

Available online at www.sciencedirect.com



Catena 65 (2006) 214 - 221

CATENA

www.elsevier.com/locate/catena

### Applicability of rare earth element oxides as a sediment tracer for coarse-textured soils

A. Kimoto<sup>a,\*</sup>, M.A. Nearing<sup>a</sup>, X.C. Zhang<sup>b</sup>, D.M. Powell<sup>c</sup>

<sup>a</sup> USDA-Agricultural Research Service, Southwest Watershed Research Center, 2000 E. Allen Rd. Tucson, AZ 85719, USA

<sup>b</sup> USDA-Agricultural Research Service, Grazinglands Research Laboratory, 7207 W. Cheyenne St., El Reno, OK 73036, USA

<sup>c</sup> University of Leicester, University Road, Leicester LE1 7RH, UK

Received 4 October 2004; received in revised form 1 September 2005; accepted 28 October 2005

#### Abstract

A leaching experiment using a mixture of five REE oxides and gravelly, sandy loam soils was conducted to examine the applicability of the REE oxides as a sediment tracer for coarse-textured soils. The experiment showed little leaching of the oxides and an enrichment of various size classes of soil particles with the oxides, which reflected the strong binding capability of the REE oxides with the gravelly, sandy loam soils. It also showed that the REE oxides preferentially bound with small size classes of soil particles. The preferential binding of the REE oxides with fine materials will cause the overestimation of the soil loss from a given area (i.e., tagged with a given REE) if aggregates are broken down during sediment transport and clay materials are preferentially delivered, and if the soil loss is computed by analyzing the REE concentrations in the whole sediment. To address the non-uniform binding issue, the method based on measuring the REE concentrations for four particle size groups was tested. The potential error of the method was evaluated by comparing the soil loss that would be computed in the case that the particle size distribution was shifted to the smallest particle size class within a particle size group and in the case that no sediment sorting occurred. The result showed that the method would produce a potential error of approximately 4% in the estimation of the total soil loss when sediment sorting occurred. The non-uniform binding of the oxides, but adjustments in the technique are required for an accurate estimation of soil loss using the REE technique.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Rare earth element oxides; Coarse-textured soils; Soil erosion; Estimation of soil loss; Non-uniform binding of the REE oxides; Particle size groups

### 1. Introduction

Various soil tracers have been used to evaluate spatially distributed soil erosion and deposition rates, to study soil and sediment movements within a study area and to determine sediment sources. In recent years, <sup>137</sup>Cs, which is an environmental radionuclide, has been extensively used as a sediment tracer at various spatial scales (e.g., Quine et al., 1999; Lu and Higgitt, 2000; Schuller et al., 2003; Walling et al., 2003). The advantage of the <sup>137</sup>Cs technique

\* Corresponding author. Tel.: +1 520 670 6381.

E-mail address: akimoto@tucson.ars.ag.gov (A. Kimoto).

is that the technique produces spatially distributed erosion and deposition data based on the loss and accumulation of <sup>137</sup>Cs over the landscape. One limitation of the <sup>137</sup>Cs technique is its inability to provide short-term estimates of erosion and deposition rates, because the redistribution of <sup>137</sup>Cs gives time-integrated decadal scale average erosion and deposition rates. Another limitation is that the technique using a single tracer cannot identify the sources of sediment from a study area nor track the fate of the eroded material.

Rare Earth Elements (REEs) are the elements of atomic number 57 through 71 with similar chemical properties. The REEs have a good potential as a sediment tracer because of their strong binding capability with soil, low mobility, low natural backgrounds in soils, and lack of toxicity problems

 $<sup>0341\</sup>text{-}8162/\$$  - see front matter 0 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.catena.2005.10.002

in the environment. The REEs are relatively easily and accurately detected with inductively coupled plasma mass spectrometry (ICP-MS). Most importantly, since the REEs constitute a suite of 14 different elements, they allow identifying the sources of sediment from a study area, evaluating the relative contribution of various positions of a study area to total soil loss and tracing the fate of eroded material by the appropriate design of the application of the tracers.

