

# Environment

# Everything goes somewhere; tracking the movement of contaminated sediments in an industrialised estuary using dual signature sediment tracers

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**Abstract.** Source control i.e. the reduction of contamination from upstream or diffuse sources, is a critical element in any management plan for contaminated waterways. If source control measures are not successfully implemented, then a situation exists in which contamination will continue through time, and the cleanup of waterway segments becomes increasingly problematic. To provide greater understanding of the issues surrounding source control, it is essential to have some knowledge of contaminant sources and transport pathways of contaminated particulates. In port areas a plethora of factors interact to control contaminant transport pathways. These include: rain and river flow; tidal circulation, surface waves and wind drift, and temporally changing water column stratification. Particle tracking offers a *practical* means to map the transport pathways of contaminated sediments under these collective influences. This paper introduces a new and novel “dual signature” tracer product, and describes the particle tracking technique on a practical level through a study example in the Lower Duwamish Waterway, Washington, USA.

## 1. INTRODUCTION

The movement of energy and materials within the geosphere is a fundamental attribute of the Earth system. Processes of atmospheric and hydrologic weathering erode the surface rocks and soils, and overland, fluvial and marine currents act to transport and redistribute particles. Anthropogenically produced particles, such as soot, urban contaminants, mine tailings and radionuclides are also subject to the same transport and re-distribution processes. An understanding of the mechanisms and processes of re-distribution is necessary to understanding both the natural geological consequences of erosion, and the transport and fate of anthropogenically produced particles (contaminants).

“Particle tracking”, or as it is sometimes referred to in the geological sciences “sediment tracing” or “sediment tracking”, offers a unique methodology with which to track the movement through space and time of environmental particulates. Utilising this methodology, information can be garnered into source – sink relationships, the nature and location of the transport pathway(s) and the rate of transport. It is a relatively straightforward, practical methodology which involves the introduction of particulate tracers into the environment (water body, sewer, beach etc.) labelled with one or more signatures in order that they may be unequivocally identified following release [1,2]. Measurable and uniquely identifiable signatures have in the past included the use of radioactive tracers [3,4] and Rare Earth elements [5], fluorescent coated sands [6], fluorescent silts [7–9]. Synthetic, polymer-based have also been developed (e.g. Black and McComb [1]). Black et al. [10] provide a comprehensive overview of the historic evolution of these differing approaches to the present day.

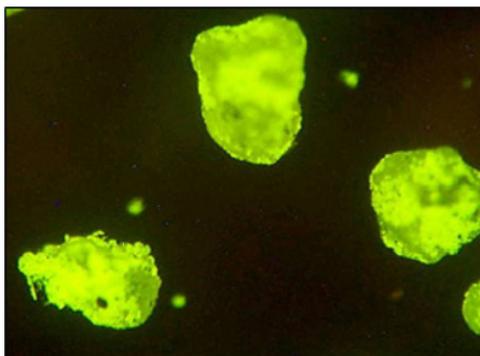
The aim of this paper is to introduce a new and novel “dual signature” tracer product and to present, from a largely practical standpoint, the set of processes involved in conducting a particle tracking study. For

present purposes we will use a recent study (tracking contaminated sediments in an industrialised waterway, the Lower Duwamish, Washington, USA) to illustrate the salient points. Whilst this specific Case Study was a suspended sediment transport problem, there is a set of steps and considerations common to all tracking studies regardless of the specific objective.

## 2. TECHNOLOGY DESCRIPTION

Partrac use proprietary tracers called “*dual signature tracers*”; this means that each particle (grain) of tracer has two signatures which are used to identify the particle unequivocally following introduction into the environment. The use of two signatures is an advancement and improvement on previously used (mono-signature) tracers. The two signatures are fluorescent colour and paramagnetic character. Two types of dual signature tracer are available: coated particles, and entirely artificial particles. Coated particles possess a fixed grain density of  $\sim 2500\text{--}2600\text{ kgm}^{-3}$  whereas that for artificial particles can be adjusted through the range 1010 to  $3750\text{ kgm}^{-3}$ . Coated particle grain sizes range from  $\sim 20\text{ }\mu\text{m}$  to 5 mm; artificial particles are commonly used to mimic low settling velocity particulates, such as biological larvae, and for engineering scale model studies. Whilst compositional data for each tracer type is commercially confidential, coated particles (used most frequently in tracking studies) are made from natural materials plus a geochemically inert fluorescent pigment.

