



Rare Earth Element Trace Method and its Application in Study of Soil Erosion

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ABSTRACT

Soil erosion continues to be one of the world's biggest environmental problems. The information on erosion process, the spatially-distributed erosion and deposition is the key to develop soil erosion prediction models that can provide a scientific basis for soil and water conservation planning. However, conventional erosion monitoring techniques did not provide enough such information. Numerous trace materials have been applied in recent decades and been successfully utilized in soil erosion research and rare earth elements (REEs) were considered as ideal tracer materials due to their special properties. The development and improvement process of REE trace method is summarized briefly in this paper. The applications of REE trace method in studying the erosion process and the spatial distribution of erosion and deposition from slope and watershed are systematically reviewed; and its application in revealing soil erosion mechanism is also overviewed. The systematic review on REE trace method in this paper could provide scientific references for understanding the REE trace method and extending its application in wider research areas.

INTRODUCTION

Soil erosion continues to be one of the world's biggest environmental problems, affecting both developed and developing countries and resulting in decreasing chemical and physical soil fertility, affecting soil productivity and resulting in the degradation of the physical and chemical properties of the soil (Zhang et al. 2012). Understanding information on erosion process and the spatially-distributed erosion and deposition is very important for developing soil erosion prediction models, which can provide a scientific basis for soil and water conservation planning (Polyakov et al. 2004, Liu et al. 2016a). The conventional technologies for measuring water erosion rate, such as runoff plots, and ground and stereo-photo-surveys have provided much information for developing strategies for soil and water conservation (Stefano et al. 2013, Nachtergaele & Poesen 1999). However, they are always relatively expensive to be maintained and hard to provide quantitative information on the temporal and spatial distribution of erosion process and the spatially-distributed erosion and deposition (Guzmán et al. 2010).

To avoid this, numerous trace methods have been ap-

plied in recent decades and been successfully utilized in soil erosion research (Guzmán et al. 2013). The trace materials can be classified as natural and artificial. Natural trace materials like ¹³⁷Cs, ⁷Be, ²¹⁰Pb were produced from the nature and can attach to the soil (Yang et al. 2006, Mabit et al. 2008, Liu et al. 2011). The exact proportion of the fallout of these materials that combines with soil surface can be greatly spatial depending on the vegetation density. In fact, variable proportions of the fallout inventory can be intercepted and sequestered by surface vegetation (Mabit et al. 2008, Greenwood et al. 2014), which may cause some error. Artificial materials such as ¹³⁴Cs and ⁶⁰Co, ⁵⁹Fe, glass particles, magnetic tracers and REEs, were incorporated into the soil body by assumption that they bind well and can transport together with the soil particles and aggregates (Young & Holt 1968, Zhang et al. 2001, Hu et al. 2011, Greenwood et al. 2014). However, their size distribution, particle density, shape, surface morphology and surface chemical properties of the glass particles and magnetic tracers were different from those for the soil particles and aggregates (Zhang et al. 2001), leading to the phenomena of separate transportation of soil and trace material. The REEs include the atomic

number for 57-71 in chemical periodic table, about 15 kinds of chemical elements, collectively referred to as lanthanum elements and the atomic number for 21 scandium (Sc) and the atomic number for 39 yttrium (Y), which have similar properties to the lanthanum elements. REEs were stable in the biogeochemical behaviour and insoluble in runoff during the erosion process (Zhou et al. 1997). The concentrations of REEs in the soil were of low background and their concentration in soil sample can be analysed readily and accurately (Mahler et al. 1998). Meanwhile, they were environmentally safe and not detected from the different plant organs, suggesting the low absorption by plant (Liu et al. 1997a). In addition, they were closely absorbed by soil particles with minimal leaching from the tagged layer to the lower layers (Zhang et al. 2001). All these properties suggested that the REEs can act as trace materials for soil erosion research, which fulfilled almost all of the properties of the ideal tracers for studying soil erosion and sediment sources (Zhang et al. 2001). Hence, they have been widely applied in research on erosion processes and attached much attention in recent decades (Xiao et al. 2017).