Zhang et al. (2001) studied the leaching and binding characteristics of REE oxides with a loess-derived, silt loam soil. They found that the oxides were uniformly incorporated into the soil from 0.053 to 6.0 mm in a diameter of soil particle, while the oxides preferentially bound with the soil material of particle size smaller than 0.053 mm. The preferential binding with fine particles has also been reported for <sup>137</sup>Cs. The fallout <sup>137</sup>Cs deposited in the soil surface is strongly adsorbed by clay materials (He and Walling, 1996; Livens and Rimmer, 1998).

Although the REE oxides have been successfully used as a multi-sediment tracer (Mahler et al., 1998; Matisoff et al., 2001; Wei et al., 2003; Zhang et al., 2003; Liu et al., 2004; Polyakov and Nearing, 2004), the method has never been used for coarse-textured soils. As mentioned above, the REE oxides strongly bind with silt and, particularly, clay materials, and are incorporated in aggregates (Zhang et al., 2001). The aggregate binding capability of coarse-textured soils is probably lower than that of the silt loam soils that were used in previous REE studies (Zhang et al., 2001, 2003; Polyakov and Nearing, 2004; Polyakov et al., 2004), due to a less clay and silt content in those soils. This suggests that the degree of the incorporation of the REE oxides into coarse-textured soils is different among different particle sizes of the soils. This also suggests that the estimation of soil loss by analyzing the REE concentration in the whole sediment, which is a method used for the silt loam soils (Zhang et al., 2003; Polyakov and Nearing, 2004; Polyakov et al., 2004), could be more problematic for coarse-textured soils. For example, soil loss from a given area (i.e., tagged with a given REE) will be overestimated if aggregates are broken down during sediment transport and clay materials are preferentially delivered, and if the soil loss is computed by analyzing the REE concentrations in the whole sediment.

The objective of this study is to examine the applicability of the REE oxides as a sediment tracer for coarsetextured soils. A leaching experiment using five REE oxides and gravelly, sandy loam soils was conducted and the leaching and binding characteristics of the oxides for the soils were examined. As mentioned above, we anticipated that there may be less uniformity of binding of the REE oxides with the different particle sizes of the coarse-textured soils. One way to help to reduce the preferential binding problem of the REE oxides is to analyze the REE concentrations for separate particle size groups of sediment samples. If each particle size group of tagged soils is measured for REE concentration, separately, and if the size distribution of the sediment is measured, then size sorting of sediment during transport processes will not affect overall results for evaluating the soil loss from a given area. In this study, the method based on measuring the REE concentrations for four particle size groups was proposed, and the potential error of the method was evaluated.

### 2. Materials and methods

#### 2.1. Sampling sites and soil characteristic

Soils were taken at the Kendall and Lucky Hills areas of the Walnut Gulch experimental watershed (31°43'N, 110°41'W), located in southeastern Arizona, USA near Tombstone. For the time period of 1963 through 2004, the mean annual precipitation measured at the Kendall area was 315 mm and that at the Lucky Hills area was 292 mm. The mean annual temperature is approximately 18 °C. The Kendall area is largely vegetated with grass with approximately 35% canopy cover, with a trace of shrubs and forbs. The dominant vegetation types are blue grama (Bouteloua gracilis (Kunth) Lag. ex Griffiths, nom. illeg.), black grama (B. eriopoda (Torr.) Torr.), snakeweed (Gutierrezia sarothrae (Pursh) Britton & Rusby), and false Mesquite (Calliandra eriophylla Benth.). The Lucky Hills area is covered with a shrub, and the dominant species are Creosote (Larrea tridentata (Sessé & Moc. ex DC.) Coville) and Whitethorn (Acacia constricta Benth.). The soil is classified as pale brown, very gravelly, sandy loam at both the Kendall and Lucky Hills areas (USDA and NRCS, 2003). The soil after physical and chemical dispersions for the Kendall area is composed of 38.2% gravel (>2 mm; USDA classification), 33.9% sand (0.05-2 mm), 12.2% silt (0.002-0.05 mm), and 15.7% clay (<0.002 mm), and that for the Lucky Hills area is composed of 38.8% gravel, 31.6% sand, 16.2% silt 13.5% clay (Dr. Ginger Paige, personal communication). The organic carbon content of the soil surface (0-2.54)cm) is 1.0-2.0% for the Kendall area and 0-1.0% for the Lucky Hills area. The calcium carbonate content of the soil surface is 5-15% for the Kendall area and 0-4% for the Lucky Hills area. The pH of the soil surface ranges 7.4 to 8.4 for the both areas. The background REE concentrations in the three different particle size classes (<0.04 mm, 0.04-2.0 mm and 2.0-4.0 mm) of the Lucky Hills soil were shown in Fig. 1. The background concentrations of the REEs were less for larger particle size classes.

