresponding tracer was the sediment source. Sediment source was statistically detected if an increase in REE concentration exceeded the 95 per cent confidence limit for the background level (Table I). The sediment from a morphological element was calculated as

$$\mathrm{CS}_i = \mathrm{MSC}\ (\mathrm{CC}_i - C_{\mathrm{b}i})/(C_{\mathrm{a}i} - C_{\mathrm{b}i}) + \mathrm{MSF}(\mathrm{CF}_i - C_{\mathrm{b}i})/(C_{\mathrm{a}i} - C_{\mathrm{b}i}) \tag{4}$$

where CS_i (kg) is the sediment from a morphological element with the ith tracer, MSC (kg) and MSF (kg) are the measured sediments from the Coshocton wheel sampler and the flume floor and CC_i (μg g^{-1}) and CF_i (μg g^{-1}) are the measured ith tracer concentrations in the sediments from the Coshocton wheel sampler and the flume floor.

Results and Discussion

Storm characteristics

The characteristics of the storms that produced sediment samples from May 2001 to September 2004 are summarized in Table III. No Coshocton wheel samples were available for REE analysis for the storms of 13 April 2002, because the collected sample volume was insufficient for analysis. Thus, the REE analysis for the event was conducted by using only the flume floor sample. A hydrograph was not available for the event of 12 July 2004, because the stilling well was clogged by sediments generated during this event. The runoff volume for this event was estimated based on the volume of water collected by the Coshocton wheel sampler.

The two largest sediment yields during the experimental period were 2757 kg for the storm of 25 July 2001 and 1299 kg for 21 May 2001 (Table III). The total amount of rainfall for the storm of 25 July 2001 was the largest during the experimental period. The peak rainfall intensities for the storms of 21 May 2001 and 25 July 2001 were relatively high, being greater than 110 mm h^{-1}. However, the sediment yields for these two storms were large compared with storms of similar size and intensity during the experimental period. For example, the amount of sediment yield for the storm of 30 August 2003 was only 318·0 kg, while the total amount of rainfall for the storm was similar to the storm of 25 July 2001 and the peak rainfall intensity was 74 per cent higher (Table III). As previously noted, the watershed is normally disked three to four times before planting; however, it was disked more intensively in 2001 to smooth the surface for tracer application and to incorporate the applied tracer. This suggested that soil was more erodible for the first few storms of 2001. The large sediment yields for the storms of 2001 probably resulted from the storm size and timing and the disturbance of soils by the intensive cultivation.

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Table III. Characteristics of storms that produced sediment samples during the experimental period

