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Environmental Restoration Project

Demonstration of Fluorescent Magnetic Particles for Linking Sources to Sediments at DoD Sites

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14. ABSTRACT
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Acronyms

ADCP – Acoustic Doppler Current Profiler
cm^2/cm^3 – square centimeter/cubic centimeter
d_{50} – Diameter of particle at 50% of the particle size distribution
DoD – Department of Defense
DZ – tracer deployment zone
EPA – United States Environmental Protection Agency
ESTCP – Environmental Security and Technology Certification Program
g – gram
g/cm3 – gram per cubic centimeter
HPS – Hunters Point Shipyard
kg – kilogram
L - liter
mg – milligram
mm – millimeter
NBSD – Naval Base San Diego
nm – nanometer
Partrac - Partrac, Ltd. (Glasgow, Scotland)
PCB – Polychlorinated biphenyl
PRP – Potential Responsible Party
PSD - Particle Size Distribution
PVC – Polyvinylchloride
RI/FS – Remedial Investigation/Feasibility Study
QA – Quality Assurance
SCCWRP - Southern California Coastal Water Research Project
SPAWAR – Space and Naval Warfare Systems Center Pacific
TMDL – Total Maximum Daily Load
TOC – Total Organic Carbon
TSS – Total Suspended Solids
UK – United Kingdom
µg/kg – microgram/kilogram (part per billion)
µm – micrometer or micron
V – Velocity

1. INTRODUCTION

Contaminated sediments are a continuing regulatory issue for DoD facilities. There is continued regulatory scrutiny of contaminated sediments located in proximity to multiple DoD discharges into aquatic environments. In complex industrial settings, both the DoD and EPA have great interest in determining which nearshore discharges contribute contaminated sediments to particular areas of the depositional environment. This project will demonstrate the efficacy of a particle tracking technology to quantitatively map the depositional footprint of particulates released from typical DoD sources into adjacent aquatic environments. Fluorescent ferrimagnetic tracer particles will be released from specific sources and tracked through the water column and collected at the sediment surface to determine the transport pathways and their depositional pattern and quantitatively demonstrate where these particle sources are most likely to impact local sediments. Demonstration and validation will show the utility of this technology to map the spatiotemporal distribution of particulates, and thus any sorbed contaminants, from specific sources which would greatly assist potential remedial efforts to focus on the appropriate source of contamination. This particle tracking technology also provides direct empirical data useful for numerical model calibration/validation purposes which are often used within sediment and contaminant transport studies.

1.1 BACKGROUND

Source control (i.e. the reduction of contamination from upstream point or diffuse sources) is a critical element in any management plan for contaminated waterways. In order to understand the issues surrounding source control, it is essential to have some understanding of the sources of contaminated particles, their transport pathways and their sinks. Particle tracking offers a practical means to investigate source – sink relationships and map the transport pathways of contaminated sediments both at the point of delivery into waterways, and following delivery, through time and across space. It is a relatively straightforward methodology which involves the introduction of particulate tracers into a water body labeled with one or more signatures in order that they may be unequivocally identified following release (McComb and Black, 2005; Forsyth, 2000). Particle tracking studies are often done as part of a larger sediment transport modeling effort to provide actual field data to validate the models (Chadwick et al., 2006). Particle tracking is not a panacea, but when applied correctly it can provide an excellent ‘tool in the box’ to assist in the validation of sediment transport models. These models can then be used to investigate sediment transport dynamics over greater spatial and temporal scales (Sloan and Gries, 2009), nominally with a greater degree of confidence in the model outputs.

Particle tracking has been used as a tool in sediment transport studies since the beginning of the last century (Crickmore, 1976; White, 1998; Black et al., 2007). The majority of historic studies have been directed towards understanding the transport pathways of sand size sediments (Black et al., 2007). However, many metal and organic contaminants are bound to surfaces of finer, silt (and clay) size particles and it is these particles that are of particular interest from regulatory and ecosystem health standpoints. Due to the demanding nature of tracking finer sediments, silt tracking historically received less scientific attention, excepting Sarma and Iya (1960) and a handful of Dutch studies (Draaijer et al., 1984; Louisse et al., 1986). More recently, studies have labelled natural clays with DNA (Mahler et al., 1998) and rare earth element oxides (Spencer et al., 2007, Spencer et al., 2011). Yet, despite these studies, tracking silt and clay sized particles remains a significant challenge (Black et al., 2007, Spencer et al., 2010). Partrac (using technology development funding) have advanced the application of the methodology for this size fraction and have conducted studies using their proprietary dual signature tracers to examine Hg-contaminated silt transport in the Falkirk Canal (UK), and contaminated silt transport in the Lower Duwamish waterway (Sloan and Gries, 2009).

