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TRANSPORTED IN CONCENTRATED OVERLAND FLOW USING RARE EARTH ELEMENT TRACERS

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Abstract

Rare earth element oxides (REOs) have excellent potential for use as tracers in erosion studies. Using laboratory and field experiments we aimed to develop and test a simple application method for spreading REOs and to use REOs to determine the source of sediment to concentrated overland flow paths.

Tracks left by farm machinery (tramlines) in fields act as concentrated flow paths, delivering a large amount of surface runoff and entrained sediment to the field boundary however little is known regarding where this sediment is sourced from.

Two field experiments were conducted to investigate this, one looking at whether
sediment is entrained from different points along the length of the tramline and one looking at the area over which sediment is entrained from either side of a tramline.

Results from leaching tests and rainfall simulations clearly demonstrated the potential of this method for tracing sediment, there was very little movement of REOs through the soil profile and they were transported with sediment in overland flow.

In the field experiment a large proportion of the sediment transported in the tramline originated within the first metre either side of it. However, the total area over which eroded sediment collects and flows into the tramline is potentially large with small amounts of sediment eroded from the between four and six metres being transported in the tramline.

REOs have an excellent potential for use as a tracer of soil erosion. They provide a quick and cheap method of identifying sources of eroded sediments and have good potential for use in determining erosion rates.

Keywords: Soil erosion, concentrated flow, tracer, rare earth oxides, sediment source

1. Introduction

Water erosion of agricultural soils has been widely recognised as a global environmental problem for many years. In the United Kingdom rates of erosion appear to have remained constant over the last 20 years (Evans, 2005). Soil surfaces that are bare or have low vegetation cover during the autumn and winter, such as winter cereal crops, are especially susceptible to erosion (Quinton and Catt, 2004). In areas where soils are readily erodible this problem can be serious with rates of erosion typically between 0.5 and 200 t ha$^{-1}$ yr$^{-1}$ (Chambers et al, 2000).
Erosion can cause a reduction in soil quality with negative impacts on soil structure and fertility potentially resulting in a loss of productivity. Eroded sediment also causes a reduction in water quality of nearby water bodies by increasing turbidity, reducing light penetration, clogging fish gills and destroying aquatic habitats through sedimentation. As soils erode they also transport other pollutants such as heavy metals (Quinton and Catt, 2007) and nutrients (e.g. Quinton et al., 2001; Heygarth, 2005) into watercourses contributing to a range of environmental problems including eutrophication.

Concentrated flow erosion, in the form of rills or gullies, is an important vector for sediment and pollutants to reach water courses as the rate of erosion is much higher from rills and gullies (Torri et al., 1987). Recently it has become apparent that the tracks left by farm machinery (tramlines) through fields are acting as concentrated flow paths and are responsible for delivering a disproportionate amount of material to the field boundary (Silgram et al., 2007). Tramlines are established at the time of sowing and are used throughout the growing season to prevent crop damage during spraying and fertilizing operations. Tramlines provide an important conduit for surface runoff and the sediment transported in it due to the bare compacted soil found within them. Earlier initiation of runoff, lack of crop cover, compaction and the channelling effect of tramlines have all been identified as factors contributing to the transport of sediment in tramlines (Reed, 1979; Fullen, 1985; Withers et al., 2006). Withers et al. (2006) found that runoff was initiated sooner in tramline areas than non-tramline areas and total runoff volumes were increased by up to 65%. Loads of suspended sediments were up to five times higher from areas with tramlines than from those without. Tramlines are clearly a very important feature in the landscape providing a pathway for the rapid transport of sediment. Despite their
importance they have received relatively little research attention and little is known about where the sediment transported in the tramlines originates from.

The collection of spatially distributed erosion data is a generic problem in soil erosion research. Spatially distributed data is important not only for understanding soil erosion processes, but also for the development and validation of soil erosion models (Zhang et al., 2003a). The need to identify sediment source areas has led to the development of a number of different tracer techniques including $^{137}$Cs (e.g. Poreba, 2006), $^7$Be (e.g. Schuller et al., 2006), $^{210}$Fe (e.g. Motha et al., 2002), magnetic susceptibility (e.g. Blake et al., 2006) and glass or plastic beads (e.g. Cochrane and Flanagan, 2006). Of these, $^{137}$Cs has received the most research attention and has become an established method for studying the redistribution of soil on hillslopes. However, many of the tracers above suffer from having poor resolving power when it comes to the identification of sediment source areas. In the case of $^{137}$Cs it is possible to identify accumulation areas and loss areas but not to explicitly link the two. For the spatial validation of models or for studies linking pollutant source with sink explicitly linking source areas with receptors is a necessity.

