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Potential use of Rare Earth Oxides as Tracers for Soil Erosion and Aggregation Studies

X. C. Zhang,* J. M. Friedrich, M. A. Nearing, and L. D. Norton

ABSTRACT

Most existing soil loss data are spatially-averaged, though various tracing techniques have been used for obtaining spatially-distributed data. Spatially-distributed soil erosion data are needed for validating physically-based erosion prediction models and for better understanding soil erosion dynamics. The objectives of this study were to evaluate the feasibility of using rare earth element (REE) oxides directly as tracers for soil erosion studies by examining their binding ability with soil materials, and also to test a quick acid-extraction procedure. Five REE oxide powders were directly mixed with a Miami silt loam soil (fine-loamy, mixed, mesic Typic Hapludalfs) and then leached with deionized water in a soil box to evaluate the mobility of REEs. Following leaching, soil samples were sectioned in 25-mm increments and analyzed for REEs. The REE-tagged soil was wet sieved to obtain REE concentrations in each aggregate size group. A simple acid-leaching method was used to extract REEs from all soil samples. The extracts were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) techniques. The data indicated that the maximum coefficient of variation of the proposed procedure was <10% for all REEs. The REE oxides were uniformly incorporated into soil aggregates of different sizes (>53 μm) and were bound with silt-size particles. This finding shows that the direct use of REE oxides is feasible, which should be superior to other REE-tagged particulate tracers because it eliminates the need of tagging exotic particles with REEs. Also, direct mixing of a trace amount of REEs does not substantially alter physicochemical properties of soil particles and aggregates. This work has shown that REE oxides have a great potential for tracing soil erosion and aggregation.

X.C. (John) Zhang, USDA-ARS, Grazinglands Research Lab., 7207 W. Cheyenne St., El Reno, OK 73036; J.M. Friedrich, Dep. of Chemistry, Purdue Univ., West Lafayette, IN 47907; M.A. Nearing and L.D. Norton, USDA-ARS, National Soil Erosion Research Lab., Purdue Univ., West Lafayette, IN 47907. Received 21 Nov. 2000. *Corresponding author (jzhang@grl.ars.usda.gov).

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SEDIMENT DELIVERY FROM SMALL WATERSHEDS OF erosion plots has been well monitored. These data are extremely useful in developing erosion prediction models, understanding erosion principles, assessing the on-site and off-site impacts, and deriving best management practices to combat soil erosion. However, these data do not contain information on soil redistribution patterns within a watershed or an erosion plot. Spatially-distributed erosion data are needed for validating physically-based erosion models and for understanding soil erosion dynamics at a process level. Since erosion processes change in time and space, physically-based models such as the Water Erosion Prediction Project model have been developed to predict soil erosion at any given time and location. Process-based models can only be thoroughly validated with spatially-distributed erosion data.

To obtain spatially-distributed data, various types of tracers have been developed and used. Most of them involve atomic bomb fallout radionuclide ¹³⁷Cs (Brown et al., 1981; Ritchie and McHenry, 1990; Martz and De Jong, 1991; Walling and He, 1999), naturally occurring radionuclides such as ²¹⁰Pb, ⁷Be, and ²³⁴Th (Wallbrink and Murray, 1993), deliberately introduced radionuclides such as ⁵⁶Fe and ⁶⁰Co (Wooldridge, 1965; Toth and Alderfer, 1960), noble metals-labeled natural particles (Olmez et al, 1994), exotic particles including glass beads, fluorescent dye coated particles (Young and

Abbreviations: ARE, average relative error; D₅₀, particle size at which 50% of particles by weight are finer than that value; DW, deionized water; ICP-MS, inductively coupled plasma-mass spectrometry; REE, rare earth element.

Holt, 1968), magnetic plastic beads (Ventura et al., 2001), steel nuts (Lindstrom et al., 1992), and rare earth element oxides (Riebe, 1995; Plante et al., 1999; Tian et al., 1994; Institute of Soil and Water Conservation, 1997). Although these tracers have proven useful, each has limitations.

Bomb-produced ^{137}Cs (half-life of 30 yr) is one of the most widely used tracers for estimating long term soil erosion rates (normally across 30 yr) and erosion patterns across a landscape. However, this method is hampered by inconsistencies and uncertainties in providing quantitative estimates due to various assumptions stemming from indeterminate input functions and indefinite spatial and depth distributions of the original deposition at the location of interest. Estimates of soil erosion rates associated with a particular level of ^{137}Cs depletion can vary by more than one order of magnitude, using different calibration relationships derived under different assumptions (Walling and Quine, 1990). Moreover, since a uniform spatial distribution of ^{137}Cs is always assumed, this tracer provides little indication regarding sediment sources.