Four spectrally distinct fluorescent colours are available with which to label tracer. These are commercially available fluorescent pigments, which themselves comprise polymer nanospheres embedded with a water insoluble dye. Each pigment is characterized by specific excitation and emission wavelengths, which facilitates a targeted sample analysis procedure, but all are consistently



**Figure 1.** Photomicrograph of coated sand fluorescent-magnetic tracer.

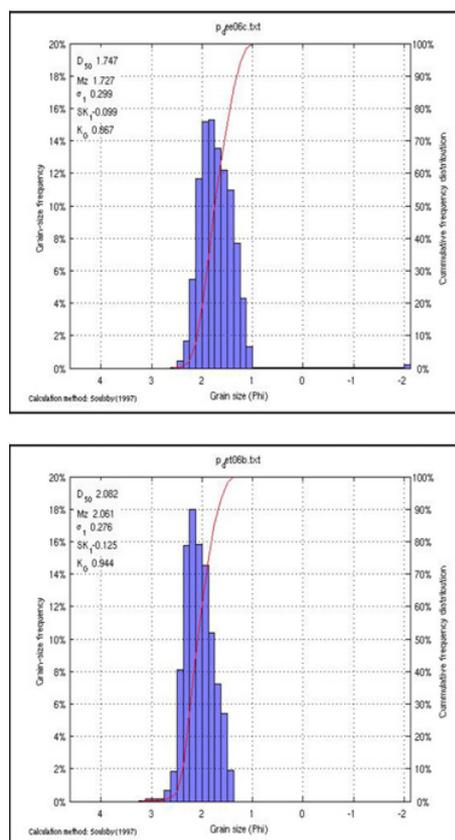
reactive upon exposure to black light (Fig. 1). Use of multiple colours means that the technology can be used to label multiple sources in the same general area, or to perform consecutive studies in the same area under differing hydrodynamic conditions (e.g. high discharge, low discharge).

Every tracer particle is also para-magnetic. Para-magnetic minerals are *not* magnetically attracted to one another (“magnetic flocculation”) but the para-magnetism gives each particle a magnetic attribute which means that particles will adhere to any permanent or electro-magnet if they come in close proximity. This facilitates a simple separation of tracer within environmental (water, sediment, soil) samples, a process which can also be exploited *in situ* (e.g. through use of submerged magnets in a water course; e.g. Guymer, et al. [11]). The integration of tiny magnetic inclusions onto the kernel particle during tracer manufacture is a substantial innovation over mono-signature, fluorescent-only tracers, for which there was no effective means of tracer separation within samples prior to analysis. This profoundly limited tracer enumeration.

The “degree of para-magnetism” of a granular material i.e. how magnetic grains are in comparison to quartz-rich beach sand, can be determined quantitatively through use of a magnetic susceptibility sensor. This essentially measures the disruption to an applied low frequency, low intensity alternating magnetic field; ferrous materials naturally possess a greater propensity to disrupt a magnetic field in comparison to all naturally occurring non-magnetic minerals and hence they can be detected using this technique. Typically manufactured tracer is  $\sim 400$ – $500$  times “more magnetic” than quartz-rich beach sand. The para-magnetic attribute of tracer can also be exploited *in situ* through use of a field-portable, hand-held magnetic susceptibility sensor (see [www.bartington.co.uk](http://www.bartington.co.uk)), which can be used in a semi-quantitative fashion to map tracer concentration on soil or sediment surfaces [10, 12].

### 3. CONDUCTING A PARTICLE TRACKING STUDY

The process of setting up and conducting a particle tracking study involves a specific set of steps regardless of the application. These are: 1) conducting a background



**Figure 2.** Example of nearly equivalent grain size spectra for (a) native sand (top) and (b) sand tracer (bottom) derived from settling velocity determinations.

survey; 2) designing a tracer(s) and similarity testing; 3) tracer introduction; 4) sampling; and 5) enumeration. A brief discussion of these is presented here.

1. **Background Survey**:- prior to any study an initial native particle properties survey is always required for two purposes (1) to determine the particle characteristics (size, density, settling velocity) that will be matched during manufacture of magnetic fluorescent particles, and (2) to determine the abundance and characteristics (e.g. size) of any naturally occurring magnetic and fluorescent particles. Information from (1) is used to design the tracer whereas information from (2) is essential ancillary information which is used during tracer enumeration.
2. **Tracer Design and Similarity Testing**:- the size and density (and sometimes settling velocity) data collected during the background survey are used to create a specification for the tracer. A final specification will include: size range; density; colour; para-magnetic attribute; and quantity (kg). The manufactured tracer is subject to a similarity analysis (using the same testing procedures as the background survey). Similarity testing or, as it is also termed, ‘hydraulic matching’ is the process in which the physical sedimentological attributes of the manufactured tracer (size, density etc.) are compared quantitatively to those of the native particles. Black et al. [10] discuss similitude tolerances



**Figure 3.** Tracer introduction (green silt) via flushing directly sub-surface through a tube, and the resulting plume.

since manufacturing constraints dictate that tracer can never be the exact copy of the native sediments.