Rare earth element oxide (REO) tracers provide a promising alternative to the approaches described above and have been successfully used in several studies (e.g. Polyakov et al., 2004; Wei et al., 2003; Lei et al., 2006). Rare earth elements, or lanthanides, range from atomic numbers 57 to 70 in the periodic table. Although called the ‘rare earths’ they are not uncommon in the natural environment and occur in a number of minerals, although concentrations in soil are generally low. The oxides of rare earth elements are very stable and non-toxic making them suitable for application in the environment. They also satisfy the characteristics of sediment tracers identified by (Zhang et al., 2001). Namely that: they should be bind strongly to
soil particles; not interfere with sediment transportation; be easy and inexpensive to measure; have low background concentrations; not be easily taken up by plants and not be damaging to the environment.

REOs were first used as a horizon marker, rather than as a tracer, by Knaus and van Gent (1989) to investigate accretion in a wetland habitat. Initial studies on the use of REOs as tracers were conducted by Tian et al. (1994) who concluded that REOs could potentially be used to accurately determine the spatial distribution of soil erosion. (Matisoff et al., 2001) also developed a similar method, determining that REOs provided a robust method for tracing soil movement with tagged particles and behaved in the same manner as untagged material. Since then considerable development work has been conducted by Nearing and his research group. (Zhang et al., 2001) determined that REO oxides were evenly incorporated in aggregates sized between <0.053mm and 6mm, but with some preference for binding with the fraction smaller than 0.053mm. They also found no REO vertical movement of REOs in the soil profile after leaching with deionised water. Laboratory studies have demonstrated the potential of this technique for generating spatially and temporally distributed data allowing quantification of soil redistribution (Zhang et al., 2003b; Polyakov et al., 2004). Field application of REOs have been successful allowing mapping of soil redistribution in a small watershed over short and multi-year timescales (Polyakov et al., 2004; Kimoto et al., 2006a). Although REOs bind strongly with silt and clay their preference for binding with small particle sizes means they are less suitable for use with coarse soils. Kimoto et al. (2006b) worked on gravelly sandy loam soils where they found errors were higher because of selective deposition in coarse materials, while this did not preclude the use of REOs as tracers in these soils, it did lead to increased complexity of analysis in order to determine
sediment loss rate and analysis costs. REOs have also been used to study the processes of rill formation (Wei et al., 2003; Xue et al., 2004, Lei et al., 2006).

In this paper we set out to do two things: to develop and test a simple application method for spreading REOs and to use REOs to determine the source of sediment to concentrated overland flow paths. This paper reports the findings of laboratory experiments on REO application method and two field experiments, one looking at whether sediment is entrained from different points along the length of the tramline and one looking at the area over which sediment is entrained from either side of a tramline.

2. Methods

2.1 Laboratory studies

A bulked soil sample was collected from three mid and lower slope areas at the study site (see below) in order to determine background concentrations of rare earth elements.

Dry soil samples were ground to <2mm, background rare earth element concentrations were determined using extraction with an aqua regia digest in open glass tubes in a block digester (McGrath and Cunicliff, 1985) followed by analysis using a Thermo Elemental X7 inductively coupled plasma-mass spectrometer (ICP-MS). Although not used in some previous studies with REOs (e.g. Polyakov and Nearing, 2004) this method is a standard method for the extraction of heavy metals from soils and is established for use with REOs (Diatioff et al., 1996). Extractions were carried out to ensure recovery was consistent between elements and comparable to the methods used in previous studies (Pryce and Quinton, unpublished data).
results of this initial survey suggested that whilst Gadolinium (Gd), Neodymium (Nd), Praseodymium (Pr) and Samarium (Sm) showed acceptable levels of variation (less than 15% variation between repeated measures) within the soil Lanthanum (La) was too variable (approximately 150% between repeated extracts from a bulked sample). Background concentrations of the REOs in the soil used in this study were 3.8 mg kg\(^{-1}\) for Gd, 24.5 mg kg\(^{-1}\) for Nd, 6.0 mg kg\(^{-1}\) for Pr and 5.1 mg kg\(^{-1}\) for Sm. The particle size distribution of the REOs investigated in this experiment and the soil used were determined in suspension with 4% calgon using a Malvern Mastersizer.

For all of the experiments conducted, REOs were applied at ten times the background concentration. Air dry soil was ground to <2 mm and mixing was carried out using a hand whisk in a covered bowl.