Rainfall event	Rainfall		Runoff		Sediment yield		
	Total (mm)	Peak (mm h^{-1})	Total (mm)	Peak (mm h^{-1})	CWS[a] (kg)	Flume floor (kg)	Total (kg)
21 May 01	29·5	189·0	8·3	54·8	1076·7	221·8	1298·5
22 May 01	17·3	46·0	7·4	9·8	46·9	0	46·9
02 Jun 01	12·4	56·0	2·2	5·2	23·9	5·7	29·6
25 Jul 01	90·2	114·0	44·9	102·4	2341·7	415·0	2756·7
13 Apr 02	31·2	20·3	10·9	15·8	204·1[b]	1·3	205·4
31 May 03	18·8	19·1	1·2	1·1	4·0	0	4·0
11 Jul 03	19·6	110·5	5·8	28·8	42·6	212·8	255·4
16 Aug 03	16·5	65·3	0·8	5·0	4·1	0	4·1
28 Aug 03	21·8	68·6	1·0	2·6	4·8	0	4·8
30 Aug 03	78·7	198·1	44·8	34·6	318·0	0	318·0
02 Sep 03	23·9	76·2	7·9	22·9	81·7	7·3	89·0
03 Sep 03	19·3	30·5	8·0	12·5	85·5	0	85·5
23 Sep 03	30·2	68·6	12·3	10·1	75·4	0	75·4
27 Sep 03	15·7	127·0	6·9	32·4	100·6	0	100·6
28 Sep 03	27·4	91·4	17·4	20·0	245·4	0	245·4
15 Oct 03	27·7	61·0	6·3	7·6	63·6	0	63·6
27 Oct 03	7·1	5·1	5·1	1·3	30·7	0	30·7
20 Nov 03	11·9	17·8	4·3	3·6	13·3	0	13·3
29 Nov 03	21·8	12·2	11·4	3·4	27·6	0	27·6
02 Jan 04	14·0	8·6	6·2	3·4	24·8	0	24·8
04 Jan 04	19·1	15·2	13·3	7·0	52·3	0	52·3
05 Jan 04	50·8	15·2	42·2	7·6	74·3	6·0	80·3
21 Mar 04	12·4	30·5	6·8	3·0	16·6	4·8	21·4
31 Mar 04	34·8	30·5	19·1	10·5	111·3	0	111·3
03 Apr 04	12·4	3·3	5·5	0·6	0·3	8·9	9·2
13 Apr 04	17·3	5·3	1·3	0·5	14·2	0	14·2
14 Apr 04	21·3	4·3	12·8	2·1	25·0	0	25·0
19 Apr 04	11·4	54·4	0·6	0·9	6·7	0	6·7
23 Apr 04	29·7	30·5	14·9	6·4	56·3	0	56·3
26 Apr 04	8·4	61·0	0·8	1·8	10·2	8·4	18·6
03 May 04	24·9	86·4	9·4	4·1	27·4	0	27·4
08 May 04	17·8	61·0	4·4	3·0	18·0	0	18·0
19 May 04	37·3	121·9	16·4	8·3	99·0	47·6	146·6
21 May 04	11·9	61·0	2·5	1·7	17·3	0	17·3
22 May 04	21·8	68·6	12·2	5·8	98·5	17·0	115·5
29 May 04	9·9	76·2	0·1	0·2	0·3	0	0·3
01 Jun 04	34·8	86·4	10·8	7·3	44·8	11·0	55·8
12 Jun 04	37·1	35·6	20·5	6·4	105·4	51·5	156·9
14 Jun 04	38·4	137·2	20·4	30·9	697·2	263·6	960·8
15 Jun 04	13·2	76·2	2·2	3·0	37·4	11·4	48·8
12 Jul 04	11·9	83·8	0·8[c]	N/A	35·1	282·7	317·9
01 Aug 04	51·1	116·8	13·7	22·9	424·5	171·2	595·7
05 Aug 04	18·0	198·1	1·0	5·3	29·2	0	29·2
20 Aug 04	54·4	137·2	27·0	61·5	942·5	0	942·5
21 Aug 04	56·6	121·9	36·4	71·7	464·2	148·1	612·3
29 Aug 04	41·9	106·7	13·7	39·5	268·9	0	268·9
30 Aug 04	14·2	101·6	5·2	13·0	45·4	45·0	90·4
05 Sep 04	18·3	50·8	1·3	6·1	17·9	0	17·9
09 Sep 04	75·7	39·6	10·1	3·8	11·9	0	11·9

[a] Coshocton wheel sampler.

[b] No sample available for REE analysis.

[c] Estimated value.

Table IV. Mass of application and depletion of REEs and tracer depletion: UC, upper channel; TS, toeslope; LBS, lower backslope; LC, lower channel; UBS, upper backslope; SH, shoulder

		REE tracer					
	Unit	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Gd**
Application section		UC	TS	LBS	LC	UBS	SH
Mass of application of REEs	kg	12·62	28·33	5·05	10·37	4·83	9·54
Mass of depletion of REEs	kg	0·56	0·41	0·09	0·85	0·08	0·08
Tracer depletion	%	4·42	1·46	1·88	8·19	1·71	0·83

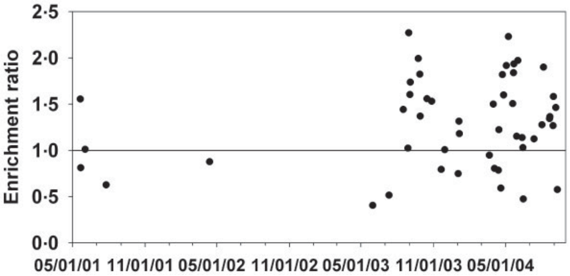

Figure 2. Tracer enrichment ratio and the measured and calculated sediment yields during the experimental period. A horizontal line shows an enrichment ratio of 1·0.

Tracer depletion

Tracer depletion was the largest on the channel elements, which was 8·2 per cent for the lower channel and 4·4 per cent for the upper channel (Table IV). Tracer depletion for the lower backslope was slightly larger than that for the upper backslope, and that for the shoulder was the least of all elements. The results were indicative of the fact that the channel elements had a relatively large soil loss compared with the other morphological elements, which was consistent with the findings of Polyakov (2002) and Polyakov *et al*. (2004). The tracer depletion for the toesplope was relatively small (Table IV). This can be explained by the fact that flows from the upper morphological elements are channeled into major rills, and most of the toeslope area has low flow concentration, although it is located adjacent to the watershed outlet (Polyakov *et al*., 2004).