#### 2.2. Leaching experiment and soil sample preparation

The leaching and preparation procedures of soil samples for the REE analysis were followed by Zhang et al. (2001).



Fig. 1. Relationships between background concentrations and the particle sizes for the Lucky Hills soil.

Five rare earth element oxides (La<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and Gd<sub>2</sub>O<sub>3</sub>) were used for the experiment. They were purchased from Tianjiao International Trading Co.<sup>1</sup> and were the same type of oxides used in former studies (Zhang et al., 2001, 2003; Polyakov and Nearing, 2004; Polyakov et al., 2004). Median diameter of the oxides were 1.23, 16.38, 3.65, 3.61 and 2.19  $\mu$ m and specific gravities were 6.51, 6.83, 7.24, 7.68, and 7.41 g cm<sup>-3</sup> for La<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and Gd<sub>2</sub>O<sub>3</sub>, respectively (Polyakov and Nearing, 2004).

Tagged soils for the Kendall and Lucky Hills areas were prepared as follows: (1) the air-dried soils were sieved to less than 8 mm; (2) approximately 300 g of the sieved soils was wetted with de-ionized water to 15% water content; and (3) the wetted soils were mixed with predetermined amounts of all the five REE oxides, and then allowed to sit for 24 h. The amounts of the REE oxides added to the soils were decided based on a target value of 10 to 12 times of the background levels of the soil surface (0 to 5 cm) for the Lucky Hills area, since we had data only on the background concentrations of the soil from the Lucky Hills area at the beginning of the experiment. The targeted REE concentrations of the soil mixtures, using a mixture depth of 5 mm, were 331, 77, 264, 66, and 54  $\mu$ g g<sup>-1</sup> for La, Pr, Nd, Sm, and Gd, respectively.

A plastic bucket with 162 mm in diameter and 155 mm in height was used for the leaching column. The plastic bucket had several holes in the bottom in order for leachate to drain. The soils tagged with the five REE oxides and untagged original soils were packed carefully in the leaching column so that the bulk density and particle distribution of each layer of the soil approached field conditions. The tagged soil was packed in the top 5-mm layer over 95 mm of untagged soil (original soil). The untagged soil was divided into four layers, with thickness of 5, 5, 10, and 75 mm for the second, third, fourth, and fifth layers, respectively. Each layer was separated by a nylon window screen. The five soil layers for the Kendall and Lucky Hills areas were leached with 0.3 L of deionized water (equivalent to 1.5 cm depth of water) every fourth day until the total amount of water reached 1.5 L (i.e., the water was applied in five increments). Leachate was collected at the bottom of the column in a plastic box. The entire set-up, including the column and leachate collection box, was covered with a plastic film to reduce evaporation. Following leaching with 1.5-L water content, all the layers were air-dried.

The first (top) layers of the soils (i.e., tagged soils) were wet-sieved using de-ionized water and divided into ten particle size classes (Class 1: <0.01 mm, Class 2: 0.01-0.02 mm, Class 3: 0.02-0.04 mm, Class 4: 0.043-0.09 mm, Class 5: 0.09-0.18, Class 6: 0.18-0.3 mm, Class 7: 0.3-0.7 mm, Class 8: 0.7-2.0 mm, Class 9: 2.0-4.7 mm, Class 10: 4.7-8.0 mm). Although we use the terminology "particle size classes", each class consists of a mixture of aggregated material and primary sand, silt, and clay particles. The second and third layers of the soils were sieved to less than 2 mm. The fourth and fifth layers of the soils were taken at a 5-mm depth from the surface of each layer, and then sieved to less than 2 mm.