3. *Tracer Introduction*:- introduction of the tracer into the environment varies according to application. For suspended sediment transport studies, commonly tracer is flushed down a tube so that it is introduced @0.5 m beneath the water surface in the form of a plume (Fig. 3). Pre-made deep frozen ( $-70^{\circ}\text{C}$ ) tracer blocks have been used to study resuspension of peat deposits in the Florida Everglades, and recently dissolving bags have been used to encapsulate tracer for a study on reef sediment impacts in Hawaii. Beach longshore transport, and soil loss to stream/bank stability studies, both involve direct placement of tracer onto the land surface (in non-windy conditions!).
4. *Sampling*:- the dual signature nature of the tracer provides for a range of sampling options. Magnets, deployed on line moorings, on bed-frames or onto fixed structures, directly within the anticipated stream flow have been used very successfully to intercept tracer (figure 4). “Dipped” magnets can be used to collect instantaneous samples. Magnets are covered with a thin acrylic sheath, which is simply removed and bagged prior to enumeration and thus sampling is very quick and simple. In the field pumped water sampling can also be used, bottom sediment cores can be collected using grabs or cores (for deposited tracer), and *in situ* or pumped fluorimetry will detect the fluorescent colour if a cloud of suspended tracer



**Figure 4.** Photographs of (top) a submersible magnet following tracer capture; and (bottom) a magnet attached to port infrastructure, with tracer.

particles passes (see Fig. 3; e.g. Guymer et al. [11]). If bottom sediment cores are collected, then post-collection separation of the tracer from the native sediment is required; this is achieved in the laboratory using a Frantz Isodynamic Separator.

5. *Tracer Enumeration*:- the dual signature permits can be undertaken using a range of differing approaches to tracer enumeration. The chief objective of the enumeration process is to ascertain the tracer dry mass (grams) rather than particle number concentration or presence/absence within each sample, simply on the basis that geologists and oceanographers most commonly work on with mass transport units [13]. A variety of analytical approaches are available. These include: dissolution of the fluorescent coating, centrifugation and spectrofluorimetric analysis (e.g. Carey [14]; Farinato and Krauss [15]; Forsyth [2]); flow cytometry [2], or FlowCam<sup>TM</sup> analysis (see <http://www.fluidimaging.com/>); and filtration/sedimentation followed by digital image analysis (e.g. Solan et al. [16]). In natural systems, and especially in industrialized estuarine and port environments, there is inevitably a population of non-fluorescent, magnetic particles within the suspended and bedded sediment pools. These constitute noise within samples. Spectrofluorimetry is the most frequently used method of choice here as use allows the natural magnetic fraction to be effectively ignored. Furthermore, the spectrofluorimetric method can measure two different tracer colours in the same sample, which increases the flexibility of the tracer technique, and is extremely sensitive (mass resolution to  $\sim 0.05\text{ g}$ ).

#### 4. CASE STUDY: TRACKING THE MOVEMENT OF CONTAMINATED SEDIMENTS IN AN INDUSTRIALISED ESTUARY (LOWER DUWAMISH WATERWAY)

Source control i.e. the reduction of contamination from upstream or diffuse sources, is a critical element in any management plan for contaminated waterways. If source control measures are not successfully implemented, then a situation exists in which contamination will continue through time, and the cleanup of waterway segments becomes increasingly problematic. For greater understanding of the issues surrounding source control, it is essential to have some appreciation of contaminant sources and transport pathways of contaminated particulates. This specific aspect formed the basis for conducting a tracking study to understand the transport pathways of PCB-contaminated sediments (principally) entering the Lower Duwamish waterway via the Green River. A sediment transport model constructed for the waterway indicates that a significant majority of the yearly sediment load entering the Lower Duwamish Waterway (LDW) is derived from the Green River (QEA, 2008). About one-half is predicted to be deposited within the LDW, an area that has now been selected by the national government for cleanup within the Superfund initiative (see [http://www.ldwg.org/rifs\\_docs9.htm#finalfs](http://www.ldwg.org/rifs_docs9.htm#finalfs)). However, the accumulation of sediment and sediment-associated contaminants differs by reach, water depth, settling velocity, and other factors. A tracking study was commissioned by the State Dept. of Ecology (Washington, USA) to identify the short-term sediment transport pathways and patterns of sediment accumulation of fluvially-derived sediment particles. Further information can be found at: <http://www.ecy.wa.gov/biblio/0903048.html>.