Our data showed that a minimum of approximately 91 per cent of the mass of the applied REEs was still available on any individual morphological element at the end of the experimental period. This result suggested that sediment sources in the watershed could be reasonably studied by the REE technique throughout the experimental period, with some caveats to be discussed in the section 'Potential sources of error'.

Tracer enrichment ratio

The tracer enrichment ratio ranged from 0·4 to 2·3 during the experimental period, and it did not significantly decrease as a function of time (Figure 2). There were no significant relationships between tracer enrichment ratio and storm size, as characterized by the amounts of rainfall, runoff or sediment yield (a probability level of 0·05). The enrichment ratio was greater than 1·0 for 73 per cent of the storms during the experimental period. This compares with a tracer enrichment ratio for ^{137}Cs reportedly ranging from 1·1 to 3·0 (Bernard *et al*., 1998; He and Walling, 1996).

Several factors may have contributed to the enrichment ratio exceeding 1·0. One factor is the preferential transport of poorly incorporated tracers, although the REE oxide powders showed a good binding across the range of different aggregate size groups of a silt loam soil (Zhang *et al*., 2001). Non-uniform application of the tracer within a morphological element may have also contributed to the high enrichment ratio. As shown in Table I, the CV of the measured REE concentrations in the soils in the areas of application varied from 21 per cent for the lower channel (tagged with Nd) and the shoulder (tagged with Gd) to 43 per cent for the upper backslope (tagged with Sm). Since the enrichment ratio was computed using the average measured concentrations in the area of tracer application, the variation of the concentration could cause an error in the evaluation of tracer enrichment. Another factor that is possibly related to the

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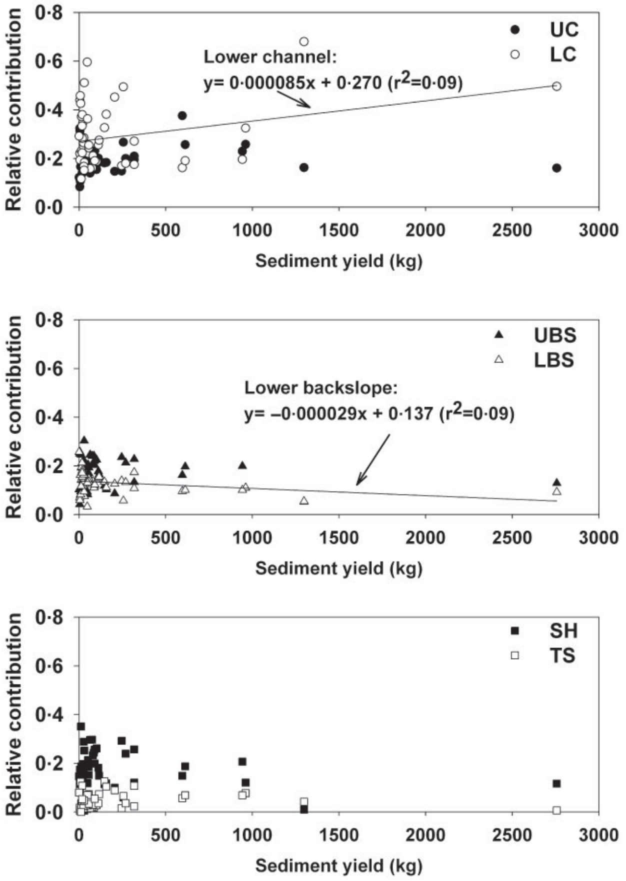

Figure 3. Relationships between sediment yield leaving the watershed and the relative contribution of individual morphological elements: UC, upper channel; TS, toeslope; LBS, lower backslope; LC, lower channel; UBS, upper backslope; SH, shoulder.

high tracer enrichment ratio is preferential transport of fine materials. Polyakov (2002) reported that the background concentrations of the REEs in the suspended sediment from the Coshocton wheel sampler were greater than those in the coarse sediment from the flume floor. He suggested that either REE elements were primarily concentrated in finer particles or that the extraction efficiency of REE for the fine particles was greater than that for the coarse ones. Our data also showed a trend of higher REE concentrations in the suspended sediment than those in the sediment deposited on the flume floor throughout the experimental period. The tracer enrichment will be overestimated if aggregates break down during transport and fine materials are preferentially delivered to the watershed outlet.