#### 2.3. REE extraction and ICP-MS analysis

A sample preparation procedure modified by Zhang et al. (2001) from USEPA standard method for extractions of metals from environmental samples (USEPA, 1995) was used in this study. Two replicated, 2 g of soil samples were taken from the original soils (untagged, no leached soils) for the Kendall and Lucky Hills areas to determine the

<sup>&</sup>lt;sup>1</sup> Trade names do not imply endorsement by the USDA or by the Agricultural Research Service.

background concentrations of the whole soils. Two replicated, 2 g of soil samples were taken from each of the 10 particle size classes of the tagged soils (the first layer) from the leaching column, as well as from the less than 2-mm soil samples from the lower four layers, except for the cases when the mass of the collected sample was not sufficient. Class 1 (<0.01 mm) for the first layer of the Kendall soil weighed only 0.04 g, and Class 1 (<0.01 mm) and Class 2 (0.01–0.02 mm) for the first layer of the soil from the Lucky Hills area weighed only 0.032 g and 0.014 g. These smaller sample sizes, with the exception of the <0.01-mm class for the Kendall soil, were sufficient to obtain REE concentration values. The measured REE concentrations in the Kendall soil for Class 1 might be less reliable.

Soil samples were placed into a 50-mL Erlenmeyer flask. Ten milliliters of concentrated HNO<sub>3</sub> (70% by weight) was added to the flask and refluxed at 85 °C for 2 h in a water bath. After cooling to less than 70 °C, 10 mL of H<sub>2</sub>O<sub>2</sub> (30% by weight) was slowly added to remove organically bound REEs. The solution was heated at 85 °C for 2 to 3 min, and then 5 mL of concentrated HCl (36% by weight) were added. The solution was refluxed again at 85 °C for 2 h 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 de-ionized water (18 M $\Omega$  cm<sup>-1</sup>), and after a 24-h waiting period was filtered through a 0.45µm membrane. It was then transferred to 50-mL centrifuge tubes. The mean of the two soil sample replicates was used in all analyses, except for the cases when there was no sufficient sample mass to obtain replicates.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis was performed at the Soil, Water and Environmental Science Department, University of Arizona, Tucson. Samples were diluted 100,000-fold in 1% nitric acid. Three replicate measurements from each extracted sample were made.

# 2.4. Soil loss estimation method and evaluation of a potential error of the method

The accuracy of the REE-estimated soil loss from a given area can be improved by measuring a greater number of particle size groups from sediment, but will be more costly. Thus, the 10 particle size classes were combined into the following four groups: Group A (<0.09 mm, which was our original particle size Classes 1–4), Group B (0.09-0.3 mm, Classes 5–6), Group C (0.3-4.7 mm, Classes 7–9), and Group D (4.7-8.0 mm, Class 10). The breakdown was based on the data of the REE concentrations for each particle size class of the soil, which is reported in Results and discussion.

The soil loss from a given area (i.e., tagged with a given REE) was computed for each particle size group

and then summed to obtain the total soil loss from the area. The proportional method used in the analysis was based on the assumption that the concentration of the tracer in bulk soil was equal to the concentration in the eroding soil (Zhang et al., 2003; Polyakov and Nearing, 2004):

$$L_{ji} = L_j (C_{mji} - C_{bji}) / (C_{aji} - C_{bji})$$
<sup>(1)</sup>

where  $L_{ii}$  is the soil loss from the area tagged with *i*-th tracer for Group  $j, L_i$  is the measured sediment for Group *j*,  $C_{mii}$  is the *i*-th tracer concentration in  $L_i$ ,  $C_{bii}$  is the *i*-th tracer background concentration for Group j and  $C_{aji}$  is the *i*-th tracer application concentration for Group j. The measured sediment for each group  $(L_i)$  was taken as 7.7, 37.5, 50.3 and 4.5 units for Groups A, B, C, and D, respectively, by assuming total soil loss is 100 units. These numbers were derived from the result that the fraction for Groups A, B, C, and D constituted 7.7%, 37.5%, 50.3% and 4.5% by weight in the soil from the Lucky Hills area, which is reported in Results and discussion. The background concentration for each group  $(C_{bii})$  was calculated by using the function shown in Fig. 1, and the tracer concentration in measured sediment of each group  $(C_{mii})$ was assumed to be three times of background concentration. (For reliable estimation, it was recommended by Tian et al., 1994 that the REE concentration measured in sediment should be at least three times that of the background concentration.) The tracer application concentration for each group  $(C_{aji})$  was the extracted REE concentration from the leaching experiment. The efficiency of the extracting method that was considered in the previous study (Zhang et al., 2001) was not a factor for sediment calculation because all REE concentrations were measured in the same manner.