Prior to application in the field it was important to determine whether the REOs would move vertically through the soil profile. To test this, a leaching experiment was set up. 200ml of soil (ground to 2mm) was placed in a 5cm diameter glass open top funnel with glass fibre wool in the base to prevent blockages. 20g of soil mixed with REOs was spread evenly over the soil surface (giving an approximate depth of 1cm) and glass fibre wool was placed in the top of the tube. 500ml of deionised water was leached through the tubes over a period of 48 hours. Three replicates were used for each of Gd, Nd, Pr and Sm. Once the leaching had been completed the soil core was carefully removed from the tubes and cut into segments for analysis. The top segment was taken at 0-0.5 cm, then 0.5-1.5, 4-5, 8-9 and 13 -14 cm. These were dried and ground for extraction and analysis as described above.

To compare the application of REOs to the soil surface mixed in either soil or sand a rainfall simulation experiment was carried out. Mixing the REOs with sand rather than soil provides a number of practical benefits when working at a large scale
in the field saving time in the preparation of REOs for spreading. Experiments were conducted using 25 x 50 cm boxes of soil with a collector at one end for surface runoff. A slope angle of 8° was used. The rainfall simulator was gravity fed and had a drop height of 287 cm, a rainfall intensity of 56 mm h⁻¹, mean drop size of 2.2 mm and used deionised water.

Boxes were half filled with sand then filled to the top with soil. The soil surface was moistened under the rainfall simulator and topped up if necessary. REOs were mixed with either dry soil or dry sand using a hand mixer. For the REO-soil mixture 0.5 kg of soil mixed with REOs at ten times the background concentration was spread evenly over the soil surface (62.5 g m⁻² of REO-soil mix). In order to achieve an application rate of ten times the background concentration for the sand mixture, a maximum depth of interaction of 4cm (determined using the leaching experiment, see results below) and a bulk density of 1.2 g cm⁻³ were used to calculate the quantity of REOs required to be mixed with sand over a given area, giving an application rate of 28.2 g m⁻² of REO-soil mix. The boxes were then placed under the rainfall simulator; surface runoff was collected for 10 minutes. The collected runoff was centrifuged, decanted and evaporated to remove excess water. Dried sediments were ground for extraction and analysis as described above.

2.2 Field studies

The field experiments were conducted at the Allerton Trust Farm at Loddington, Leicestershire (52.60N, 0.83W). Soils were heavy clays belonging to the Hanslope and Denchworth series (Haplaquept, suborder Aquents) on a slope of approximately 5°. The area selected for the investigation had been ploughed up and down the slope with one 100m long tramline and was sown with an oat crop. The
experiment was conducted between 30th November 2006 and 14th December 2006. During this time there was a total of 25.6mm rain with one particularly large rainfall event on the 11th December when 9.2mm of rain fell in 24 hours. Runoff was collected in covered drains at the base of the slope and was stored in 500 l tanks for sub-sampling. Sediments were sub-sampled by taking 1l mixed water and sediment samples from the tanks which were centrifuged, decanted and evaporated to remove excess water. Additional sediments were collected by allowing sediment in the tanks to settle and carefully pumping water out then collecting deposited sediment. This method ensured that both the fine and coarse sediments were sampled. Sediments were dried and ground prior to REE analysis as described above.

REO sand mixtures were spread in the field using a push along fertiliser spreader. This was calibrated to spread the REO-sand mix at a rate of 28.2 g m$^{-2}$, giving an even coverage at a low rate. Experiments were conducted 5 m upslope of the runoff collection drains which were sunk to a level flush with the soil surface.

Experiment 1 was used to investigate distance over which soil moves into tramlines from either side of the tramlines. Bands of REOs were spread parallel to the tramline. Figure 2a shows the layout of the experiment in the field. A 1 m wide, 5 m long band of Sm was spread either side of the tramline (the tramline was masked with a plastic sheet to prevent REOs to prevent contamination), a 1m wide band of Nd was spread either side of this followed by 2 m wide bands of Nd and Gd. Only one wheeling of the tramline was established so the experiment was repeated on both sides of this wheeling.

Experiment 2 was used to investigate whether sediment collected from the tramline was entering along the whole length of the tramline. Bands of REOs were placed along the contour perpendicular to the tramline (Figure 2b). Bands of REOs
were 1 m wide and 1 m long placed either side of the tramline. The tramline was masked with a plastic sheet to ensure the REOs collected came from outside the tramline.