Cosmogenic radionuclides such as ^{210}Pb (half-life of 20.2 yr) and ^7Be (half-life of 53 d) are naturally formed in the atmosphere and are brought to the earth's surface as precipitation. Due to differential depth distributions between ^{210}Pb and ^7Be , these tracers, when used in conjunction, have a potential for identifying the predominant erosion processes such as interrill or rill erosion (Wallbrink and Murray, 1993). However, because of uncertainties associated with the continuous input functions, as well as their spatial and depth distributions, these tracers, similar to ^{137}Cs , necessitate similar assumptions and therefore suffer from similar drawbacks.

Unlike bomb-produced and naturally occurring radionuclides, radioactive ions can be manipulated and deliberately introduced for studying soil erosion. For example, Wooldridge (1965) sprayed ^{56}Fe solution to the soil surfaces to study soil translocation. Toth and Alderfer (1960) tagged soil aggregates with ^{60}Co solution for studying soil aggregation. A major concern with this type of tracer is the radiological risks to both researchers and the environment. Exotic particles such as fluorescent glass beads and magnetic plastic beads have been used to overcome this concern, but pose new problems. The major criticisms for the exotic particles are that (i) exotic particles differ in size distribution, particle density, shape, surface morphology, and surface chemical properties from ambient soil particles and aggregates; (ii) these particles may not bind with soil particles and soil aggregates, and therefore are transported independently; and (iii) sensitivity of quantitative analysis is normally low, which means that a large quantity of tracers are needed to trace soil and sediment movement in a sizeable area such as in a small watershed.

Labeling natural particles of interest with noble metals (e.g., Au, Ag, In, Ir), which can be activated by neutron irradiation only during measurements, circumvents most of the drawbacks discussed above. Olmez et al. (1994) labeled natural sediment particles with Au and Ag by heating Au- or Ag-treated sediment at a

high temperature. The heating allows the labeling elements to diffuse into sediment crystalline lattice. However, this procedure may not be applicable to soils because excessive heating would dramatically alter soil chemical compositions, especially clay and organic matter fractions. Moreover, labeling procedures can be tedious and time consuming if a large quantity of tracers is needed.

Ideal tracers for studying soil erosion and sediment sources should overcome the drawbacks discussed above and possess the following properties: be strongly bound with soil particles or easily incorporated into soil aggregates, have great sensitivity in analyses, be easy and inexpensive to measure, possess low background concentration in soils, not interfere with sediment transport, have low plant uptake, be environmentally benign, and have availability of multiple tracers that are similar in physicochemical properties but are distinct in signature.

The Lanthanide elements, defined as REEs of atomic number 57 through 71 with similar chemical properties, are good candidates for use in sediment source studies. Rare earth oxides, which are insoluble in water, have been tested and used in a few pioneer studies. Tian et al. (1994) tagged soils at different slope positions with different rare earth oxides by directly mixing REE oxide powders with soils to track sediment sources and movement. Their results were satisfactory and the method was promising. Riebe (1995) used europium-labeled glass particles to monitor soil translocation. Europium oxide was fused with glass and other ingredients at 1100°C for 5 h to produce a homogenous material that had a particle density of 2.65 Mg m^{-3} . The material was further ground into sand- and silt-size fractions, and was then mixed with bulk soils. Plante et al. (1999) developed a particulate tracer by incorporating dysprosium oxide into various-size ceramic prills during prill manufacture. The use of ceramic prills was based on the assumption that surface properties of the prills would be similar to those of soil aggregates.

Availability of a sensitive, rapid, and inexpensive analysis method is another concern for selecting ideal tracers. Traditional instrumental methods of analysis include instrumental neutron activation analysis, x-ray fluorescence, atomic absorption spectrometry, and inductively coupled plasma atomic emission spectrometry. Instrumental neutron activation analysis was widely used for REE measurement for many years. However, it is relatively insensitive to the middle mass REE and is expensive to implement due to the requirement of a nuclear reactor. X-ray fluorescence is another widely used technique, but the sensitivity for REE is relatively poor (detection limits $>1 \mu\text{g g}^{-1}$). Atomic absorption spectrometry has not been widely used for REE measurement because (i) it is less sensitive to the REE than the light elements and (ii) it lacks in multi-element capability. Inductively coupled plasma atomic emission spectrometry is now widely used for measuring REE because of its low detection limits, but it can require extensive sample pretreatments, including ionic separation.

Inductively coupled plasma-mass spectrometry is a

relatively new technique that overcomes many of the above limitations. Jarvis (1989) identified the following advantages: exceptional detection limits (in the range of ng kg^{-1} to $\mu\text{g kg}^{-1}$), uniform sensitivity across the mass range, simple spectra, wide linear dynamic range (≈ 6 orders), simultaneous measurement of all REE elements, rapid analysis time (minutes per sample), and no need for chemical separation. A disadvantage of ICP-MS is the requirement to introduce the sample as an aqueous solution. Conventional sample dissolution procedures are time-consuming, which can substantially limit sample throughput. If rapid acid-leaching of the sample can be done, the high throughput of ICP-MS would be better utilized.