Relative contribution of morphological elements

The relative contribution of the lower channel to sediment yield from the watershed as a whole significantly increased as a function of the amount of sediment yield for a given storm ($p = 0{\cdot}03$, $r^2 = 0{\cdot}09$, $\alpha = 0{\cdot}05$; Figure 3), while the relative contribution of the lower backslope significantly decreased ($p = 0{\cdot}04$, $r^2 = 0{\cdot}09$). For all morphological elements, the variations in the relative contributions were greater for smaller storms than for larger ones (Figure 3). Quinton *et al*. (2001) indicated that clay percentage in sediment for small events was disproportionate to the size of storms and that there was more variation in clay percentage in sediment for smaller events than for larger ones. As noted before, we observed a trend of higher tracer concentration in fine materials is higher than that in coarse ones. The high variation in the relative contributions for smaller storms (Figure 3) might be related to the variability in clay content in sediment for small events.

In general, splash or sheet erosion on hillslopes is the greatest contributor to sediment loss when the storm is not large enough to generate concentrated flows, while the contribution of rill or channel erosion to sediment loss

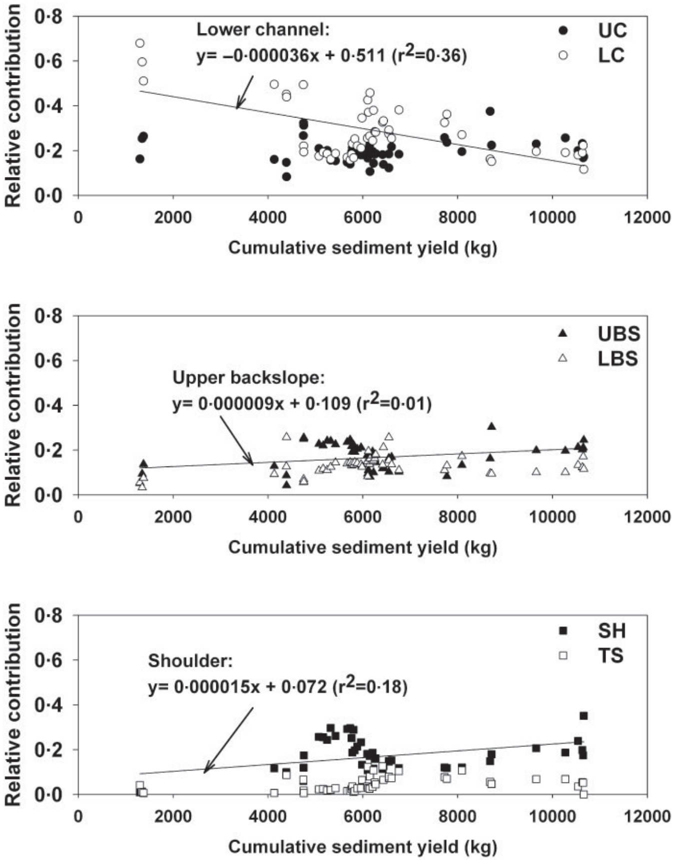

Figure 4. Relationships between cumulative sediment yield and the relative contribution of individual morphological elements: UC, upper channel; TS, toeslope; LBS, lower backslope; LC, lower channel; UBS, upper backslope; SH, shoulder.

increases with storm size (see, e.g., Morgan, 1995). The positive linear relation for the lower channel as a function of the sediment yield (Figure 3) may reflect the fact that the contribution of rill or channel erosion to sediment yield becomes greater for larger storms, while the negative linear relation for the lower backslope may result from the greater contribution of splash or sheet erosion for smaller storms. The relation was significant only for the lower channel and the lower backslope, which was probably related to the fact that these elements are relatively close to the outlet.

There is another possible explanation for the significant positive relationship for the lower channel. The correlation is obviously dependent on the two largest storms (Figure 3). These storms occurred on 21 May and 25 July 2001, and the storm of 21 May was the first one after the application of tracers (Table II). Polyakov (2002) pointed out that a partial flushing of tracer particles from the tagged soil probably occurred due to the inadequate binding of the REEs with soil aggregates. Laboratory experiments (Zhang *et al*., 2003; Polyakov and Nearing, 2004) showed the initial flushing of poorly incorporated tracers and decrease in the tracer enrichment with cumulative rainfall. The significant relationship for the lower channel may have been the result of the initial flushing of poorly incorporated tracers during the large storms of 2001. The flushing of tracer could be remarkable on the lower channel, since the sediment transport efficiency for the element is higher than for any of the other morphological elements in the watershed (Polyakov, 2002; Polyakov *et al*., 2004).