The method using the four separate particle size groups should provide a better estimation of soil loss from a given area. However, the method could still overestimate the soil loss when the particle size distribution within a size group is changed by sediment sorting during transport processes. The potential error of the method based on measuring the REE concentrations for the four different particle size groups was examined by comparing the soil loss that would be computed in the case that the particle size distribution was shifted to the smallest particle size class within a group (e.g., Class 5 for Group B) and in the case that no sediment sorting occurred (i.e., particle size distribution within a group did not change). Except for Group A, the REE concentrations for the smallest particle size class within a group were used for the computation of soil loss in the case with sediment sorting. For Group A, we assumed that the two large particle size classes (Classes 3 and 4) were evenly shifted to the two small particle size classes (Classes 1 and 2), because the smallest aggregate size class (Class 1) was only 0.01% of the whole soil. The weighted averages of REE

Table 1	
Background REE concentrations in the whole soil and extracted concentrations in the leached soils	

	REE conce	REE concentration ( $\mu g g^{-1}$ )												
	Kendall ar	ea				Lucky Hills area								
	La	Pr	Nd	Sm	Gd	La	Pr	Nd	Sm	Gd				
Background for whole soil	21.0	5.2	19.0	3.7	3.6	21.4	5.3	19.6	3.8	3.8				
First layer	204.5	62.7	287.8	51.0	119.2	178.1	45.2	267.8	55.0	96.2				
Second layer	32.9	33.2	18.4	12.4	8.9	33.0	22.7	20.4	11.0	8.4				
Third layer	26.7	10.9	18.0	5.0	5.1	22.5	6.3	16.1	4.3	4.1				
Fourth layer	24.9	7.5	18.4	4.1	3.9	20.3	5.1	17.3	3.0	2.8				
Fifth layer	26.6	6.8	21.5	4.7	4.5	26.2	6.3	23.0	4.3	4.1				
Leachate	0.036	0	0.025	0	0.008	0.069	0.006	0.025	0.003	0.014				

concentrations were used for the computation in the case with no sediment sorting.

#### 3. Results and discussion

#### 3.1. REE concentrations for leached soil layers

The extracted REE concentrations for each leached soil layer and leachate and the background concentrations in the original soils were shown in Table 1. The concentrations of all the REE oxides for the first layer were the highest for the Kendall and Lucky Hills soils. The REE concentrations for the second layer were slightly higher than the third, fourth and fifth layers, but they were not nearly as high as the first layer. The concentrations for the third layer and the lower layers were not apparently different from the background concentrations in the whole soils for the Kendall and Lucky Hills areas. The REE concentrations in the leachate, except for Pr and Sm for the Kendall soil, were higher than that for de-ionized water (<0.000005  $\mu$ g<sup>-1</sup>; Zhang et al., 2001), but they were still quite small. Those results indicated that most of the REE oxides still left in the first layers soils after

leaching. The higher concentrations for the second layer than those for the lower layers was probably resulted from some cross contamination by the tagged first layer, since the second layer was in direct contact with the overlying tagged first soil layer.

The leaching results showed that the REEs bound well with the gravelly, sandy loam soils from the Kendall and Lucky Hills areas and the leaching of the oxides from the tagged layer to lower layers was minimal.

## 3.2. REE concentrations for different particle size classes of tagged, leached soils

The fractions of 10 particle size classes of the leached, REE-tagged soils (first layer) for the Kendall and Lucky Hills areas after wet-sieving were shown in Fig. 2. The extracted REE concentrations for the 10 particle size classes of the tagged soils are shown in Table 2. As noted before, the silt and clay fraction (<0.05 mm; USDA classification) after dispersion was 27.9% by weight for the Kendall area and 29.7% for the Lucky Hills area. The leached soil after wet-sieving contained only 3.2% of the fractions smaller than 0.043 mm (Classes 1, 2 and 3) for the Kendall area and



Fig. 2. Particle size distribution of the leached, tagged soils for the Kendall and Lucky Hills areas: Class 1, <0.01 mm; Class 2, 0.01-0.02 mm; Class 3, 0.02-0.04 mm; Class 4, 0.043-0.09 mm; Class 5, 0.09-0.18; Class 6, 0.18-0.3 mm; Class 7, 0.3-0.7 mm; Class 8, 0.7-2.0 mm; Class 9, 2.0-4.7 mm; Class 10, 4.7-8.0 mm.