Therefore, in this article, we provide an overview of development and improvement process of REE trace method and its application in spatial and temporal distribution of soil erosion from slope and watershed and in the soil erosion mechanism.

Development and Improvement Process of REE Trace Method

The stable REEs were successfully used as a tracer to study the erosion and deposition rate in the wetland by Knaus & Van Gent (1989). Some physical properties of the commonly used REE oxide in soil erosion are listed in Table 1. Tian et al. (1992) applied different kinds of REE to different slope position and determined the method for calculating the

applied REEs concentrations and the concentration of trace area to total soil erosion. The results indicated that the REE trace method can precisely distinguish the sources of the erosion from different slope position with error less than 15%, suggesting the feasibility of the REE as trace material for soil erosion. Shi et al. (1996) analysed and verified the feasibility of using REE trace method in the watershed area. Wu et al. (1997) certified the reliability of erosion distribution obtained by the REE trace method by comparing with the results obtained by measure method. Zhou et al. (1997) further verified the effectiveness of the REE trace method in soil erosion research after successfully applying the method in the indoor and field watershed area. All of these results were satisfactory and suggesting the promising of the REE trace method.

The REEs should initially be mixed thoroughly with the soil to the target application concentration. Progressive dilution method, sieving method, spreading method and spraying method were tried to incorporate REEs into the soil (Liu et al. 2004, Guzmán et al. 2013). The main idea of the progressive dilution method is to dilute the high concentration of REEs by gradually added soil and mixed them for several times until it reached the target application concentration, it has been widely used due to the uniform mixture of REEs and target soil (Liu et al. 2004, Yang et al. 2008, Xiao et al. 2017). The REEs were scattered on the soil surface and sieved multiple times to achieve a uniform mixture in the sieving method. Practically, the progressive dilution method and sieving method were time and labour consuming, leading to a limitation in large scale application. When applying in larger field experiments, spreading method and spraying methods were often applied. Polyakov et al. (2004) mixed the REEs with air-dried soil and spread them on the watershed after wetting and air-drying circle. To better associate the tagged material with the soil and to

Table 1: The physical properties of the commonly used REE oxides in soil erosion.

Chemical formula of the REE oxide	Atomic number of the REE	Molecular weight of the REE	Molecular weight of the REE oxide	Median particle diameter (μm)	Density (g/cm^3)
La_2O_3	57	138.91	325.81	4.68	6.51
CeO_2	58	140.12	172.11	20.50	7.13
Pr_6O_{11}	59	140.91	1021.44	16.38	6.83
Nd_2O_3	60	144.24	336.48	4.17	7.24
Sm_2O_3	62	150.36	348.72	5.15	7.54
Eu_2O_3	63	151.96	351.93	5.59	7.42
Gd_2O_3	64	157.25	362.50	2.12	7.41
Tb_4O_7	65	158.93	747.69	6.16	8.33
Dy_2O_3	66	162.50	373.00	4.02	7.81
Ho_2O_3	67	164.93	377.86	4.88	8.54
Tm_2O_3	69	168.93	385.87	5.73	9.32
Yb_2O_3	70	173.05	394.11	6.56	9.17

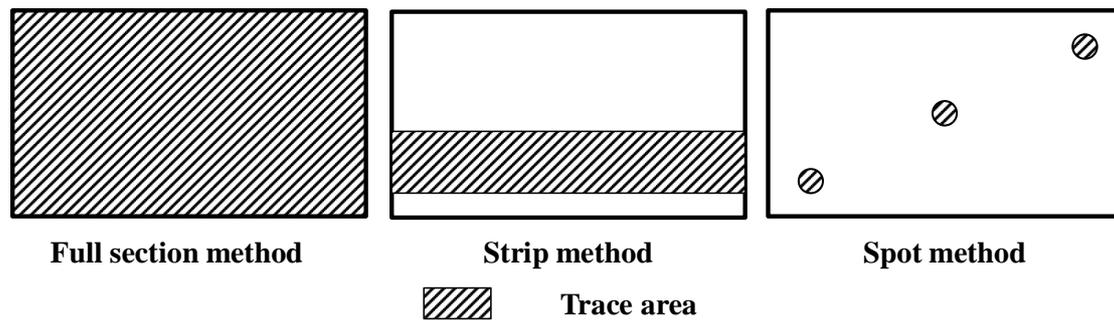


Fig. 1: Schematic representation of full section method, strip method and spot method.

