Evaluation of two sediment tracers under simulated rainfall

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Abstract A number of different tracing approaches have already been established, including the use of rare earth oxides or environmental radionuclides. However, since existing techniques face various limitations, the search for alternative procedures continues. Two alternative tracing approaches involve the use of organophilic clays and magnetic iron oxides. This study performed a combined test of these tracers to assess potential contrasts in their behaviour under a controlled rainfall simulation experiment. The experiment consisted of a simulated rainfall event of 55 $mm \cdot h^{-1}$ applied to a bed–shoulder system (2 × 1.14 m). The results highlighted differences between the tracers in terms of their enrichment in sediment and different soil aggregate classes. Comparison of the contribution of the different plot sections to the total sediment export using both tracers suggested that most of the sediment originated from the shoulders.

Key words erosion; tracer; magnetic iron oxide; rainfall simulation; organophilic clays

INTRODUCTION

Sediment tracing techniques offer potential solutions to the cost and technical limitations associated with deploying traditional erosion measurement and monitoring procedures. Accordingly, there is a growing number of studies using different tracers applied in a broad variety of environmental settings. Existing approaches comprise the use of radionuclides, sediment fingerprinting, rare earths, magnetics and other tracers (Guzmán, 2012). However, new tracers are under continuous development because these existing approaches have their own limitations and problems.

Another potentially suitable tracer for erosion studies is the use of organophilic clays that are tagged with quaternary ammonium compounds. The early work of McAtee (1959) recognized that even primary amine can react with montmorillonite by the base exchange mechanism. Nowadays, ammonium compounds are widely used in industry and are easy to incorporate into soils for sediment tracing experiments. A key advantage from the analytical perspective is that the detection limit is extremely low and the background concentration is zero. On the basis of the above context, the main objective of this study was to compare the potential of organophilic clays and magnetic iron oxide as sediment tracers, using a rainfall simulation experiment.

MATERIALS AND METHODS

Tracer characteristics

Magnetic iron oxide The magnetic iron oxide or magnetite (Fe_3O_4) is mainly used as a black powder pigment and can be easily and inexpensively quantified through magnetic susceptibility (χ) measurements. More than 95% of the total weight of the magnetite is represented by the silt size range and its D_{50} is 6.5 µm, with a corresponding density of 4.6 $g \cdot cm^{-3}$. More details on this specific magnetic iron oxide can be found in Guzmán *et al*. (2010).

Organophilic clays The commercially available product Tixogel VZ (Southern Clay Products, Inc., Gonzales, Texas 78629, USA) was used as an organophilic clay tracer. For the production of Tixogel VZ, the inorganic cations of natural bentonites are substituted with quaternary ammonium cations of different chain lengths. These quaternary ammonium compounds are mainly composed of nitrogen as NH_4, carbon chains (C_{16}-C_{18}) and an unidentified alkyl rest (C_nH_{2n+1}) or cyclic/heterocyclic compounds. Four different chain lengths/masses of Tixogel VZ have been identified which can be used as a tracer after successful extraction and analytical determination. However, for the purpose of this study, only the total mass of the different chains was used for sediment tracing. Tracer analysis provided a density of 1.84 $g \cdot cm^{-3}$ and a particle size distribution of 10.5% < 1 µm, 68% < 63 µm and 99.2% < 200 µm.

Soil characteristics and tracer preparation

An Ap horizon (0–15 cm depth) of a Gleyic Luvisol which had been under arable cultivation was used as the host soil during the rainfall simulation experiment. All textural analyses were performed with the pipette method. Organic carbon was measured using wet combustion. The host soil did not contain $CaCO_3$ and had a pH ($CaCl_2$) of 5.62. Table 1 summarises the basic properties of the host soil. Approximately 300 kg of this soil was transported to the laboratory, air dried and sieved using a 5 mm mesh.

Table 1 Soil and sediment property summary.