The Lower Duwamish Waterway Superfund site is a 5.5 mile stretch of the Duwamish River that flows into Elliott Bay in Seattle, Washington (Fig. 5). The waterway is flanked by numerous industrial corridors, as well as several residential neighbourhoods. It is 150 – 215 m wide with a mean depth of ~ 6 m. It is tidally influenced well beyond River Mile 12.4. Fluvial discharges to the waterway range < 10 to 340 m<sup>3</sup> s<sup>-1</sup> with a median value of approximately 40 m<sup>3</sup> s<sup>-1</sup>. The specific project objectives were:

- To show how far into or beyond (up- or downstream) the cleanup site (fluorescent) sediment particles can be transported when released into the water column.
- To trace the movement of these particles into, and possibly through, the waterway and, in particular, to trace where they can settle to, and be deposited upon, the bottom.

##### 4.1. Tracer specification

The principal focus of the study was on the fate of silt-sized particles (< 63 μm in diameter), but since sand sized material is also flushed down the Green River this size fraction was also included in the study. Table 1 summarises the tracer specification (particle size,

Table 1. Tracer specification.

Fluorescent Colour	Size Range (μm)	Density (kg m <sup>-3</sup> )	Settling Velocity (m s <sup>-1</sup> )
Red Sand	60–250	2600	0.013 ± 0.01
Yellow Silt	30–60	1200	0.00013–0.00024

density, settling velocity); these were derived from both laboratory and field measurements of the size, density, and settling velocity of native sediments that were in the river and within the estuary. 100 kg of each of the fractions was provided. The sand sized fraction was a coated sand product, whereas the silt sized fraction was a density-adjusted LDPE (polyethylene) biodegradable artificial particle, for which the settling velocity was matched to the settling velocity of bedded silts. Both tracers were paramagnetic. A comprehensive suite of similarity tests were undertaken to confirm the tracer physical-hydraulic attributes matched those of the native sediments.