reduce potential dust removal by wind, the entire area was then sprayed with water with taking care that no runoff was generated (Polyakov et al. 2009). Stevens & Quinton (2008) spread the REEs to the topsoil after mixing them with sand rather than soil for providing a number of practical benefits when working at a large scale in the field. Deasy & Quinton (2010) sprayed suspension liquid of REEs and deionized water to the hillslope by using a calibrated manual knapsack sprayer with a constant pressure valve. The spreading method and spraying method can effectively improve the mixing process in practice. However, the REEs were restricted to the upper few millimetre or centimetre, therefore, they were suitable only for short-term studies as the tagged soil layer may be rapidly eroded (Polyakov et al. 2009).

The REEs were discharged in the research area according to the design of the experiment. Full section method, strip method and spot method were frequently used by researchers (Fig. 1). The REEs were discharged to the research area in the full section method, and to a representative strip or spot area with an assumption that the erosion can represent the characteristic of the full research area in strip method and spot method, respectively. The full section method is the most commonly used because of its high precision (Tian et al. 1992). However, it was time and labour consuming when applied in large scale area. The strip method and spot method were introduced for the purpose of saving time and labour, although the selection of representative strip or spot area was difficult. Wu et al. (1997) tried to use the strip method and spot method in the field experiment, the results indicated that the strip method has a relatively higher accuracy compared to the spot method. Yang et al. (2008) used the spot method to study spatial erosion and deposition distributions on the hillslope. Liu et al. (1997b) summarized the advantages and disadvantages for these methods and pointed out that the cautions should be paid attention in practice.

Both, instrumental neutron activation analysis (INNA) and inductively coupled plasma-mass spectrometry (ICP-

MS) provided high precision in REE analysis for soil erosion research. Knaus & Van Gent (1989) and Li et al. (1997) systematically introduced the principle and method of the INNA for REE measurement, the results showed that INNA can accurately and sensitively detected the REEs in the eroded soil sample. However, it is relatively insensitive to the middle mass REE like Pr and Dy and is expensive to implement due to the requirement of a nuclear reactor (Tang et al. 2011). Zhang et al. (2001) presented the sample preparation and method for ICP-MS to analysis the REEs in the eroded soil sample. It is a relatively new technique that can detect all REEs simultaneously and rapidly with exceptional detection limits. Moreover, REEs are rare in other substances, so it can guarantee a high precision in REE analysis due to barely any disturbance during the test process. However, conventional sample dissolution procedures are time-consuming (more than 28 hours) and complex in operation, substantially leading to poor efficiency. Recently, Masselink et al. (2017) introduced a method named the Aqua Regia, in which the sample dissolution procedure is easy and fast, the high throughput of ICP-MS would be better utilized in further.

The adsorption capacity of different particle size were uneven for REEs, thus the concentration of the REEs significantly differed in each soil particle size class. Zhang et al. (2001) reported that the REEs preferentially bond with the soil particles <0.053 mm in fine-textured soil. Kimoto et al. (2006) found REEs bond well with the soil particles <0.09 mm in coarse-textured soil. Liu et al. (2016b) manifested that the <0.075 mm particle size class had the strongest adsorption capacity for REEs in the purple soil from the Three Gorges Area in China. All these results showed that the REEs preferred to bond with small soil particles. The small particles are usually preferentially eroded due to the preferential mobilization of the finer particles and the preferential deposition of the coarser fractions during the soil erosion process (Walling & Moorehead 1989, Shi et al. 2012, Shi et al. 2017). The combined effect of REEs preferentially

bond with the small particles and the preferential mobilization of the finer particles during erosion may cause systemic error for using REE trace method in soil erosion, especially when using in coarse-textured soil. The experimental errors in Liu et al. (2016a) were 35%, 25%, and 18% for rainfall intensity of 1.0, 1.5 or 2.0 mm min⁻¹, respectively. And a big experimental error was also observed from the result of Wang et al. (2008). To overcome these shortcomings, Liu et al. (2016b) improved REE trace method for soil erosion by introducing new calculation formulae, which consider the differences in adsorption ability for REEs among soil particle classes and the PSDs among the sediment and parent soil samples. The new formulae were proved to improve the accuracy of the soil loss calculation by using REEs as tracers in coarse-textured soil.

