



A novel fluorescent tracer for real-time tracing of clay transport over soil surfaces



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ABSTRACT

Clay is an important vector for the transport of pollutants in the environment, including nutrients, pesticides and metals; therefore, the fate of many chemicals in soil systems is closely linked to that of clay. Understanding the mechanisms responsible for clay transport has been hampered by the lack of a suitable tracer. Producing a tracer that accurately mimics clay transport is challenging, due to the small size of the particles and their unique physical properties. Here we describe the design and synthesis of a tracer using natural clay particles as a foundation, exploiting the natural ability of clay to sorb molecules to coat the clay with a thin layer of fluorophore. Application of the tracer has been demonstrated through the collection of real-time images of the tracer moving over the surface of a soil box during a rainfall event. These images allow, for the first time, clay to be tracked spatially and temporally without need to remove soil for analysis, thus resulting in minimal experimental artefacts. Custom written software has been used to extract high resolution data describing tracer movement and extent throughout the experiment.

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1. Introduction

Clay is a key component of many of the world's soils. Its ability to sorb nutrients, such as phosphorus (Sharpley et al., 1984; Sumner, 2000; Syers et al., 1971), potassium (Petrofanov, 2012), metals (Quinton and Catt, 2007) and organic pollutants (Homenauth and McBride, 1994; Sumner, 2000), and its ease of transport in flowing water makes clay an important vector for contaminant transport. Clay particles are moved by both overland flow (Quinton and Catt, 2007; Quinton et al., 2001) and by subsurface flow (McCarthy and Zachara, 1989), which may connect with rivers and lakes. Although studies have developed an empirical understanding of clay movement (Quinton and Catt, 2007; Quinton et al., 2001) and there have been attempts to model clay transport over and through soils (Jarvis et al., 1999; Jomaa et al., 2010), deriving spatial and temporal distributions of clay movement in response to rainfall has proved elusive. In this paper we describe a methodology, which, for the first time, allows the tracking of clay in time and space across a soil surface.

1.1. Tracing clay movement

Tracing clay movement has proved very challenging (Armstrong et al., 2012). One aspect of this challenge is the small size of the particles

being traced. For larger particles (grains of sand size) there has been success in mixing a dye with a binding agent and then applying this mixture to the surface of the particles (Black et al., 2007). However, this technique has limitations for particles that have a diameter of a few microns, as the coating significantly alters the size and density of the particles. Therefore, for clay an alternative method of tracing is required.

This has led researchers to develop a range of techniques for tracing clay, including the use of fluorescent microspheres (Burkhardt et al., 2008; Nielsen et al., 2011), rare earth oxides (REOs), which, strictly speaking, are fine silt particles (Stevens and Quinton, 2008; Zhang et al., 2001), and the labelling of clay particles with organic molecules (Selvam et al., 2008). The majority of methods require sampling (via physical removal of material) of the soil after the experiment to determine the tracer concentration (Mabit et al., 2013; Parsons and Foster, 2011). However, it is desirable to understand how a process changes over time requiring the collection of dynamic data. Sampling interferes with detachment and transport processes, limiting the use of existing techniques for process studies. Therefore a method that does not require removal of material is required if progress is to be made in understanding the dynamics of these processes. Additionally there are significant density differences between tracers (such as microspheres and REOs) and native clay particles, which are likely to affect their transport. Therefore a clay tracer with the same physical and chemical properties as the native soil clay, and that can be manufactured easily and analysed using a non-invasive, non-destructive and in-situ analysis

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technique operating at moderate to high temporal resolution, is desirable. Some progress has been made in the nano-particle community with the creation of fluorescent nano-clays, however, no environmental application of the material has been reported (Diaz et al., 2013).

1.2. Fluorescence

Fluorescence detection often allows for a high signal to noise ratio permitting single molecule detection (Lakowicz, 2006). This sensitivity enables minimal fluorophore to be used in tracer production, resulting in negligible modification of the coated particle. Traditionally, fluorescence is measured on discrete samples using a fluorimeter, providing detailed spectral information. Two previous studies have captured images of fluorescent tracers using film cameras. In the first, silt-sized glass particles (44 to 2000 μm) labelled with uranium salts, which fluoresce under UV light, were monitored on a 10 m slope inclined at 5.5% (Young and Holt, 1968). Later, fluorescently-labelled pesticide granules (size unknown) were detected in soil, with each photograph imaging 0.63 m^2 (Woods et al., 1999). This work assessed how soil tillage methods affect incorporation of pesticide granules into soil; no effort was made to acquire images of the pesticide moving.