3. Results

3.1 Particle size analysis

The particle size distributions of the REO and the soil used are given in Figure 1. All of the samples had similar median particle sizes: 6.7 µm, 5.7 µm, 5.7 µm 7.2 µm and 6.6µm for Pr, Gd, Sm, Nd and the soil respectively. Pr had a second peak at 23 µm and a together with the soil greater proportion of particles in the 60 -100 µm range.

3.2 Leaching experiment

Analysis of the soil core segments from the leaching experiment consistently showed that levels of REOs in the soils was elevated in the first few centimetres (Figure 3). For all of the elements investigated this had returned to background levels by 4 cm (figure 3). This was taken as the maximum zone of interaction.

3.3 Rainfall simulator experiments

Results of the rainfall simulator experiments using REOs mixed in soil and sand showed that REOs were enriched in the sediment (Table 1). Concentrations of REOs in sediment applied in soil were not significantly different to concentrations when REOs were applied with sand (Mann-Whitney U-test: Gd p=0.82, Nd p=0.59, Sm p=0.48, Pr p=0.59). Variability in the concentration of REOs in eroded sediment was considerably higher for REOs applied in sand than when applied in soil (Table 1).
The variability was approximately constant for the different elements applied when applied mixed in soil whereas, when applied mixed in sand, some elements showed a greater variability than others. There was no difference in total sediment losses between the sand and sediment applications which suggests that the difference in particle size of the application medium was responsible for the difference in variability. Although application in sand has some benefits the greater variability with the sand-REO mix than with the soil-REO mix suggests that more replicates are needed if the former is used.

3.4 Field experiments

The enrichment ratio for Pr from experiment 1 was clearly different from that for Gd, Nd and Sm (Table 2). Figure 4 shows the concentration of the REOs in soil and sediment eroded from experiment 1. The enrichment of Pr in samples is much higher than for the other REOs, indicating that more sediment is sourced from one metre either side of the tramline than from 2-4 m, but that sediment is transported by up to 4 m before being delivered to the tramline. The assumption has been made that all REOs tag similarly across different aggregate sizes (proven in Zhang et al., 2001) and that aggregate sizes transported from different areas are similar. As the particle sizes of the REOs are similar to each other and the soil (figure 1) we believe that the enrichment ratios in Table 2 are a result of transport from different source areas rather than selective erosion of REOs already within the soil. This is corroborated by the concentrations of REOs in sediment collected from different parts of the hillside (from a different event), but without any applied REOs, where background concentrations of REOs were slightly lower than the soil indicating that they were not concentrated by selective transport of eroded sediment (3.5 mg kg\(^{-1}\) for Gd, 21.7 mg kg\(^{-1}\) for Nd, 5.2 mg kg\(^{-1}\) for Pr and 4.8 mg kg\(^{-1}\) for Sm).
Enrichment ratios in experiment 2 (Table 2) showed very little variation between elements. This suggests that all four areas along the length of the tramline are contributing equal amounts to the sediment collected in runoff. Even though the application of REOs was adjacent to the tramlines (between zero and one metre) enrichment ratios are lower than for experiment 1. However, enrichment per unit area of application is similar.

4. Discussion

Initial laboratory experiments demonstrated the suitability of REOs for identifying sediment sources. Leaching experiments showed that in this soil type REOs only interacted with the soil surface and there were not significant losses due to leaching. This is an essential characteristic of a tracer but the shallow zone of interaction is problematic where rills form causing soils to erode from below the zone of interaction diluting the tracer concentration. Mixing the soil by ploughing could reduce this problem.

The rainfall simulator studies showed that REOs are eroded with soils (whether they are applied mixed with soil or sand). When applied to the soil surface, mixed with soil, results were consistent between rainfall simulations which suggest that the REOs bind with the soil and are eroded at the same rate. These findings are as expected from previous work by Zhang et al. (2001, 2003), Polyakov et al. (2004) and Polyakov and Nearing (2004) who have shown rare earth elements make very good tracers in fine textured soils such as these. When applied mixed with sand however, there was considerable variability in the concentrations of REOs being eroded with the soil although the means were similar to the soil REO applications. The most likely explanation for the high variability in REO retrieval when applied in sand is
inadequate mixing settling out or the formation of aggregates as a result of the differing textures of the REOs and sand. A more consistent result was obtained when mixing the REOs in soil for application which suggests that there is good potential for the use of REOs to estimate erosion rates in the future on soils with similar particle size distributions.