A. Kimoto et al. / Catena 65 (2006) 214-221

Table 2	
Extracted REE concentrations in the leached.	tagged soils among the 10 particle size classes

	Particle size (mm)	e (mm) Extracted REE concentration ( $\mu g g^{-1}$ )											
		Kendall a	Kendall area					Lucky Hills area					
		La	Pr	Nd	Sm	Gd	La	Pr	Nd	Sm	Gd		
Class 1	< 0.01	1027.0	297.2	869.0	114.0	281.2	1259.8	339.7	1003.3	124.4	408.4		
Class 2	0.01 - 0.02	2231.2	601.7	1727.4	339.6	852.0	1149.3	612.7	1144.1	171.6	683.9		
Class 3	0.02 - 0.04	2145.4	610.4	1658.4	424.5	880.5	1219.8	308.9	1138.5	208.0	494.2		
Class 4	0.04 - 0.09	692.1	270.2	886.4	183.9	450.5	405.0	94.7	558.9	134.5	217.2		
Class 5	0.09 - 0.18	133.2	44.5	264.6	45.0	106.0	168.8	35.6	290.1	71.5	102.1		
Class 6	0.18-0.3	107.2	33.8	209.3	34.8	75.5	131.9	24.5	277.1	58.3	80.5		
Class 7	0.3 - 0.7	132.4	40.3	256.1	39.4	95.8	79.0	14.3	166.4	33.8	49.9		
Class 8	0.7 - 2.0	94.9	26.7	173.1	24.5	64.4	70.7	12.1	145.4	25.8	39.7		
Class 9	2.0 - 4.7	61.7	14.4	115.6	12.9	30.3	59.5	10.1	102.7	16.8	26.3		
Class 10	4.7 - 8.0	34.5	6.3	87.2	4.9	13.9	28.4	4.9	52.8	7.3	13.1		

2.9% for the Lucky Hills areas (Fig. 2). The results suggested that the aggregates of the silt and clay materials of those gravelly, sandy loam soils were not destroyed by the wet-sieving in this experiment.

All the REE concentrations in the tagged soils for the Kendall and Lucky Hills areas tended to decrease with increasing particle size (Table 2). The ratio of the extracted REE concentration to background concentration for each particle size class was computed (Table 3). The background concentration for each particle size class was estimated by using the functions shown in Fig. 1, on the assumption that the functions for the Lucky Hills soil could be applied for the Kendall soil as well. An enrichment of all the size classes of soil particles with the REEs was observed for the Kendall and Lucky Hills soils (Table 3). This showed that the REE oxides bound well with all the particle size classes of those gravelly, sandy loam soils. However, there was a trend that the REE concentrations for the smaller particle size classes were higher than those for the large ones for the Kendall and Lucky Hills soils. The exception was that the REE concentrations for Class 1 were generally less than the concentrations for Class 2, especially for the Kendall soil. This might have been resulted partially from the small sample amount of only 0.04 g in that case.

The results showed that the REE oxides were incorporated in all the size classes of soil particles for the Kendall and Lucky Hills areas, but the oxides preferentially bound with finer materials for the both soils. The non-uniform distribution of REE oxides was probably associated with less degree of aggregation of these soils as compared to previously used loess-derived soils.