1.1.1 DUAL SIGNATURE TRACERS

For this study both coated natural silt particles and coated artificial particles were used in the demonstrations. Coated natural particles possess a fixed grain density of ~2.6 grams per cubic centimeter (g/cm^3) whereas that for artificial particles can be adjusted through the range 1.01 to 3.75 g/cm^3. Dual signature tracers, as the name suggests, have the characteristic that each tracer grain has two signatures which are used to identify the particle unequivocally following introduction into the environment. In the present study, tracers were labeled with both *fluorescent color* and *magnetic character* as signatures (for more discussion see Section 2).

The development of dual signature tracers for use in geological studies by Partrac has occurred over a 10 year period. This development was based on a review of previous research, methodologies and technologies so that the current approach is built on a foundation of this previous work (see Black et al., 2007). This review paper formed a foundation upon which to improve the technology based upon what was known historically to work and not work, and where there were technological or scientific gaps. The major innovation which arose over the 10 year period was the invention of the dual-signature particle, which added ferrimagnetic properties to the traditional fluorescent tracer approach. Significant practical methodological advantages arose from this innovation which substantially improved and simplified the technology and associated sampling methodologies. During the past five years an extensive series of laboratory and field investigations have been undertaken to refine and improve all areas of the tracking methodology, including deployment methods and approaches, sampling techniques and statistical methods, tracer recovery and analysis.

1.2 OBJECTIVE OF THE DEMONSTRATION

This project demonstrated a particle tracking technology to quantitatively map the spatiotemporal distribution and depositional footprint of particles released from typical DoD contaminant sources into adjacent aquatic environments. Fluorescent ferrimagnetic particles were released from specific sources and tracked through the water column and collected at the sediment surface to determine their spatial distribution and depositional pattern and quantitatively demonstrate the linkage between sources and receiving water areas where these particle sources are most likely to impact the sediments.

Demonstrations show the utility of this technology to map the distribution of particles, and therefore any sorbed contaminants, from specific sources to assist potential remedial efforts in focusing on the appropriate source of particular contaminants. This is important to the DoD and EPA in complex industrial settings with multiple discharges in close proximity. The performance objectives focused on hydraulic matching (i.e. matching the physical characteristics of the tracer to the native particles being investigated), validating collection and analysis (enumeration) methods, and the potential of the technique in determining material flux utilizing a mass balance approach.

At the first demonstration site, the project focused on using the tracer to track a plume of particles released from a stormwater outfall. The transport pathway(s) of released particles was determined as the plume dispersed through the water column (both vertically and laterally) adjacent to the outfall. The depositional pattern onto the surrounding bottom sediments was also successfully mapped. Utilizing dual signature tracers in this manner provided a clear picture of where contaminated particles from a point source, such as an outfall, are deposited in the sediments and therefore demonstrated which particular sediments were impacted by specific sources, enabling the site authorities to implement targeted pollution prevention practices more efficiently. Direct comparison of the particle tracking data and a sediment transport model showed strong correlation (i.e. the tracer deposited where the model predicted the tracer would deposit). This is a good example of how the technology/technique can be used to validate sediment transport models.

At the second demonstration site, two tracers (of different colors) were released (as opposed to the one tracer color used within the first demonstration study) to assess the movement of two hydraulically different materials. A pink tracer was manufactured to hydraulically match the properties of activated carbon amendment material and a green tracer was manufactured to hydraulically match the properties of the contaminated (native) sediment. The primary objectives of the study were:

1) To examine the potential for ‘loss from source’ of the activated carbon amendment material (as mimicked by the pink tracer), to identify the subsequent transport pathway (and potential depositional zone) for this lost material; and
2) To examine if contaminated materials (as mimicked by a green tracer) from the sediments upland of capped areas are being mobilized and deposited onto the capped areas thus resulting in recontamination of the site.