One advantage of direct mixing of REE oxide powders with soils is to eliminate the need of manufacturing REE-tagged exotic particles. Although Tian et al. (1994) and his colleagues (Institute of Soil and Water Conservation, 1997) have conducted some pioneer research in this aspect, the feasibility of direct use of REE oxide powders as tracers for erosion studies has not yet been fully examined. There is little information in the literature regarding the binding ability between REE oxide powders and soil particles or aggregates, which is the most important criterion in selecting ideal tracers for erosion studies. The objectives of this study were to evaluate the feasibility of direct use of REE oxide powders as tracers for soil erosion studies by examining their binding abilities with soil particles and the mobility in a soil matrix, and also to develop a quick method for sample extraction for ICP-MS analysis.

MATERIALS AND METHODS

Soil Characteristics

A Miami silt loam soil, collected from the Ap horizon near West Lafayette, IN, was air-dried and passed through a 6-mm sieve. The Miami soil had $\approx 13\%$ sand, 18% clay, 69% silt, and 1.3% organic carbon. Clay mineralogy consisted in a decreasing order illite, kaolinite, vermiculite, and smectite. Soil pH in water and 0.01 M CaCl_2 solution (1:1 solid:water ratio) was 5.7 and 5.24, respectively (Franzmeier et al., 1977). Particle size distribution was measured with a pipette method (Franzmeier et al., 1977). Organic C was measured by a dry combustion method (model CHN-60, Leco Corp., St Joseph, MI).

Rare Earth Oxide Characteristics

Five REE oxides (La_2O_3 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , and Gd_2O_3), selected mainly on the basis of their costs, were imported from the People's Republic of China. Price ranged from 4 to 25 US dollars per kilogram of oxides, depending on element and purity. Selected physical and chemical properties of REE oxides were given in Table 1. The particle density ranged from 6.5 to 7.7 Mg m^{-3} .

Particle size distribution of REE oxide powders was measured by a pipette method following Stokes' law assumptions. Two grams of each REE oxide was suspended in 45 g of deionized water (DW) in 50-mL centrifuge tubes. The tubes were gently inverted by hand several times and then allowed to settle. Five milliliters of the suspension was taken at the 50-mm depth at predetermined time intervals, calculated for the sizes of 1, 2, 4, 8, 12, and $25\ \mu\text{m}$. Several additional sizes were measured

for Pr and Sm oxides. The time intervals varied from 20 s for $25\text{-}\mu\text{m}$ to $\approx 4\text{ h}$ for the $1\text{-}\mu\text{m}$ size. All measurements were conducted at room temperature ($\approx 25^\circ\text{C}$). A logistic function was fitted to cumulative particle size distribution curves. The function takes the form of:

$$M = \frac{100}{1 + a \times \exp(-c \times d)} \quad [1]$$

where M is the cumulative mass in percent, d is the particle size, and a and c are fitted coefficients. The fitted curve was then used to calculate D_{50} (i.e., particle size at which 50% of particles by weight are finer than that value) for each oxide.

Sample Preparation and Leaching

Ten kilograms of air-dried Miami soil, which was sieved through a 6-mm sieve, was prewetted with DW to $\approx 15\%$ water content. To ensure complete mixing, soil and REE oxides were mixed by serial dilutions. Predetermined amounts of REE were first mixed with $\approx 1\text{ kg}$ of Miami soil. Additional blank soil was sequentially introduced and mixed completely. Expected REE concentrations resulted from REE addition were 177, 196, 90, 102, and $102\ \mu\text{g g}^{-1}$ for La, Pr, Nd, Sm, and Gd, respectively. Following 2 d of incubation at a temperature of 25°C , 25 mm of the REE-tagged soil was packed over a 150-mm layer of air-dried, untreated Miami soil in a 450 by 350 mm box, separated by a Nylon window screen. The soil was leached progressively with 20 liters of DW ($\approx 130\text{-mm}$ depth of water) in a period of 40 d. Two liters of DW were slowly poured into the soil box approximately every 4 d. During leaching, the box was covered with a plastic sheet to prevent evaporation, and leachate was collected from the bottom of the soil box.

Following leaching, the tagged soil layer was removed at field water capacity, air-dried, and wet-sieved to determine REE concentration in each size class. The soil below the tagged layer was sampled in 25-mm depth increments, and air-dried, sieved ($< 2\text{ mm}$), and analyzed for REE concentration.

Wet-Sieving

A wet-sieving machine similar to Yoder's device (1936) with a displacement of 38 mm and a frequency of 36 cycles min^{-1} was used to obtain aggregate size distributions. After passing through an 8-mm sieve, 580 g of air-dried, leached REE-soil was prewetted with DW under 0.5 J kg^{-1} suction on a 0.033 MPa suction plate for $> 6\text{ h}$. Following wetting, the tagged soil was sieved in DW for 25 min using a series of five 127-mm sieves (4.75, 2, 1, 0.5, and 0.21 mm). After sieving, the materials $< 0.21\text{ mm}$ were sequentially sieved through 53-, 38-, 25-, and $10\text{-}\mu\text{m}$ sieves to obtain additional size classes. These materials were oven-dried and analyzed for REE concentration.