# 3.3. Sediment estimation using four separate particle size groups

The ratios of the soil loss in the case that no sediment sorting occurred versus the soil loss in the case that particle size distribution was shifted to the smallest particle size class(es) were shown in Table 4. The calculated ratio of soil loss for every tracer in Group D is 1.0 because the group had only one particle size class. The results showed that the total soil loss could be overestimated or underestimated by approximately 4% if the particle size distribution was shifted to the smallest particle size class(es) in the group, due to selective deposition of coarse materials during sediment transport. The estimation of soil loss was the poorest for Group A, since the differences of extracted REE concentrations within the group were larger than those of the other groups. However, the fraction of this group of the

Table 3

Ratios of extracted REE concentrations in the leached,	tagged soils to	background	concentrations	for the 10	particle si	ize classes
--	-----------------	------------	----------------	------------	-------------	-------------

	Particle size (mm)	Ratio										
		Kendall	Kendall area					Lucky Hills area				
		La	Pr	Nd	Sm	Gd	La	Pr	Nd	Sm	Gd	
Class 1	< 0.01	41.0	47.3	35.3	24.1	66.5	50.3	54.0	40.8	26.3	96.5	
Class 2	0.01 - 0.02	95.7	103.1	76.0	77.9	215.8	49.3	104.9	50.4	39.3	173.2	
Class 3	0.02 - 0.04	96.9	110.3	77.3	103.2	234.4	55.1	55.8	53.1	50.6	131.5	
Class 4	0.04 - 0.09	33.0	51.6	43.9	47.5	126.3	19.3	18.1	27.7	34.8	60.9	
Class 5	0.09 - 0.18	6.7	9.0	14.0	12.4	31.3	8.5	7.2	15.3	19.7	30.2	
Class 6	0.18-0.3	5.7	7.2	11.7	10.1	23.3	7.0	5.2	15.4	17.0	24.9	
Class 7	0.3 - 0.7	7.4	9.2	15.3	12.4	31.5	4.4	3.3	10.0	10.6	16.4	
Class 8	0.7 - 2.0	5.8	6.7	11.5	8.6	23.1	4.4	3.0	9.7	9.0	14.2	
Class 9	2.0 - 4.7	4.2	4.0	8.6	5.0	11.9	4.0	2.8	7.6	6.6	10.3	
Class 10	4.7 - 8.0	2.5	1.9	7.1	2.1	5.8	2.1	1.4	4.3	3.1	5.5	

Table 4 Ratios of the soil loss in the case that no sediment sorting occurred versus the soil loss in the case that particle size distribution was shifted to the smallest aggregate size class(es)

	Ratio of sediment amount										
	La	Pr	Nd	Sm	Gd						
Group A	1.30	1.69	1.11	0.80	1.28						
Group B	1.09	1.15	0.99	1.06	1.08						
Group C	0.92	0.93	0.94	1.01	1.03						
Group D	1.00	1.00	1.00	1.00	1.00						
Total soil loss	0.97	0.99	0.96	1.01	1.04						

whole soil is only 7.7% (Fig. 2), and therefore the effect of the poor estimation of soil loss for this group on the estimation of the total soil loss must be small.

The above result showed that the method using the four separate particle size groups would produce a potential error of approximately 4% in the estimation of the total soil loss for the soils used in this study, when selective deposition of coarse materials occurs during sediment transport. Of course, changing the number of particle size classes within our defined groups would change this estimation, and our groupings are somewhat arbitrary. Nonetheless, this calculation provided the information on the magnitude of an error of making the calculation of soil loss using four particle size groups for coarse-textured soils in the presence of nonuniform binding of the tracer.

#### 4. Conclusions

A leaching experiment was conducted by using a mixture of the five REE oxide powders and the gravelly, sandy loam soils. The experiment showed the strong binding capability of the REE oxides with those gravelly, sandy loam soils, which is an important prerequisite for the use of the REE oxides as a sediment tracer for those soils. It also showed the non-uniform binding of the REE oxides with the gravelly, sandy loam soils. This suggested that the estimation of soil loss by analyzing the REE concentration in the whole sediment could be problematic for these coarse-textured soils when the particle size distribution of the original soils is changed by sediment sorting during sediment transport. To address the preferential binding issue, we tested the method based on measuring the REE concentrations for four particle size groups. The potential error of the method was examined by comparing the soil loss that would be computed in the case that the particle size distribution was shifted to the smallest particle size class within a particle size group by sediment sorting and the case that no sediment sorting occurred. The result showed that the method could produce a potential error of approximately 4% in the estimation of the total soil loss for the soils used in this study when selective deposition of coarse materials occurs during sediment transport.