Inspection of the data, and supporting oceanographic data, revealed that currents (tidally and wind driven) mobilized tracer particles which were subsequently transported across the site. High field magnets placed in a grid pattern around the cap area, and sediment grabs, were able to collect both tracers at the same time, and analysis methods back at the laboratory were able to discriminate between the two tracers using a spectrofluorometric approach. In this study we were able to demonstrate the use of multiple colored tracer particles to independently track different sources at the same time.

1.3 REGULATORY DRIVERS AND CONCERNS

The demonstration sites contain contaminated sediments associated with continuing inputs from stormwater and other upstream discharges, and therefore fall under Section 303(d) of the Clean Water Act. The Federal Clean Water Act, Section 303(d) requires states to identify all water bodies that do not meet water quality standards. Impaired water bodies are included on the 303(d) list and water cleanup plans or Total Maximum Daily Loads (TMDLs) must be developed to bring the water body back into compliance. SPAWAR is currently working at the demonstration sites on TMDL related studies, and this ESTCP project will assist the sites by determining which contaminant source areas impact specific surrounding sediment areas.

At the first demonstration site a regulatory cleanup order has been issued for sediments at a commercial shipyard just north of the navy site, and the commercial shipyard has implicated the navy as an additional PRP (potential responsible party) for contributing contamination to their sediments. SPAWAR has performed a number of modeling studies to estimate less than 1% of the contaminated sediments can be transported from the navy site to the commercial shipyard. This ESTCP study provided additional empirical data to support those model results. The regulatory drivers at this site are characteristic of many DoD harbor areas where complex comingling of multiple DoD and non-DoD sources may be present and their linkage to nearby sediments represents a challenging aspect of characterization and source control that is essential to effective remediation.

At the second demonstration site, feasibility studies are being conducted to evaluate possible capping methods to limit/reduce transport of contaminated sediments at the site. Previous studies (Luthy et al., 2005) have suggested that recontamination of cap areas by upland contaminated sediments may occur. Results from this demonstration may assist in evaluating possible recontamination issues at the site.

Due to the concerns of potential tracer ecological effects, additional biological effects studies were added during the first year of the project and are reported in Appendix 4. These biological effects studies consisted of a number of elutriate bioassay tests that all showed no adverse biological effects under a range of typical tracer exposure levels. Additional environmental issues are discussed at the end of Section 8 Implementation Issues.

2. TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

‘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. Utilizing this methodology, information can be garnered into source – sink relationships (‘connectivity’), 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 (Forsyth, 2000; McComb and Black, 2005). Sampling at strategic locations and timings is used to collect the tracer which is then returned to the laboratory for analysis. Measurable and uniquely identifiable signatures have in the past included the use of radioactive tracers (Courtois and Monaco, 1969; Heathershaw and Carr, 1987), fluorescent coated sands (Vila-Conjeco et al., 2004), and fluorescent silts (Sarma and Iya, 1960; Draaijer et al., 1984; Louisse et al., 1986). Synthetic, polymer-based tracers have also been developed (e.g. McComb and Black, 2005) but synthetic and radioactive tracers are now considered less desirable on economic and environmental grounds. Black et al. (2007) provide a comprehensive overview of the historic evolution of these differing approaches to the present day. The state-of-the-art for particle tracking technology, and the focus of this demonstration, utilizes dual (rather than mono) signature tracers. A general description of the dual signature tracer technology is provided below.