In the field experiment a large proportion of the sediment transported in the tramline originated within the first metre either side of it. This would suggest that the majority of material is transported over relatively short distances before entering the tramlines. Enrichment (per m$^2$) was twice as high for the second band at 1-2 metres (Sm) than for the 2-4 and 4 to 6 metre bands suggesting that much of the remaining sediment comes from the next metre either side. However, the total area over which eroded sediment collects and flows into the tramline is potentially large with small amounts of sediment eroded from the between four and six metres being transported in the tramline. As tramlines are frequently spaced every 12 metres these results imply that tramlines act as conduits for sediment generated over the entire field.

Almost equal amounts of REO enrichment were found from the four source areas along the length of the tramline showing that over the 4m length of the experiment all areas contributed an approximately equal amount of sediment despite variation in the topography. This would imply that detachment and transport processes are occurring at approximately the same rate in all areas to the side of the tramlines and that once delivered to the tramline that there is little selective deposition of the different elements in the overland flow.

Monitoring over three subsequent events (data not presented here) showed declining levels of REO tracer in eroded sediment with each event. After three events they had not returned to background levels. REOs may be suitable for identifying
source areas over longer periods of time but not for calculating rates of sediment erosion over multiple events. Re-mobilisation may be an issue in considering losses from multiple events.

REOs have an excellent potential for use as a tracer of soil erosion. The use of a sand REO mixture in our work was partially successful. It provides a rapid cost effective means of preparing the tracer for field application, avoiding the need to dry and grind large quantities of soil. However, mixing the samples was problematic leading to more variability in tracer delivery than when the REOs were mixed with soil. Combined with the shallow application depth this means we can only derive qualitative data at this stage. When applied to the soil surface mixed with soils there is very good potential for use as a tracer for both identifying sediment source areas and estimating total sediment losses. These techniques are very promising and have a great number of potential applications in the areas of soil erosion and diffuse pollution.

Acknowledgements

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Table 1. Mean concentration (mg kg\(^{-1}\)) and enrichment ratio (REO concentration in eroded sediment divided by REO concentration in soil) of rare earth elements in eroded sediments in the rainfall simulation experiments (co-efficient of variance for concentration (%) is shown in parentheses) where the rare earth elements were applied either mixed in sand or soil (three replicates for each).

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration in eroded sediment (soil) (mg kg(^{-1}))</th>
<th>Enrichment ratio (soil)</th>
<th>Concentration in eroded sediment (sand) (mg kg(^{-1}))</th>
<th>Enrichment ratio (sand)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>37.38 (14.2)</td>
<td>3.99</td>
<td>32.50 (49.9)</td>
<td>5.38</td>
</tr>
<tr>
<td>Sm</td>
<td>26.85 (18.6)</td>
<td>6.62</td>
<td>36.89 (68.4)</td>
<td>7.28</td>
</tr>
<tr>
<td>Nd</td>
<td>142.06 (16.6)</td>
<td>4.53</td>
<td>163.14 (59.0)</td>
<td>6.65</td>
</tr>
<tr>
<td>Gd</td>
<td>30.20 (16.7)</td>
<td>5.34</td>
<td>22.03 (56.0)</td>
<td>5.75</td>
</tr>
</tbody>
</table>
Table 2. Enrichment ratio of REOs in experiments 1 and 2 (standard deviation is shown in parentheses).

<table>
<thead>
<tr>
<th>Element</th>
<th>Enrichment ratio (Exp. 1)</th>
<th>Enrichment ratio (Exp. 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>2.84 (+/-0.17)</td>
<td>1.27 (+/-0.11)</td>
</tr>
<tr>
<td>Sm</td>
<td>1.37 (+/-0.14)</td>
<td>1.30 (+/-0.12)</td>
</tr>
<tr>
<td>Nd</td>
<td>1.34 (+/-0.15)</td>
<td>1.32 (+/-0.13)</td>
</tr>
<tr>
<td>Gd</td>
<td>1.48 (+/-0.14)</td>
<td>1.38 (+/-0.13)</td>
</tr>
</tbody>
</table>
Figure 1. Particle size distribution of the REOs and soil taken from the experimental site.

Figure 2. Plan of field experiments. Experiment 1 (A) used to investigate distance over which soil moves into tramlines from either side of the tramlines and experiment 2 (B) to investigate whether sediment collected from the tramline was entering along the whole length of the tramline.

Figure 3. Graph to show concentration of REOs at different depths in the leaching experiment.

Figure 4. Mean concentration (mg kg$^{-1}$) of REOs in eroded sediment from Experiments 1 and 2 and background concentrations in the soil. Error bars show standard deviations for replicate samples (n=3).