The aforementioned development process, mixing method, discharging method, REE measurement method and improvement process related to REE trace method provide technology and theory support for using this method in soil erosion under both fine-textured and coarse-textured soils.

Application of REE Trace Method in Slope Erosion

Spatially-distributed erosion data are needed for validating physically based erosion models and for understanding soil erosion dynamics at a process level (Zhang et al. 2001). It is also useful in assessing the on-site and off-site impacts, and providing basic information for management practice to combat soil erosion.

The REE trace method was tried to quantitatively study the spatially-distributed erosion information on slope since it was developed. The REEs were applied to different position to trace the erosion source (Fig. 2). Tian et al. (1992) used several REEs to divide the slope into three sections, the results showed that the erosion rate followed the ordering of downslope area, mid-slope area and up-slope area. The result was verified by Wang et al. (2008) and Zhu et al. (2011) by using REE trace method in field slope. Zhao & Shi (2003) measured the erosion and deposition rate along a much longer slope (60 m) in simulated rainfall. The results indicated that the erosion and deposition mainly concentrated in mid-slope and down-slope area, respectively. This result is consistent with the conclusions in the Polyakov & Nearing (2004). Wu et al. (1997) demonstrated the erosion rate along the slope varied by applying six kinds of REE on the field slope. Increasing trend, increasing followed by decreasing trend and wave type were observed in their research. Shi et al. (1997a) observed Weibull probability function can describe the erosion rate along the slope well. Yang et al. (2008) found soil erosion could occur at the steep slope and deposition could occur with low gradients. The

above mentioned inconsistent results can attribute to the difference in rainfall characteristics, slope gradient and length, which can result in different erosion type (i.e. interrill erosion, rill erosion or gully erosion). Stevens & Quinton (2008) applied the REEs to trace the erosion along the tramline. Michaelides et al. (2010) traced the sediment redistribution across a break in slope with gradient of 15°C declining to 2°C using rare earth elements to quantify the erosion spatially, in addition they also quantified the deposition depths spatially and the relative source contributions to deposited sediment by measuring the REE in the slope surface soil sample. Based on these, it was straightforward to conclude that the spatially-distributed erosion and deposition data can be accurately obtained by using REE trace method.

The spatial and temporal distribution of erosion information can be obtained by measuring the REEs in the eroded soil (Ju et al. 1997). Xue et al. (2005) applied different REEs to different slope position, the results indicated that the erosion rate for different position changed with the rainfall duration. Since, interrill erosion generally occurs from the upper 10 mm of soil (Liu et al. 2011, Greenwood 2012), REEs applied at different depths have the potential to distinguish erosion type during rainstorms. Song et al. (2003) studied the process of interrill erosion developed to rill erosion and the related contribution to total erosion by tracing different soil depth with different REE. Zheng et al. (2010) divided the slope erosion process into sheet (interrill ero-

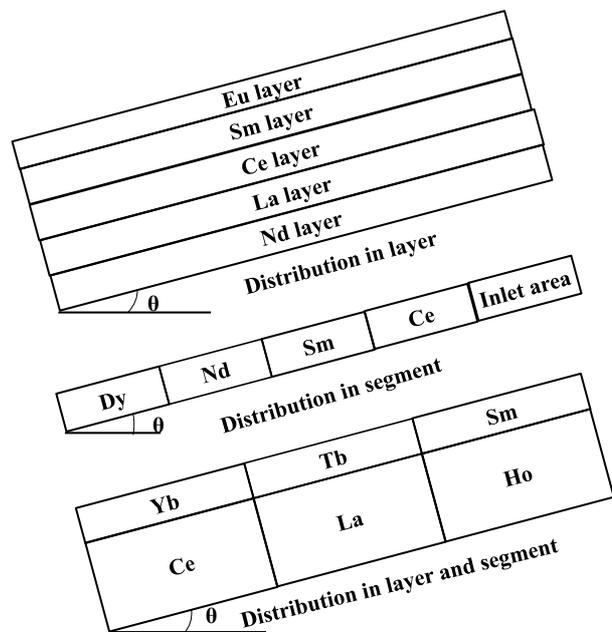


Fig. 2: The common distribution of REE styles on slope.