Table 1. Selected physical and chemical properties of five rare earth element (REE) oxide powders.

Chemical formula	REE oxide	Purity†	$D_{50}\ddagger$	Particle density
		%	μm	Mg m^{-3}
La_2O_3	80.09	98.44	1.23	6.51
Pr_6O_{11}	91.86	95.53	16.38	6.83
Nd_2O_3	84.63	99.02	3.65	7.24
Sm_2O_3	95.91	98.14	3.61	7.68
Gd_2O_3	96.54	98.97	2.19	7.41

† RE oxide of interest divided by total of the five RE oxides.

‡ D_{50} = particle size at which 50% of particles by weight are finer than that value.

Acid-Extraction of Rare Earth Elements

A simple, quick acid leaching procedure, similar to a standard method used by the USEPA for extractions of metals from environmental samples (USEPA, 1995), was proposed. The procedure includes: (i) weigh 2 g of soil sample into a 50-mL Erlenmeyer flask; (ii) add 10 mL concentrated HNO₃ (70%, w/w), and reflux at 85 °C in a water bath for 1 h; (iii) after cooling to <70°C, add 10 mL H₂O₂ (30%) slowly to remove organically-bound REEs, and heat the solution for 2 to 3 min after effervescence subsided; (iv) add 5-mL concentrated HCl (36%, w/w), and reflux at 85°C in water bath for 1 h; (v) after cooling to room temperature, filter through a No. 5 Whatman (Clifton, NJ) filter paper, and elute with 5 mL DW (18 MΩ cm⁻¹); (vi) filter through a 0.45 μm membrane.

Inductively Coupled Plasma-Mass Spectrometry Sample and Standard Preparations

A 250-mg aliquot of each extract was transferred to a 50-mL polyethylene centrifuge tube and massed exactly. Stock internal standard solution containing In and Tl was added to the tube, and the volume was brought to 50 mL with 18 MΩ cm⁻¹ water. Final internal standard concentration was ≈10 ng g⁻¹ for all samples and standards. Total acid concentration of final analyzed solution was ≈1.5%.

External calibration standards were prepared from a certified stock REE solution (SPEX Sample Preparation, Metuchen, NJ; 10 μg g⁻¹) by serial dilutions in concentrations of 0, 10, 20, 50, and 80 ng g⁻¹. Calibration standards were matched in acid concentration (1.5%) and composition (HCl and HNO₃) to a typical sample. With these standards, all sample concentrations fell within the calibration range. Three replicates of each dilution were prepared for each sample, and each dilution sample was analyzed once using ICP-MS technology (Table 2).

Inductively Coupled Plasma-Mass Spectrometry Data Analysis

Raw, integrated counts per second data were manipulated in three sequential steps by a computer program. First, the program normalized the differences in internal standard concentrations between individual samples and standards. A linear scaling was used to normalize internal standard concentration of standards, samples, and blanks. Second, correction for intersample instrument response was done by linear interpolation between the two internal standards based on mass (adjusted for mass-dependent drift). Third, blank counts were

Table 2. Inductively coupled plasma-mass spectrometry (ICP-MS) operating parameters, instrument settings, and isotope monitored.

ICP-MS system: VG Elemental PQ3
RF forward power: 1400 W
RF reflected power: 2–5 W
Argon outer gas flow rate: 13.7 L/min
Argon intermediate gas flow rate: 0.7 L/min
Argon nebulizer gas flow rate: 0.73 L/min
Nebulizer gas pressure: 28–29 psi
Nebulizer type: Standard concentric (quartz)
Sampler: Ni, 1.0 mm orifice
Skimmer: Ni, 0.7 mm orifice
Scanning mode: peak jump
Replicates: 3
Points/mass: 3
Dwell time/mass: 10 ms
Collection time/replicate: 15 s
Internal standards: ¹¹⁵ In, ²⁰⁸ Tl
Analytes: ¹³⁹ La, ¹⁴¹ Pr, ¹⁴³ Nd, ¹⁴⁷ Sm, ¹⁵⁷ Gd

subtracted from the samples and standards, and the modified counts were used to compute a linear calibration of response versus concentration. From this equation, concentrations in initial soil samples were calculated by accounting for dilutions and soil sample masses.