Properties	Soil	Sediment
Clay (%)	28.3 ± 0.4	32.2 ± 3.5
Silt (%)	56.9 ± 1.6	58.1 ± 1.0
Sand (%)	14.9 ± 1.7	9.7 ± 4.1
Organic carbon (%)	1.46 ± 0.1	2.1 ± 0.7

Magnetic iron oxide and organophilic clays were both mixed with the host soil using serial dilution with a concrete mixer and 2 h of mixing time. Magnetic iron oxide was added at a rate of 24.4 g kg^{-1} of host soil to increase magnetic susceptibility background values (~1.76×10^{-7} $m^3 \cdot kg^{-1}$) by approximately two orders of magnitude. Organophilic clays were added to the host soil at a concentration of 0.14 $g \cdot kg^{-1}$ soil.

Rainfall simulation experiment

A box laboratory flume (200 × 114 cm) was used during the rainfall simulation experiment. This was divided in two smaller plots of 200 × 57 cm, to obtain two replicates. The flume was layered with 20 cm of sand and a sheet of fine mesh. The top 5 cm of the box was filled with tagged soil. Each replicate was constructed as a bed–shoulder. Only the shoulders contained tagged soil.

Careful and slow wetting by increasing the water table was used to saturate the soil. The experiment then started after three days of free drainage. A total of 140 soil samples from each replicate were taken across a sampling grid before the rainfall simulation to determine the soil content of both tracers. The slope of the flume was adjusted to 7%, the simulated rainfall intensity was 55 $mm \cdot h^{-1}$ and the duration of the rainfall application was 45 min. Further details of the rainfall simulator are provided by Strauss *et al*. (2000). Figure 1 shows the layout of the experiment and presents some construction details. Runoff and mobilised sediment were collected in buckets, weighed to calculate runoff and air dried to estimate soil loss. Sediment was also analysed for tracer concentrations. Three sediment samples taken at the beginning, the middle and at the end of the experiment were bulked to assess sediment texture and organic carbon content.

The distribution of the tracers in the host soil

To assess the tracer distributions in the host soil, tagged soil was wet and dry sieved manually to separate six different aggregate sizes (>630, 200, 125, 63, 25 and <25 µm). Tracer concentrations in each fraction were measured using the aliquots provided by both sieving procedures.

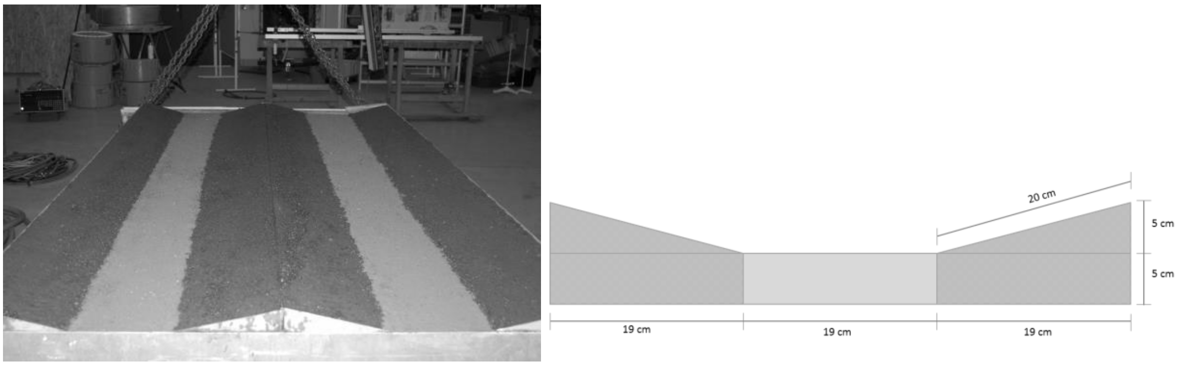

Fig. 1 Layout and dimensions of the plot experiment. Each replicate consisted of two shoulders and one bed formed with tagged and untagged soil, respectively.

The analytical determination of the tracers

Magnetic iron oxide The magnetic susceptibility of air dried soil samples was measured at a low frequency (0.47 kHz) using a Bartington® meter and an MS2B® dual frequency sensor. The relative contribution from shoulders and beds was calculated according to the methodology described by Guzmán (2012).