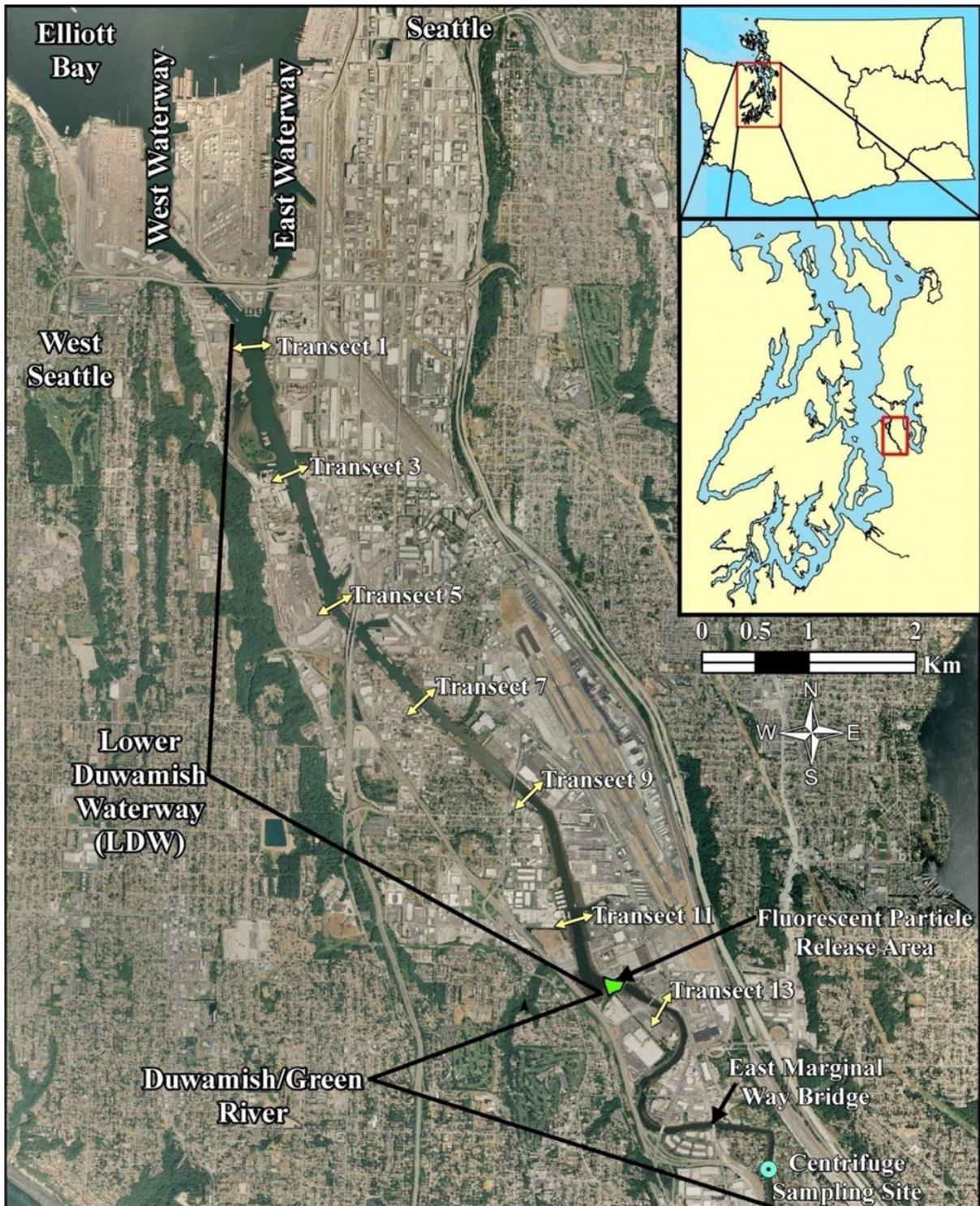
Tracer was introduced at River Mile 4.4 (see Fig. 5) synchronous with high water during a median flow event using the method shown in Fig. 3. A geospatial sampling program covering the length (to River Mile 0) and width of the waterway was devised which comprised: magnets fixed onto port infrastructure (see Fig. 4; 18 sites with 6 of the 18 sites comprising a triple magnet arrangement); *in situ* pumped sampling and dipped magnets via transects (13 on Day 1 only; transects are shown on Fig. 5), and bed sampling (63 sites) using a van Veen grab. The waterway was sampled at the end of the first day, after 1 week, after 1 month, and after 2 months.

##### 4.2. Principal study findings

The Day 1 findings indicated that both sands and silts had been transported downstream, however the sand sized material was almost entirely deposited within ~ 500 m of the tracer injection point. *In situ* pumped water samples showed that by the turn of the tide silt material had been carried in suspension down to River Mile 0 i.e. the length of the study reach (Fig. 7).

Data from fixed magnets, which were only mounted along the riverbank infrastructure and not mid-channel, showed that the silt material was mixed laterally the length of the waterway. These data unequivocally confirm that (for the given hydrologic-tidal circumstances) sands are carried only a limited distance into the waterway, whereas contaminated natural silts flushed into the waterway are mixed longitudinally and laterally. Thereafter, sands were never found in suspension indicating no or highly limited subsequent resuspension under normal conditions.

After Day 1 the sheaths on all magnets were replaced. Silt sized particles continued to be collected by the magnets and were therefore by inference found to be in suspension throughout the subsequent sampling campaigns (week 1, months 1 and 2), though a general reduction in concentration occurred through time, and by Month 2 the silt particles in suspension were noted to be finer grained, suggesting some deposition of the coarser silt



**Figure 5.** Aerial photograph of the Lower Duwamish Waterway showing the tracer release site and location of transect and other sampling areas.

fraction. A hypothesis proposed for the continued presence of tracer in suspension is that a well-mixed, quasi-permanently suspended pool of tracer remained within the waterway, and was simply advected by tidal action on a daily basis and retained in the study area by the tidal excursion distances. Some deposition evidently occurred (see Fig. 6) as bed samples were found to

contain tracer, and therefore some of the silt found in suspension over the longer term could be derived from resuspension of deposited tracer. The sediment transport model [17] identifies propeller induced resuspension as a process likely to occur in the waterway on account of the shallow water depths. Silt tracer was also found in bottom samples *upstream* of the tracer injection point,