RESULTS AND DISCUSSION

Cumulative particle size distribution of REE oxides is shown in Fig. 1A. A logistic function fitted to the data, gave coefficients of determination >0.95 for all REEs. The fit was less satisfactory for Pr, with the first peak (<10% by weight) being underrepresented. The derivative of the fitted function (i.e., particle size distribution) is plotted in Fig. 1B. The D₅₀ of Pr oxide was the coarsest, and La oxide had the finest, while the remainder ranged from 2 to 4 μm. The particle size was relatively uniform for La and Gd oxides with the maximum size being <5 μm (Fig. 1B). In comparison, Sm and Nd oxides had a wider distribution with ≈99%

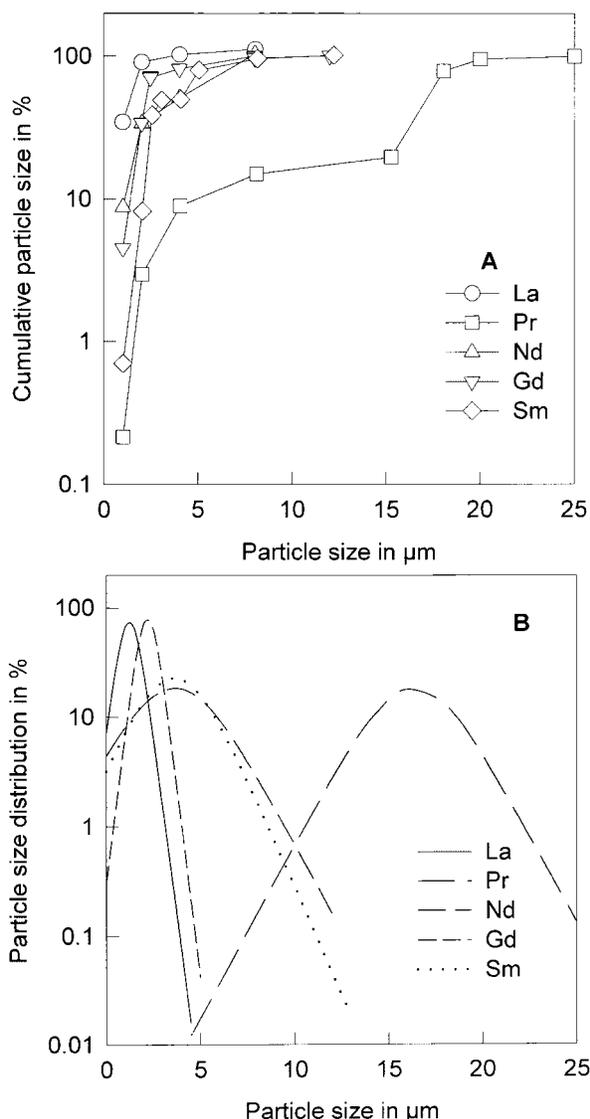


Fig. 1. Cumulative (A) and particle size (B) distributions of five rare earth oxide powders.

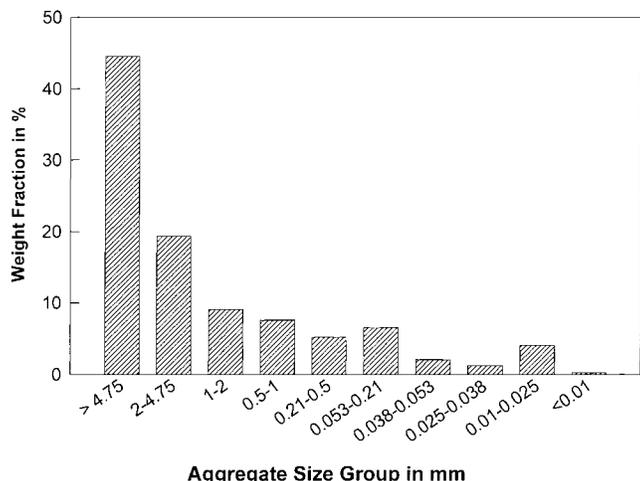


Fig. 2. Aggregate size distribution of the leached rare earth element (REE)-tagged soil after 25 min of wet sieving.

of REE oxides by weight being smaller than 10 μm . The Pr oxide had the widest and coarsest particle size distribution (Fig. 1A), ranging from 2 to 25 μm , with $\approx 90\%$ by weight being larger than 5 μm .

The leached REE-tagged soil, which was passed through an 8-mm sieve after air dried, was wet sieved to partition the whole soil into different size classes. Aggregate size distribution derived from the wet sieving (Fig. 2) indicates that most soil particles were still present in aggregated forms after 25 min of sieving. Forty-five percent of soil aggregates by weight (not corrected for sand content) were larger than 4.75 mm, and 65% were larger than 2 mm. Overall, macroaggregates (>0.25 mm) accounted for $\approx 86\%$ of the total mass, while the fraction <25 μm accounted for $<5\%$.