Organophilic clays The extraction of the organophilic compounds of Tixogel VZ from soil and sediment was performed using a mixture of $BaCl_2$ and CH_3OH (10/90). After shaking for 1 h and filtration through a 0.45 µm nylon membrane filter, the determination of the extracted quaternary ammonium compounds was performed via high performance liquid chromatography (Agilent 1200 SL HPLC) – mass spectrometry (6220 TOF MS). A quantitative determination of the different masses was subsequently performed using an additional triple quad MS-MS system (Agilent 6410) with electro spray ionisation (ESI). The linear working range of the method was 25 to 1000 $\mu g \cdot L^{-1}$. All measurements were performed with five replicates. Since the bed did not contain any organophilic clay tracer, the relative contribution from the shoulders and bed was calculated using the following equations:

$$f_{sh} = \frac{c_{sed}}{c_{sh} \cdot e}$$

$$f_b = 1 - f_{sh}$$

where f_{sh} and f_b are the fractions of sediment from the shoulders and bed, respectively, c_{sed} and c_{sh} are the concentrations of organophilic clays in the sediment and shoulders and e is an enrichment factor. To calculate the enrichment factor e we used, as a first approximation, the results from a similar previous experiment conducted with the same soil but without untagged areas. For this former experiment the mean enrichment of c_{sed} compared to the concentration of the original soil was 1.33 (Strauss *et al*., in prep.).

RESULTS AND DISCUSSION

The distribution of the tracers in the host soil fractions

Figure 2 shows the enrichment of magnetic susceptibility and organophilic clay in six different soil size fractions as compared to the host soil concentrations.

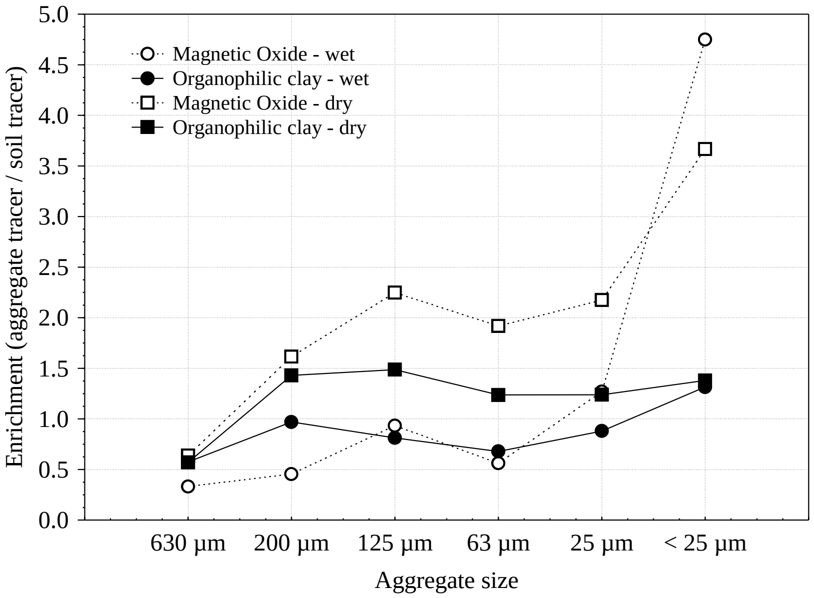

Fig. 2 The enrichment of magnetic susceptibility and organophilic clay of six different soil aggregate size classes obtained by dry and wet sieving.

For dry sieving, enrichment was higher for all aggregate size classes, except the aggregates >630 µm and those <25 µm, compared to wet sieving. The increase in enrichment for the smaller aggregate size fractions may be explained by the corresponding larger specific surface area. This is in accordance with the results reported for other tracers including rare earth oxides (Zhang *et al*. 2001). The degree of enrichment did differ, however, for the two tracers. Enrichment of magnetic susceptibility was about 2–3 times higher than that measured for the organophilic clays. This may be attributed to the smaller particle size of the magnetic oxides compared to organophilic clays.

Behaviour of the tracers under simulated rainfall

During the rainfall simulation experiment total runoff, sediment mass and the concentrations of both artificial tracers were measured every 2 minutes (Fig. 3).