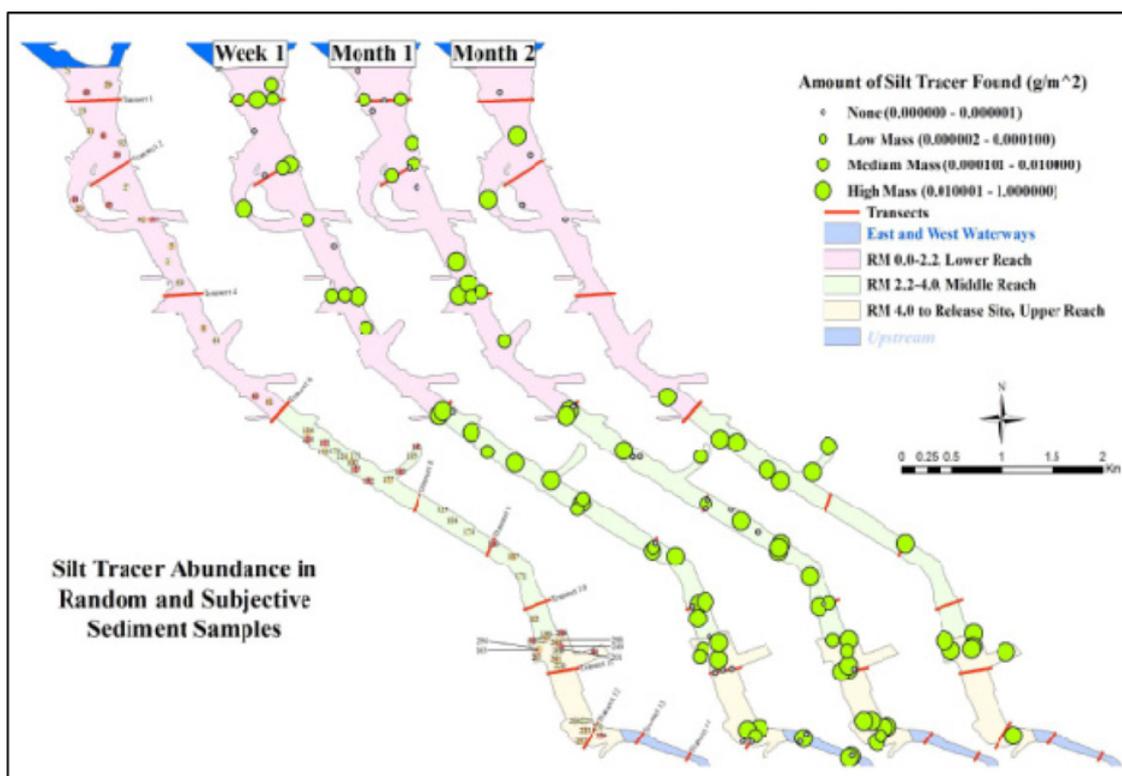


Figure 6. Distribution of (silt) tracer in bottom sediment samples through time.

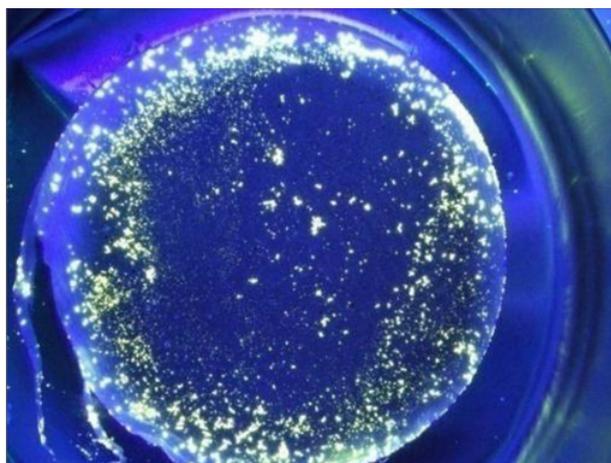


Figure 7. Fluorescence microphotograph of pumped surface water at River Mile 0.5 showing the presence of suspended silt tracer.

indicating a degree of upstream transport (by flood tides) and deposition.

## 5. GENERAL CONCLUSIONS

- Hydraulically matched tracer fractions were successfully manufactured.
- The study has demonstrated the ability to recover magnetic tracers from a relatively large, complex, diluting system using limited tracer mass and with different sampling methods.

- Specific data demonstrate tracer transport into the waterway as well as how far into or beyond the cleanup site particles have travelled (for the hydrologic-hydrodynamic conditions present during the 2 month study period) and deposition. The findings generally support the sediment transport model for the site.

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