Extractable REE concentrations of the whole soil and individual aggregate size groups (Fig. 3) show generally a 'uniform' distribution across different size groups, indicating that these oxides were evenly incorporated into soil aggregates of the various size groups. For the size

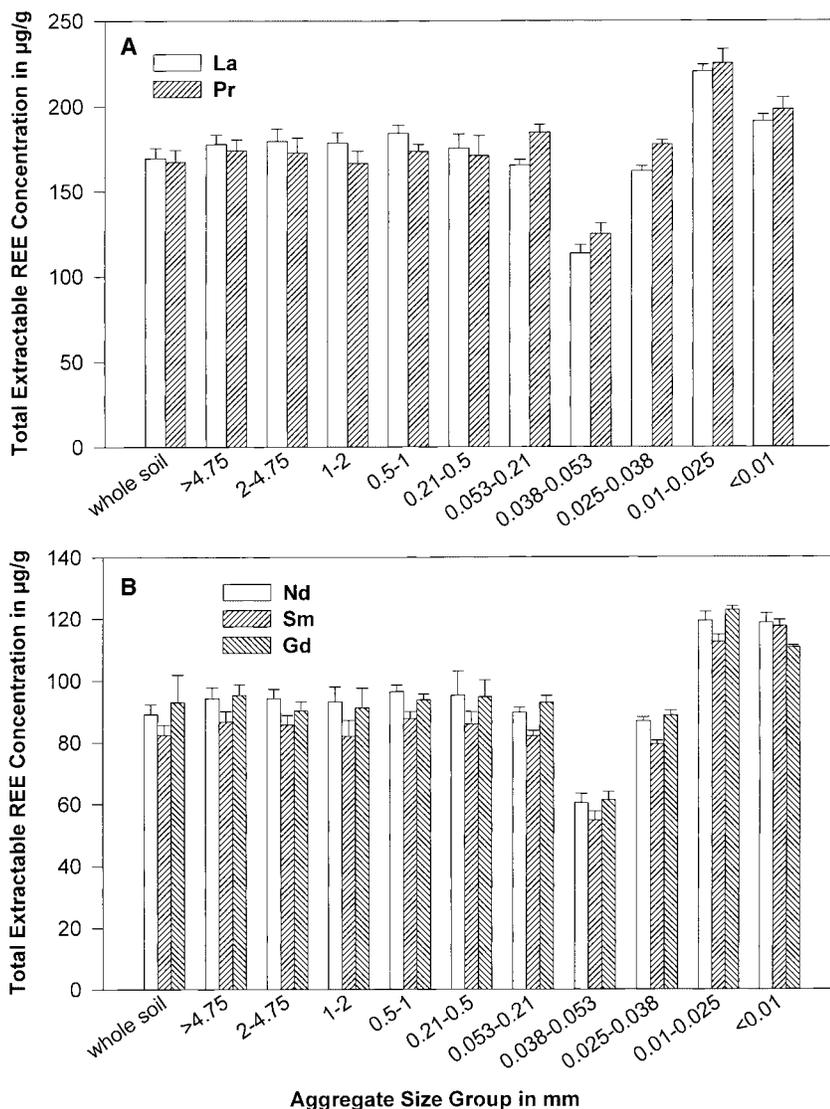


Fig. 3. Total extractable rare earth element (REE) concentrations of the leached REE-tagged soil (whole) and individual aggregate size groups after wet-sieving.

groups $>53 \mu\text{m}$, the relative concentration difference (difference in REE concentrations between a size group and whole soil divided by that of the whole soil) were within $\pm 5\%$ for most of REE oxides, suggesting that constituents that made up soil aggregates were similar to those of soil matrix. Based on the wet-sieved aggregate size distribution, these size groups ($>53 \mu\text{m}$) accounted for $\approx 92\%$ of the total soil mass.

A weak association existed between REE oxides and soil particles in the 38- to $53\text{-}\mu\text{m}$ range. The REE concentrations in this group were $\approx 30\%$ less than the whole soil. This trend was consistent for all five REEs. We do not have a satisfactory explanation for these results. The REE concentrations increased as particle and microaggregate sizes decreased ($<38 \mu\text{m}$) and peaked at the 10- to $25\text{-}\mu\text{m}$ fraction, which were $\approx 30\%$ greater than the whole soil for all REEs. This indicated that the degree of oxide-particle association apparently increased as the size decreased from 53 to $10 \mu\text{m}$. Apparently, for the $<10\text{-}\mu\text{m}$ group, concentrations were lower than those of the 10- to $25\text{-}\mu\text{m}$ group. Since 99% of all REEs excluding Pr by weight were smaller than $10 \mu\text{m}$, we do not have information on quantity of REE oxides that were actually bound with primary particles or microaggregates in this fraction. However, this fraction accounted for only 0.24% of the total soil mass. If the REE oxides had not bound with soil materials, the REE concentrations in this fraction would have been at least 400 times that of the whole soil. Overall, results demonstrated that REE oxides were uniformly incorporated into soil aggregates that were larger than $53 \mu\text{m}$, and the oxides were bound well with silt-size particles or aggregates, except for sizes between 38 and $53 \mu\text{m}$.