There was a significant negative linear relationship between cumulative sediment yield over the experimental period and the relative contribution of the lower channel ($\alpha = 0{\cdot}05$, $p < 0{\cdot}0001$, $r^2 = 0{\cdot}36$; Figure 4). This may have been the result of a selective depletion of the tracer in portions of the lower channel element. The first storm after the tracer application (21 May 2001) caused soil loss to the depth of tracer incorporation depth (8 cm) in portions of the channel elements (Figure 5). Although these incisions were filled by subsequent tillage operation in the following crop year (Table II), incisions with depth over 50 cm were observed on the channel elements at the end of the experiment period

Figure 5. Incision observed in the watershed as a result of the storm of 21 May 2001. This figure is available in colour online at www.interscience.wiley.com/journal/espl

Figure 6. Deeply incised area on the channel element at the end of the experimental period. This figure is available in colour online at www.interscience.wiley.com/journal/espl

(Figure 6). Although approximately 91 per cent of the applied tracer was still available on the lower channel element at the end of the experimental period (Table III), the depletion percentage in the incised areas must have been greater than the average for the channel element.

The relative contributions of the shoulder and the upper backslope as a whole increased with cumulative sediment yield ($p = 0{\cdot}002$, $r^2 = 0{\cdot}18$ for the shoulder, $p = 0{\cdot}03$, $r^2 = 0{\cdot}01$ for the upper backslope; Figure 4). This probably reflected that the sediments eroded on those upslope elements moved toward the outlet from the original positions and the re-deposited locations. The increases were significant only for the shoulder and the upper backslope, which was probably related to the fact that these elements were relatively large in area and remote from the outlet.

Potential sources of error using the REE technique for a longer time period

Our results showed that the REE technique has a reasonable potential for studying sediment sources for nearly four years. However, there were two major potential sources of error associated with using the REE technique over a longer time period. One is a selective depletion of a tracer from an element with incised areas in which concentrated flow causes soil loss below the depth of tracer incorporation, which causes the underestimation of the proportion of sediment from that area. The other potential source of error is the contamination of downslope elements with tagged sediments from upslope elements. Previous work on this watershed (Polyakov, 2002; Polyakov *et al*., 2004) showed that the lower channel was a site of deposition while at the same time it was the largest source of sediment, indicating that a large turnover of soil occurred on this element. Eroded sediments may move down-slope in a series of movements involving entrainment, deposition and possible re-entrainment, after which some of the sediment will reach the outlet. Although the REE technique allows identification of the original sediment source area, it is not capable of differentiating sediment directly transported from the original positions and re-entrained sediment from re-deposited locations. The problem becomes greater over time as more soil is displaced downslope.

Conclusion

The REE technique was applied to a small agricultural watershed in Ohio, USA, for nearly four years. The evaluation of the relative source contributions of sediment yield showed the movement of sediments originally eroded on the upslope areas toward the watershed outlet. A long-term monitoring of the relative source contributions of sediment yield will help to understand surface evolution processes. The technique may contribute to identifying dominant erosion processes during rainfall. Furthermore, it will allow validating spatially distributed erosion and sediment yield models and determining the origin of contaminants and tracing the fate and transport of agrochemicals if certain conditions are met. The REE technique has a reasonable potential for studying sediment sources for a relatively long (multi-year) period of time. However, our study pointed out that it cannot differentiate the sediments directly transported from the original positions and re-entrained sediments from re-deposited locations and it will underestimate the relative sediment amount from a morphological position if a partial depletion of tracer occurs due to flow concentration in portions of channel areas. Our study also showed other potential sources of error related to initial flushing of poorly incorporated tracers, preferential transport of fine materials and non-uniform application of a tracer within a morphological element. The preferential transport of tracer due to initial flushing will cause the overestimation of sediment yield from a morphological element. The preferential transport of fine materials will also lead to the overestimation of sediment, since either REE elements are primarily concentrated in finer particles or the extraction efficiency of REE for the fine particles is greater than that for the coarse ones (Polyakov, 2002). The variation of tracer concentration within a morphological element due to non-uniform application will result in an error in sediment estimation. Another possible limitation of the technique is the dilution of tracers. The sediment source will not be detected if the tracer concentration is diluted during transport and it falls below the detection limit (95% confidence limit for the background level in this study). This may occur, especially when the technique is applied to a large watershed. The limitations or the potential sources of error of the REE technique must be considered for studying sediment sources.

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