2.1.1 DUAL SIGNATURE TRACERS

The technology to be demonstrated uses proprietary tracers called ‘dual signature’ tracers (Figure 1); 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 color* and *ferrimagnetic character*. Two types of dual signature tracer are available: coated particles, and entirely artificial particles. Coated particles, which are simply samples of natural sands or silts directly coated with a fluorescent-magnetic mono-layer, possess a fixed grain density of 2.6 g/cm^3 (i.e. the mineral density) whereas that for artificial particles can be adjusted through the range 1.01 to 3.75 g/cm^3. Coated particle grain sizes range from 20 to 5000 μm (micrometers or microns) and are commonly used in sediment transport/particulate contamination studies. Artificial particles are commonly used to mimic low settling velocity particulates, such as biological larvae and activated carbon, 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 entirely natural materials plus a geochemically inert fluorescent pigment. A coated particle was used at each of the demonstration sites, and each grain possessed a density of ~2.6 g/cm^3. A second artificial particle tracer was used at the second demonstration site to simulate the activated carbon amendment at the cap site.

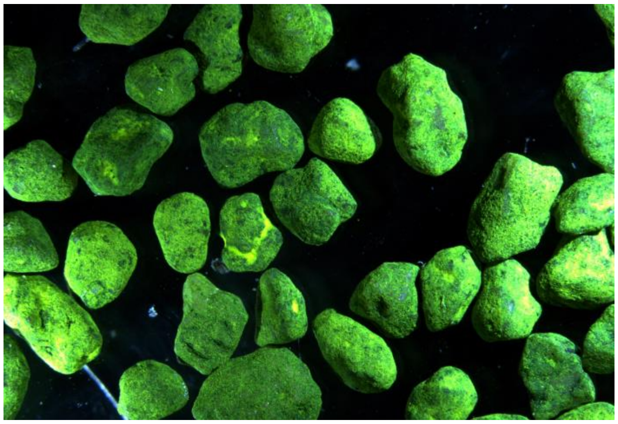


Figure 1. Photomicrograph of coated sand (mineral kernel) fluorescent-magnetic tracer grains. The grains pictured are ~ 150 - 200 microns in size (Partrac files).

Four spectrally distinct fluorescent colors are available with which to label tracers. The colors are commercially available fluorescent pigments, which themselves comprise polymer nano-spheres embedded with a water insoluble dye. This means that, aside from a very minor dust fraction produced by the tracer manufacturing process, no free dye is released into the aquatic system (the dust fraction can be removed/minimized by prior screening/washing).

Each pigment is characterized by specific excitation and emission wavelengths, which facilitates a targeted sample analysis procedure. The emission and excitation spectra of the pink and chartreuse (visually green and referred to as 'green' hereafter) tracers are presented in Figure 2. The peak emission wavelength (λ) for each dye is λ_{pink} =625 nanometers (nm) and λ_{green}=530 nm. Use of multiple colors 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).

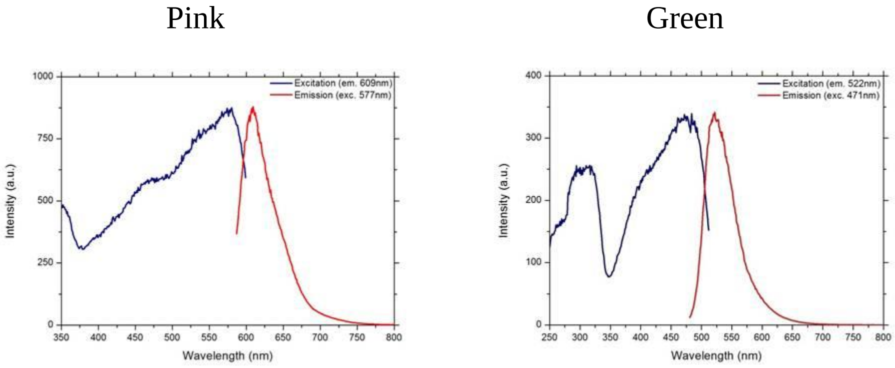


Figure 2. Excitation – emission spectra for pink (left) and green (right) pigment tracer particles (Partrac files). The fluorescence excitation spectrum (blue line) is obtained by fixing the fluorescence detector wavelength at 523nm then scanning the excitation wavelengths. Inversely, the fluorescence emission spectrum (red line) was obtained by fixing the excitation wavelength at 485nm then scanning the emission wavelengths. The peak excitation and emission spectra for each tracer color are noted.