Concentration-depth profiles of REE oxides after leaching with 130 mm of DW are presented in Table 3. The REE-tagged soil was packed in the top 25-mm layer. The REE concentrations below the tagged soil layer ($>25 \text{ mm}$ in depth) were not significantly different from the background soil values. There was no apparent trend of REE movement within the soil profile. However, average concentrations of the five REEs in the leachate (Table 3) were higher than those in DW, which were $<0.005 \text{ ng mL}^{-1}$ for all REEs. This result suggested that REE oxides were slightly soluble at pH 5 to 6 conditions, under which this experiment was conducted. It also implies that REE mobility may increase with an increase in soil acidity. Thus, cumulative downward

Table 4. Variability of the proposed procedure as indicated by SD, CV, average relative error (ARE), and relative change (RC) due to heating and extracting time.

Element	Mean	SD	CV	ARE	RC
	$\mu\text{g g}^{-1}$		%		
Blank soil ($n = 14$)					
La	12.82	0.63	4.95	3.91	11.52
Pr	3.19	0.16	4.94	3.46	10.90
Nd	11.00	0.41	3.73	2.87	10.79
Sm	2.19	0.13	5.85	4.43	10.21
Gd	2.07	0.11	5.46	3.91	7.03
REE-tagged soil ($n = 12$)					
La	181.64	10.59	5.83	4.86	-1.59
Pr	187.43	12.58	6.71	5.63	1.89
Nd	97.92	9.05	9.24	7.28	1.97
Sm	87.01	5.72	6.57	5.16	1.96
Gd	95.24	7.30	7.66	5.86	5.38

leaching of REEs could be significant across long periods of acidic conditions. Leaching or redistribution of REEs could cause a problem for tracing soil erosion in soils with very low pH.

Parameters related to precision and consistency of the proposed extraction procedure appear in Table 4 for blank and REE-tagged soils. Standard deviations of all five REEs were $<0.63 \mu\text{g g}^{-1}$. Coefficients of variation were $<6\%$ for all REEs. Similar to CVs, average relative errors (AREs), which were calculated as averaged absolute differences between individual samples and mean value divided by the mean, were $<5\%$ for all REEs. Standard deviations of REE-tagged soil ranged from 5 to $13 \mu\text{g g}^{-1}$ for all REEs (Table 4). The CVs ranged from 5.8 to 9.2%, which were slightly greater than those of the blank soil, but were still relatively small. The ARE of all REE oxides were between 4.7 and 7.3%. Since AREs and CVs are good indicators of method precision and variability, these data indicated that the proposed extraction method was highly consistent and reproducible across individual samples within a wide range of concentrations. Considering the fact that the relative errors included inherent variations between sample replicates and errors introduced during extraction and sample dilution for ICP-MS analysis, the $<10\%$ of CVs and AREs were satisfactorily low, indicating that the method was sufficient for use in soil erosion and aggregation studies.

To evaluate the effects of heating length and extracting time on extraction efficiency, one batch of sam-

Table 3. Rare earth element (REE) concentration-depth distributions after leaching with a 130-mm depth of deionized water. Mean concentrations and SDs of REE-tagged and blank soils are also given.

Depth	La	Pr	Nd	Sm	Gd
mm					
Concentration in soil ($\mu\text{g g}^{-1}$)					
0-25	169.56	167.43	89.07	82.37	92.99
25-50	13.31	3.27	10.98	2.25	2.13
50-75	12.46	3.15	10.93	2.13	2.04
75-100	12.44	3.13	11.02	2.14	2.02
100-125	12.34	3.12	11.02	2.13	2.01
125-150	12.56	3.13	11.11	2.14	2.03
Tagged soil	181.6 \pm 10.6	187.4 \pm 12.6	97.9 \pm 9.1	87.0 \pm 5.7	95.2 \pm 7.3
Blank soil	12.8 \pm 0.6	3.2 \pm 0.2	11.0 \pm 0.4	2.2 \pm 0.1	2.1 \pm 0.1
Concentration in leachate (ng mL^{-1})					
Leachate	0.188	0.138	0.248	0.173	0.137

Table 5. Mean, SD, and CV of percentage recovery of five rare earth elements (REEs).

Element	Recovery rate [†]	SD	CV
	%		
La	95.31	5.98	6.27
Pr	94.20	6.43	6.83
Nd	96.93	10.09	10.41
Sm	83.45	5.63	6.74
Gd	91.00	7.13	7.83

[†] Percentage of added REE that has been recovered or extracted by the proposed procedure.

ples was heated for 1 h after each addition of HNO₃ and HCl, and was completed in 12 h, while the other was heated for 2 h after each addition and was completed in 24 h. The longer heating and extracting time increased extraction efficiency considerably for the blank soil, but not for the tagged soil (Table 4). This is because REE oxides dissolve in acids rapidly, so heating and extracting time is not a factor for added REE oxides. In contrast, background REEs that may exist in various soil minerals dissolve slowly with time. As a result, longer heating and extracting time increases extraction efficiency. However, this problem can be avoided by standardizing heating and extracting time. In addition, most soils have low amounts of REEs, compared with doped levels, so heating and extracting time would not be an issue.