At the beginning of the experiment, higher concentrations were measured for both artificial tracers. Polyakov & Nearing (2004) explained this response on the basis of an initial flush of poorly-incorporated tracer material. During the rainfall simulation experiment, the magnetic susceptibility of mobilised sediment exhibited an exponential decrease. A similar trend was measured for the clay and organic carbon content of the collected sediment. This trend probably reflected limitations in supply on the plot, as supported by some photographs. Organophilic clay concentrations remained constant or slightly increased after the initial flush. It is hypothesized that this different response may reflect either the different sizes of the artificial tracers or their different propensity for particle attachment, but further exploratory work is needed.

Average runoff of the rainfall simulation was 0.9 $L \cdot min^{-1} \cdot m^{-2}$ with a sediment concentration of 17.4 $g \cdot L^{-1}$. Average tracer concentration in the original tagged soil was 5.6 $mg \cdot kg^{-1}$ for organophilic clays and 1.2×10^{-5} $m^3 \cdot kg^{-1}$ for the magnetic iron oxide. The corresponding concentrations in mobilised sediment were enriched (7.0 $mg \cdot kg^{-1}$ and 2.1×10^{-5} $m^3 \cdot kg^{-1}$) compared to the host soil tracer concentrations.

The average relative contributions from shoulders and furrow to total sediment export determined by organophilic clays were 61 and 39%, respectively. The agreement between the tracer-based estimation of source area proportions was surprisingly high. Both tracers suggested a higher contribution from the shoulders compared to the bed. This could reflect the larger area of the shoulders which represented 66% of the total plot area. In addition shoulder slope was about 26%, whereas bed slope was only 7%.

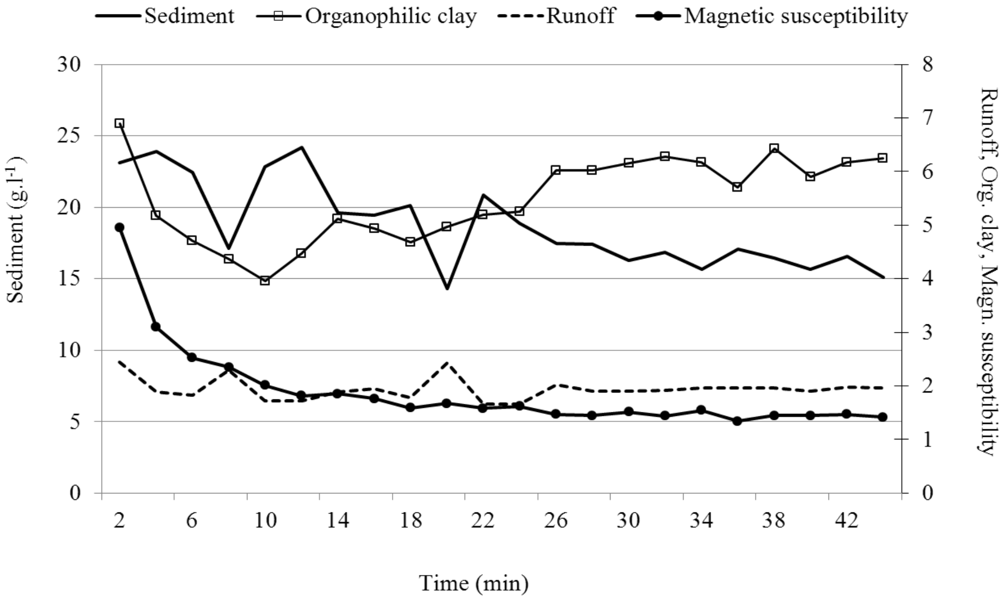

Fig. 3 The dynamic behaviour of runoff (L·min^{-1}), sediment export, magnetic susceptibility (×10^{-5} m^{3}·kg^{-1}) and the concentration of organophilic clay (mg·kg^{-1}) for one replicate during rainfall simulation.

CONCLUSIONS

This experimental comparison of an established (magnetic iron oxide) and more novel tracer method (organophilic clays) underscores the potential suitability of the latter for soil erosion studies.

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