Every tracer particle is also ferrimagnetic. Magnetism is controlled by the forces created by the spin and orbital angular states of the electrons within atoms (Dearing, 1994). The manner in which these motions are aligned, the number of electrons and the type of motions determine the magnetic moment of the atoms. Ferrimagnetic materials have populations of atoms which are strongly aligned, but exist as two sets of opposing forces. These materials display high susceptibility and are considered (colloquially) highly 'magnetic' materials insofar as tracer 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., 2010). 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 has profoundly limited tracer enumeration in previous studies.

The degree of magnetization 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 provides a comparative measure of the relative ease with which a material can acquire a magnetic field when exposed to a low frequency, low intensity alternating magnetic field; Iron (Fe) or Fe bearing materials acquire a magnetic field far more easily than non Fe bearing materials (Oldfield et al., 1999), hence they can be detected using this technique. Typically manufactured tracer is ~50-100 times 'more magnetic' than quartz-rich beach sand. Within this study the magnetic susceptibility of manufactured tracers was determined (see more discussion in Appendix 1 and 2 Field Reports).

2.1.2 TRACER COMPOSITION

The precise composition of tracer is commercially confidential. However, the major constituents of each tracer particle can be disclosed. The kernel of each tracer particle is a quartzitic sand (or silt) size grain, most usually derived from crushed quarry rock. This, in general terms, has the properties of quartz-rich beach particles. An ultra-thin (< 10 microns in size) coating is applied to the surface of every grain during tracer manufacture. The coating comprises a fluorescent pigment, a finely milled naturally occurring ferrimagnetic mineral, and a binding agent. The fluorescent pigments are commercially produced and are of themselves an inorganic dye encapsulated within millions of wax microcapsules. The sulphate-based binding agent is used to impart continuity and structure to the coating. In both sea- and fresh-water, the coating is stable and does not leach into the water. However, it can be removed by using a polar solvent, a feature exploited during the analytical stage. The tracers are benign and non-toxic. The dyes used (rhodamine-red (visually pink) and fluorescein-yellow (visually green)) are wholly encapsulated within the surface coating and not available to the environment. Through time any surface coating is eventually removed via abrasion leaving only the naturally occurring mineral kernel and the milled ferrimagnetic mineral.

2.1.3 TRACER STUDY BASIC ELEMENTS

Conducting a tracer study involves a specific set of steps (Black et al., 2017). These steps include: conducting a background study and tracer manufacture; tracer introduction; tracer sampling; and enumeration of tracer from environmental samples. The following is a brief description of these steps.

BACKGROUND STUDY

A background study is necessary to establish there are no fluorescent, magnetic particulate entities in the environment of interest (or if there are these can be accounted for in the analysis stage). Samples of the particles to be tracked are also collected and tested to establish grain size distribution and grain density (and sometimes settling velocity). This information is used to specify tracer characteristics. Assessment of the quantity of tracer required usually examines the volumes of water and length scales of interest to be sampled, and the sample design and analytical detection level. However, as a rule, as much tracer should be used as budgetary constraints allow (this is discussed further in Section 2.3.2).

The manufactured tracer is then subject to a similarity analysis (using the same testing procedures). Similarity testing or, as it is also termed, *'hydraulic matching'* is the process in which the physical attributes of the manufactured tracer (size, density etc.) are compared quantitatively to those of the native sediments. Black et al. (2007) developed a set of tolerances in relation to the hydraulic matching process. This approach was used successfully in studies in the Lower Duwamish Waterway (Sloan and Gries, 2009), and has also been used in studies of larval and peat transport (Black et al., 2005).

TRACER INTRODUCTION

Introduction of the tracer into the environment varies according to application. Previous usage in a similar context to that proposed here (in a study to determine the physical impact of highway derived particulates on nearby stream quality; Guymer et al., 2010) introduced the tracer directly into a roadside culvert/drainage pipe (Figure 3). Subsequent flow transported the tracer downstream (Figure 4).

TRACER COLLECTION (SAMPLING)

The dual signature nature of Partrac's tracer provides for a range of sampling options. High field 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, and provide an effective approach to sampling tracer particles travelling in suspension. The magnets are covered with a thin acrylic sheath, which is simply removed and bagged prior to enumeration. In addition to the fixed magnet collections, vessels with pumped water sampling can also be used (for suspended tracer) and bottom sediment grabs/cores can be collected and/or sediment traps deployed (for deposited tracer collections).