1.3. Fluorophore selection

Four principle criteria were used to select the fluorophore. It should: bind strongly to clay; fluoresce at a wavelength different to the auto-fluorescence of soil; be well characterized; and be detectable using a CMOS (Complementary Metal Oxide Sensor) detector in a digital camera. Successful binding relies on matching the fluorophore to the clay of interest; in general the fluorophore should carry the opposite charge to the clay and be lipophilic. Soil auto-fluorescence, due, in part, to the large quantity of organic aromatic acids that are present (excitation maximum at 465 nm, emission maximum at 517 nm) (Milori et al., 2002; Rinnan and Rinnan, 2007), can result in high background fluorescence and therefore interfere with detection of the tracer. Therefore to reduce the impact of natural fluorescence a fluorophore that excites between 520 and 600 nm was desired. Having a well characterized fluorophore allows more rapid progress to be made as its chemical properties are already well described. Finally, we wanted to use a CMOS detector array, commonly found in consumer grade cameras, as they acquire images within the visible range (400–700 nm). A fluorophore that fluoresces in this range was therefore required.

Rhodamine B was selected as the fluorophore, because: it binds to clay, e.g. Rhodamine B has been shown to bond organically-modified montmorillonite (Diaz et al., 2013), and sodium montmorillonite has been shown to be a successful remediation method for water contaminated with Rhodamine B (Selvam et al., 2008); it typically has an excitation maximum around 570 nm and emission maxima of around 590 nm (Beija et al., 2009), avoiding the most intense soil auto-fluorescence; and it fluoresces within the range detectable by a CMOS detector. Many derivatives have been synthesized, which could allow fine tuning of the clay tracer's fluorescent properties (Beija et al., 2009), and it is commercially available and inexpensive.

2. Materials and methods

Here we describe the materials and methods used to produce the clay-sized fluorescent tracer, tests of its stability and its application to a laboratory scale erosion experiment.

The instruments used were an Agilent Technologies Cary Eclipse fluorescence spectrometer and an Agilent Technologies Cary 60 UV/vis absorbance spectrophotometer. Disposable plastic cuvettes were used throughout (Fisher Scientific). The water used was deionized water, unless otherwise specified, and Rhodamine refers to Rhodamine B from Acros Organics (132311000).

2.1. Tracer production

The tracer was produced by sorbing Rhodamine onto the surface of clay particles. Twelve grammes (69904 ALDRICH) was ground to a fine powder, and sonicated for 30 min in water. Rhodamine (0.2 g) was added and the volume made up to 1 L. The mixture was sonicated for a further 45 min, stirred for 2 h, then allowed to settle. The supernatant was clear and colourless, and a vivid red-purple powder was visible at the bottom of the beaker. Excess supernatant was decanted off and the powder collected using vacuum filtration through two Whatman #5 filters. The filtrate was clear and colourless to the eye. The tracer was then thoroughly rinsed using a 50:50 mixture of saturated NaCl and ethanol and then repeatedly with water. The resulting tracer was dried at room temperature in a desiccator and protected from light. If required, the tracer was gently disaggregated by hand before use.

2.2. Tracer stability

Stability tests were carried out to ensure the tracer would not degrade over the duration of the trial (less than 24 h). One gramme of tracer (equivalent to 16.7 mg Rhodamine) was placed into 100 mL of solvent (either High Ionic Activity Solution (HIAS) or distilled water), and stirred to mix. The HIAS was prepared by combining 25 g NaCl, 4.1 g Na_2SO_4 , 0.7 g KCl, 11.2 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 2.3 g $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ with deionized water to give a final volume of 1 L (Sverdrup et al., 1942). The aim was to produce a simulated natural water of high ionic activity with respect to the major elements. The concentrations used in this solution are extreme compared to those normally found in terrestrial waters; if the tracer is stable under these conditions, we assume that it will be stable in the vast majority of soil environments.

After a period of time (>40 h), during which the tracer was allowed to settle, 3 mL of the supernate was placed in a plastic cuvette to assess desorption of Rhodamine from the tracer, using UV/vis absorbance spectrophotometry and fluorescence spectrometry. No attempt to separate the tracer from the water was made, as any particles remaining in suspension were too fine to remove by filtration.

To make calibration standards, first a stock solution was prepared by dissolving 18.2 mg Rhodamine in 100 mL deionized water. Standards for UV/vis spectrophotometry and fluorescence spectrometry were prepared by diluting the stock 1:250 for fluorescence measurements and 1:125 for UV/vis measurements, using either HIAS or deionized water. Thus, the UV/vis standards contained 0.144 mg Rhodamine per 100 mL, and the fluorescence standards contained 0.072 mg Rhodamine per 100 mL. These are the concentrations that would be achieved had 1% or 0.5% Rhodamine dissolved off the tracer during the stability experiments.

2.3. Physical properties of tracer

A Leica confocal microscope was used to record images of clay and tracer particles. Images were taken using a 63 \times optical lens under oil. The size range of particles was measured using a Malvern Mastersizer 2000.

2.4. Acquiring fluorescent images

Images were acquired using a Canon 500-D DSLR camera mounted on a tripod. (See Supplementary information (SI) 1: Camera setup, for further details of the camera settings and filters). A ~75 mW, 532 nm (green) laser was used to illuminate the soil box, after passing through a rotating diffuser (SI 2: Laser lighting setup, SI: Fig. S1). Achieving uniform illumination is critical to producing accurate images (Waters, 2009). Visual and photographic assessment of the light showed an acceptable degree of uniformity (SI: Fig. S2).

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