Average percentage of recoveries along with SDs and CVs are shown in Table 5. Recovery rates were satisfactorily high (>91%) for La, Pr, Nd, and Gd, and somewhat low for Sm (≈83%). Reasons for the low recovery of Sm are unknown at this stage. More importantly, the SDs and CVs of the recovery rates were between 5 to 8% for all REEs except for Nd, whose values were around 10%. This showed that the inter-sample variations of the proposed extraction method were small, and the method was able to produce a coherent recovery rate across samples. Actually, the magnitude of percentage recovery is not a critical factor; as long as the percentage recovery is consistent, actual amounts of REEs in soils or sediments can be accurately estimated by considering the recovery rate for a particular soil in question.

Wendt et al. (1986) measured soil loss from 40 replicated field plots (differed somewhat in land use history) and found that the CV for 25 storms ranged from 18 to 91%. Nearing et al. (1999), analyzed soil losses of 2061 storms from replicated natural runoff plots at seven locations under several cropping systems, and reported that CV ranged on the order of 14 to 150%. Considering the large variability associated with measured soil loss data, a CV of <10% for the proposed procedure would provide a satisfactory means for obtaining quantitative soil erosion data.

Aggregate size distribution of eroded sediment from runoff plots depends on factors such as soil properties (e.g., soil texture and aggregate stability), rainfall and runoff characteristics, topography, surface cover and roughness, time, and predominant erosion processes (Nearing et al., 2001). However, the general consensus is that most sediment from either interrill or rill areas on a hillslope were eroded and transported in aggregates

(Alberts et al., 1980; Gabriels and Moldenhauer, 1978; Meyer et al., 1980). Meyer et al. (1980) also reported that particle size distribution of eroded sediment from interrill area resembled those of dispersed surface soil from which sediment was eroded. These results indicated that the proportion of particles that made up soil aggregates was similar to that of ambient soil. Based on these findings, REE oxide powders, which can be easily incorporated into soil by tillage operations such as disks, may be ideal tracers for studying upland erosion and sediment transport dynamics along a hillslope or within a small watershed where sediments are transported mainly in aggregates. Tian et al. (1994) and his coworkers (Institute of Soil and Water Conservation, 1997) have conducted several laboratory and field test experiments using REE oxides to trace soil erosion. Their results indicate that the REE oxide tracing technique is promising and has a great potential of studying soil erosion mechanisms and sediment transport processes.

For soil aggregation and translocation studies, Plante et al. (1999) developed a sphere tracer by tagging ceramic prills with Dy₂O₃, and Riebe (1995) produced a particle tracer by fusing Eu₂O₃ with glass. Although satisfactory results were achieved by those researchers, major concerns of using exotic particle tracers for soil erosion and aggregation studies remain as the particle tracers should possess similar particle density, size distribution, and surface reactivity to those of soil aggregates or objects of interests. This work has shown that the direct use of REE oxide powder is feasible and will eliminate the need of artificially reproducing the size and density distribution of the soil. Since REE oxide powder is very fine and only a trace amount is needed for tagging soil aggregates, it will not substantially alter the aggregate density and surface reactivity. Moreover, the aggregate size distributions will be the same as those of the soil matrix and the eroded sediment. This is critical, especially for studying upland soil erosion by water in which sediments are eroded and transported in aggregates and those aggregates are in fact varying dynamically in response to detachment and transport processes, management operations, and other changes in natural conditions.

CONCLUSIONS

The proposed extraction procedure is fast, easy, and reliable. The method was consistent across a wide range of REE concentrations for the five REEs, with CVs ranging between 6 and 11%. In conjunction with the sensitive, inexpensive, and quick (14 REE elements at a time) analysis by ICP-MS, this method makes REE tracer technique even more attractive for obtaining spatially-distributed soil erosion data.

The REE oxide powders when directly mixed with soil were uniformly incorporated into various-size soil aggregates (>53 μm), and were bound with soil particles or aggregates. Since soil aggregates always change dynamically with time, the direct use of REE oxides has the potential to mimic the real time aggregate size distribution of soil in question. This finding has shown that

the direct use of REE oxides is not only feasible, but also superior to REE-tagged particulate tracers. This is because trace amounts of REE oxides introduced would not alter physicochemical properties of soil aggregates such as density, size, shape, and surface reactivity, and it will also eliminate the problems in manufacturing artificial REE-tagged particle tracers.

Lanthanide oxides may be ideal tracers for studying soil erosion and aggregation because of their strong binding ability, low mobility, great sensitivity in analysis, quick and inexpensive determination, low backgrounds in soils, non-hazard to environment, and availability of multiple tracers that are similar in properties but distinct in signature. This work has shown that further tests of these REE tracers at plot and small watershed scales are desirable. Overall results indicate that REE tracers have a great potential for tracing soil erosion and aggregation in nonacidic moderate and heavy texture soils. However, the feasibility for tracing sandy soils needs to be further explored because of low aggregate-forming abilities.

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