Figure 3. Example tracer introduction (Partrac files).

Figure 4. Example downstream tracer transport (Partrac files).

TRACER ANALYSIS (ENUMERATION)

The analytical objective of studies using tracers is to determine the dry mass of tracer within a sample. In situations where there are no native magnetic particles, once the tracer has been recovered it can be dried and weighed. However, in many industrial areas where samples contain a magnetic but non-fluorescent fraction a different analytical method (spectrofluorometry) is used.

A spectrofluorometer is a device used to measure parameters of fluorescence: its intensity and wavelength distribution of emission spectrum after excitation by a certain spectrum of light (Figure 2). These parameters can be used to identify the presence, and the emission intensity of specific dye molecules in a fluid medium. Modern fluorimeters are capable of detecting fluorescent molecule concentrations as low as 1 part per trillion. This approach offers a means with which to obviate the additional mass due to the presence of magnetic but non-fluorescent particulates simply and directly. It also provides a very high analytic resolution which facilitates detection of very low (milligram quantities) tracer mass. The fluorimeter signal output can be empirically related to tracer mass through a series of tracer (color) specific, reference standards. The methodology can be used where there are multiple tracer colors in environmental samples.

2.2 TECHNOLOGY DEVELOPMENT

Until 2005 particle tracking studies largely used mono signature fluorescent tracers (Black et al., 2007). Encapsulation of magnetic inclusions within particles was an innovation implemented by Partrac and introduced expressly to facilitate *in situ* interception and recovery of tracer in aquatic environments, thereby simplify tracking studies. This Partrac technology was developed over five years under research funding from the Scottish government. However, the technology still requires demonstration to show its innovative use for efficiently mapping the transport of finer sized particles that sorb contaminants and thus, dictate where contaminants are deposited. At the Duwamish Superfund site, much of the finer silt sized material left the immediate area where the tracer was released, but the utility of *in situ* magnets as (point, passive) sampling devices over time periods extending over months was demonstrated (Sloan and Gries, 2009).

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

2.3.1 ADVANTAGES OF THE TECHNOLOGY

Two principal and practical advantageous elements, both related to sampling and separation, arise through the addition of ferrimagnetic character to particles. These provide for a more cost-effective sample collection and analysis, in comparison to previous technical approaches. In combination, the use of magnets and tracer particles with ferrimagnetic character permit *separation* of tracer from environmental samples which can then be passed on for analysis. No previous techniques have been able to effectively separate particulate tracers from the native sediment load.

Firstly, the use of *in situ* magnets intercepts tracer moving in a fluid body obviating what in a conventional approach would require collection of a water sample, return to a laboratory, water removal (e.g. by sieving, filtration) and manual inspection. *In situ* magnets avoid these processes entirely as tracer separation *from* the environment occurs *within* the environment (Fig. 5). The use of magnets offers an elegant and better technical solution to tracer recovery, and because it avoids time-consuming and repetitious post-processing of samples it is also more cost-effective. During deployment each magnet is covered by a clear acrylic sheath; at the moment of sample recovery this sheath is simply removed and bagged.

Studies have shown the cross-sectional (sampling) area each magnet offers is 225 cm^2, and the corresponding volume is ~1125 cm^3 (i.e. 1.125 liters). Studies in a laboratory flow channel have investigated the capture efficiency of the magnets under controlled flow conditions. These show that tracer entering the magnetic field will become irreversibly attached where ambient currents are < 0.4 meters/second.

Further magnets, if dipped into the ocean, can act as point samples analogous to point water samplers (Figure 6). This provides a simple and ready means of assessing tracer presence in the water column. Studies have shown that sampling in this fashion has a tracer retrieval/capture efficiency of >90% and is highly comparable with conventional water sampling. Pole magnets can also be used as Eulerian passive (*time-integrating*) samplers if left unattended for a period of time (e.g. on a vertical mooring; see Fig. 5), an approach utilized in this demonstration. Equally, they can act as *time series* samplers if they can be sequentially re-sampled.