This study indicated that the REE oxides can be reasonably used as a sediment tracer on coarse-textured soils in the presence of non-uniform binding of the oxides. The non-uniform binding of the REE oxides does not preclude the use of the oxides on those coarse-textured soils. However, the non-uniformity of binding may increase the time and cost of the analyses of the REE data, and it will further complicate the analyses if preferential deposition is active.

#### Acknowledgments

This study was partially supported by the grants from the Fund of the Japanese Ministry of Education and Culture for Science Research and by the USDA Agricultural Research Service. We gratefully appreciate Dr. Bill Emmerich, Ms. Charmaine Verdugo, Ms. Terri Kelly, Mr. Kevin Loeffelman, and Ms. Mary Kay Amistadi for helping in the laboratory work. We also appreciate Dr. Jeff Stone for helpful comments and suggestions.

#### References

- He, Q., Walling, D.E., 1996. Interpreting particle size effects in the adsorption of <sup>137</sup>Cs and unsupported <sup>210</sup>Pb by mineral soils and sediments. Journal of Environmental Radioactivity 30, 117–137.
- Liu, P.-L., Tian, J.-L., Zhou, P.-H., Yang, M.-Y., Shi, H., 2004. Sable rare earth element tracers to evaluate soil erosion. Soil and Tillage Research 76, 147–155.
- Livens, F.R., Rimmer, D.L., 1998. Physico-chemical controls on artificial radionuclides in soil. Soil Use and Management 4, 63–69.
- Lu, X.X., Higgitt, D.L., 2000. Estimating erosion rates on sloping agricultural land in Yangtze Three Gorges, China, from caesium-137 measurements. Catena 39, 33–51.
- Mahler, B.J., Bennett, P.C., Zimmerman, M., 1998. Lanthanide-labeled clay: a new method for tracing sediment transport in karst. Ground Water 36, 835–843.
- Matisoff, G., Ketterer, M.E., Wilson, C.G., Layman, R., Whiting, P.J., 2001. Transport of rare earth element-tagged soil particles in response to thunderstorm runoff. Environmental Science and Technology 35, 3356–3362.
- Polyakov, V.O., Nearing, M.A., 2004. Rare earth element oxides for tracing sediment movement. Catena 55, 255–276.
- Polyakov, V.O., Nearing, M.A., Shipitalo, M., 2004. Tracking sediment redistribution in a small watershed: implications for agro-landscape evolution. Earth Surface Processes and Landforms 29, 1275–1291.
- Quine, T.A., Walling, D.E., Chakela, Q.K., Mandiringana, O.T., Zhang, X., 1999. Rates and patterns of tillage and water erosion on terraces and contour strips: evidence from caesium-137 measurements. Catena 36, 115–142.
- Schuller, P., Ellies, A., Castillo, A., Salazar, I., 2003. Use of 137Cs to estimate tillage- and water-induced soil redistribution rates on agricultural land under different use and management in central-south Chile. Soil and Tillage Research 69, 69–83.
- Tian, J.L., Zhou, P.H., Liu, P.L., 1994. REE tracer method for studies on soil erosion. International Journal of Sediment Research 9, 39–46.
- USDA, NRCS, 2003. Soil Survey of Cochise County, Arizona, Douglas-Tombstone part. 733 pp.
- USEPA, 1995. Test Methods for Evaluating Solid Waste-SW846, Update III, 3rd ed. US Gov. Print. Office, Washington, DC.

- Walling, D.E., Collins, A.L., Sichingabula, H.M., 2003. Using unsupported lead-210 measurements to investigate soil erosion and sediment delivery in a small Zambian catchment. Geomorphology 52, 193–213.
- Wei, S., Puling, L., Mingyi, Y., Yazhou, X., 2003. Using REE tracers to measure sheet erosion changing to rill erosion. Journal of Rare Earths 21, 587–590.
- Zhang, X.C., Friedrich, J.M., Nearing, M.A., Norton, L.D., 2001. Potential use of rare earth oxides as tracers for soil erosion and aggregation studies. Soil Science Society of America Journal 65, 1508–1515.
- Zhang, X.C., Nearing, M.A., Polyakov, V.O., Friedrich, J.M., 2003. Using rare-earth oxide tracers for studying soil erosion dynamics. Soil Science Society of America Journal 67, 279–288.