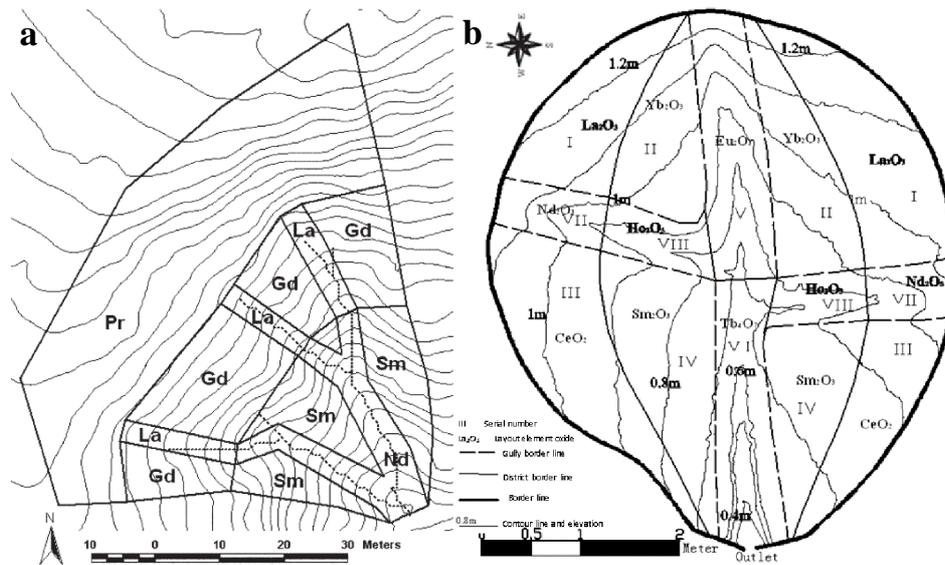


Fig. 3: The Schematic representation of REEs applied in field watershed (a-Polyakov et al. 2009) and indoor experiment (b-Liu et al. 2016a).

sion) stage, the development of rill erosion stage and the rill erosion stable stage according to the change law for contribution of interrill and rill erosion to total erosion during the rainfall duration. Furthermore, the dynamically varied data on temporal and spatial distributions in the rill erosion process under scouring test can also be monitored by using REE trace method (Li et al. 2006). They also divided the rill erosion process into the formation stage, the development stage and the decline stage based on the characteristic of erosion rate during scouring and analysed the characteristic of the amount and contribution of different trace position in different rill erosion stage. All of these findings proved that the REE tracing method was significant and helpful for understanding and disclosing the innate processes of slope erosion and rill erosion.

Application of REE Trace Method in Watershed Erosion

Watershed is the basic unit for soil and water conservation planning. It is necessary to understand the erosion process in watersheds for modelling and practice (Polyakov et al. 2004, Liu et al. 2016b). The REE trace method was also applied to investigate the spatially-distributed erosion and deposition data from the indoor and field watershed used for agricultural and rangeland (Fig. 3) (Polyakov et al. 2004, 2009, Kimoto et al. 2006, Liu et al. 2016b).