The second advantage of the use of magnets relates to recovery of tracer from within sediment samples (e.g. in instances where cores or grabs of the seabed are collected, Fig.7). For these sampling methods, a surface scrape approximating the oxic layer depth is removed and bagged. Upon return to the laboratory, a sediment sample can simply be flushed across a magnet and this will recover any magnetic particles, including tracer, that are in the sample. This process is >98% efficient at capturing a known amount of released tracer. The use of magnets allows concentration of deposited tracer within a sediment matrix which can then be passed for analysis, and it is here that the magnetic character of the dual signature tracer provides substantial benefit in terms of time, and therefore also of cost.

Magnets can be arranged into a flat, broad frame which can be emplaced onto the seafloor. In this manner, any tracer depositing onto the sediment surface will be captured. Equally, magnets can be mounted vertically on a bedframe/plate to indicate tracer presence within the bottom boundary layer (Fig. 8).

2.3.2 LIMITATIONS OF THE TECHNOLOGY

The most significant limitation of particle tracking is the potential for tracers to not effectively simulate the behavior of the target sediment (contaminated particulates). To ensure the tracer particles replicate the behavior of the target sediment the manufactured tracer is subject to a similarity analysis for comparison to the native particles. Similarity testing or, as it is also termed ‘hydraulic matching’, is the process in which the physical attributes of the manufactured tracer (size, density etc.) are compared quantitatively to those of the native particles. Figure 9 shows grain size spectra derived from settling velocity determinations for native sand and for a manufactured tracer from a previous study as an example of similarity testing. Two hydraulically matched particles will be cycled (i.e. eroded, mobilized, transported and deposited) in the same fashion to ensure the tracer is suitable for deployment.

Black et al. (2007) developed a set of tolerances in relation to the hydraulic matching process. Evaluations of the success criteria includes statistical analyses to compare the mean and standard deviation of the grain size distribution. For example, the mean grain size of the tracer should be within half a phi unit of the native particles and the ratio of densities (tracer/native) should be equal to one (±10%). The overall grain size distribution will also be compared with measures of skewness and kurtosis.

Figure 5. *In situ* capture of tracer using a submersible magnet.

Figure 6. Sampling suspended tracer can be done directly using a pole magnet dipped into this cloud of green tracer.

Figure 7. Use of sediment grab to monitor deposition of tracer at the first demonstration site.

Figure 8. A vertical bed-frame mounted magnet to capture tracer moving in the bottom boundary layer at the second demonstration site.

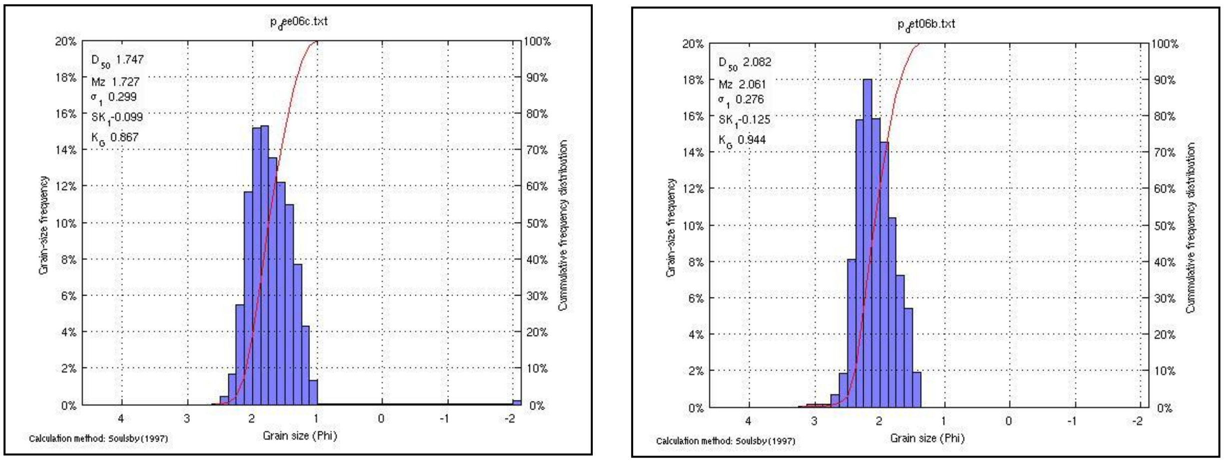


Figure 9. Example of nearly equivalent grain size spectra for (a) native and (b) tracer particles derived from settling velocity determinations (Partrac files).