Gully-slope system is very common in the watershed, and the research on the erosion processes in gully-slope system would provide basic information to study soil erosion in watershed. Wei et al. (2009) used two continuous

slopes with two different gradients to simulate the gully-slope system for studying the soil erosion process in under scouring condition. The results showed that the erosion rate on slope was much greater than that on gully, and the erosion in this system mainly derived from the slope. Shi et al. (1996, 1997b) used REEs as tracer to study the information on the spatial and temporal erosion distribution in a small simulated watershed under simulated rainfall. Seven kinds of REEs were applied to trace the lower gully, middle gully, upper gully, lower slope, middle slope, upper slope and headward erosion areas in the watershed. The results showed that the severely eroded area changed with the development of gully in the watershed. Liu et al. (2016a) applied eight kinds of REEs to monitor the sediment sources from a miniature model of a small watershed in the Three Gorges area of China. The temporal and spatial variation of the amount and contribution of each trace area change with the rainfall duration, was quantified. The result indicated that the contribution of the gully system was greater than that of the slope, and the contributions of the gully system tended to decrease with increasing rainfall intensity and rainstorm duration. Polyakov et al. (2004) used six kinds of REEs to subdivide the natural agricultural watershed into toeslope, upper backslope, lower backslope, shoulder, upper channel and lower channel. The result indicated that the erosion rate for channels and backslopes was greater compared to the shoulder and the toeslope and the soil erode from the upper positions generally deposit on lower positions. Kimoto et al. (2006) conducted a nearly four-year field experiment on a small agricultural watershed similar to Polyakov et al.

(2004) to evaluate the relative contributions of sediment sources in the agricultural watershed by using REE trace method. The results indicated that 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 results from Kimoto et al. (2006) demonstrated that REE trace method has a reasonable potential for studying sediment sources in the field watershed experiment for a relatively long (multi-year) period of time. Polyakov et al. (2009) used five kinds of REEs as trace to divide a rangeland watershed with coarse soil into upper slope, middle slope, lower slope, upper channel and lower channel. The results showed that upper and middle channels of the watershed were eroded at a much greater rate compared with slopes, and the deposition in the lower channel was minimal because of an efficient transport system in the watershed. The results from Polyakov et al. (2009) proved that the REE trace method is a useful tool for measuring sediment redistribution in rangeland watershed with coarse soil.

Application of REE Trace Method in Soil Erosion Mechanism

The REE trace method has performed well in providing data on the spatial distribution of erosion and deposition and the amount and contribution of each trace area changed with rainfall duration in the slope and watershed. It is also applied to reveal the soil erosion mechanism by some special experimental design and analysis. Zhang et al. (2005) validated the sediment feedback relationships of the Water Erosion Prediction Project (WEPP) by quantitatively evaluating the distributed instantaneous rill erosion data using REE trace method. Tang et al. (2004) quantitatively evaluated the critical distance for soil erosion and the corresponding critical shear force for slope and analysed the relation between soil erosion and runoff hydrodynamics parameters to disclose the detachment mechanism by using this method. Lei et al. (2006) analysed the sediment concentration under different rill length during rill erosion by using REE trace method. Based on this information, Zhang et al. (2017) obtained the sediment transport capacity in eroding rills after establishing a single two-parameter exponential equation to describe the relationship between sediment concentration under different rill lengths and downslope distance. Xiao et al. (2017) established equations using an aggregate stability index to replace the erodibility factor of interrill and rill erosion in the WEPP model when the interrill and rill erosion synchronously occurred. Masselink et al. (2017) used four kinds of REEs to observe the field data on hillslope-channel connectivity and within-channel sediment dynamics.

CONCLUSIONS

A systematic review on development and improvement process of REE trace method and its application in the slope and watershed to study the spatial distribution of erosion and deposition and in soil erosion mechanism were conducted. Based on the literatures, it was straightforward to conclude that REE trace method was significant and helpful for obtaining information about the erosion and deposition and demonstrating that the spatial and temporal distribution of erosion information varied with rainfall duration in the slope and watershed. It also can be used to reveal the soil erosion mechanism by some special experimental design and analysis. The spreading method and spraying method were often used to apply for effectively improving the mixing process in practice, however, the REEs were restricted to the upper few millimetre or centimetre, thus a long-term monitor is impossible as the tagged soil layer may be rapidly eroded. Further, the REEs should be mixed in deeper depth by other method to provide more information on the spatial and temporal distribution of erosion in the field slope and watershed for long-term monitoring. And other special experimental should be designed to reveal soil erosion mechanism by using the REE trace method.

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