A second potential limitation is related to dilution of the tracer and loss of tracer material beyond/below the limit of detection. To mitigate this the appropriate mass of tracer (for the system and to achieve the aims and objectives of the project) must be utilized during the study. A typical rough calculation to estimate the mass of tracer required might consider the extent of the source area (i.e. the spatial area over which the tracer is introduced), the tracer introduction methodology and receiving environment and definition of a site boundary (sample limit). An appropriate quantity of tracer required (T_{Mass}) can then be determined by multiplying the bulk density of the native sediment (D_{Bulk}) within the source area by the spatial extent of the source area (S) or to achieve a desired tracer concentration post-deployment.

$$T_{Mass} = D_{Bulk}\, S \tag{1}$$

3. PERFORMANCE OBJECTIVES

3.1 SUMMARY OF PERFORMANCE OBJECTIVES

Performance objectives for this demonstration provide a basis for evaluating the success of the technology during the demonstration. The performance objectives for the project are shown in Table 1 and results are evaluated in Section 6. Section 6 results show all performance objectives were successfully passed.

Table 1. Performance Objectives

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Hydraulic matching of tracer material with native sediments.	Particle size distribution (PSD) and density analyses of tracer material and native sediments.	- PSD to be within 20% of native sediment metrics e.g. d_{50} - $\rho_{tracer}/\rho_{native}$ ≤±6%, with overlapping std deviation values.	Section 6.2.1
Comparison of magnets with conventional methods to determine total suspended solids (TSS) concentration for suspended tracer.	Laboratory tests and analyses on varying TSS concentrations to compare conventional and magnet methods and assess effectiveness.	Maximum difference between conventional and magnet methods to be < 30%.	Section 6.2.2
Retention capacity of material captured by the deployed magnets.	Expected flow speed magnitudes at the tracer dispersion study site.	Retention capacity of magnet to be >90% for expected study site flow magnitudes.	Section 6.2.3
Demonstrate effectiveness of the magnet frame technique for tracer collection in sediments.	Controlled comparison of magnet frame and conventional sediment grab methods.	Maximum difference between conventional and magnet sampling methods to be < 30%.	Section 6.2.4
Effectiveness and accuracy of spectrofluorometric method, running of spikes and laboratory blanks, bias, standard curve.	Controlled laboratory based spectrofluorometric measurement and analysis of study specific tracer materials.	Differences within spikes and blanks to be < 25% of true value. Bias data to be within 10%. Standard curve regression, scatter to be within 40% of best fit line.	Section 6.2.5
Demonstrate a mass balance approach through interpolation among discrete sampling locations.	Tracer mass at sampling locations, interpolation methods for suspended and deposited tracer.	Closed mass balance >50% (fair); >70% (good); or >90% (excellent).	Section 6.2.6
Qualitative Performance Objectives			
Ease of use for technique.	Feedback from technician and/or project team undertaking field survey.	Technician and/or project team consider technique to be more effective than conventional methods / techniques.	Section 6.2.7

3.2 PERFORMANCE OBJECTIVES DESCRIPTIONS

3.2.1 HYDRAULIC MATCHING OF TRACER TO NATIVE PARTICLES

In order for a specific study to be scientifically robust the tracer used must have the same hydraulic properties as the particulates/sediments it is aiming to mimic. Hydraulic matching is the process whereby the behavior in water of the native sediments and the tracer are compared. This is achieved by performing tests such as measuring particle density (specific gravity) and determining the particle size distribution (PSD) of the tracer and the native sediments, and comparing these. Success criteria will include PSD within ±20% of native sediment metrics (e.g. d_{50}), and density ratios ($\rho_{tracer}/\rho_{native}$) within ±6%, with overlapping standard deviation values.

3.2.2 COMPARISON OF TRACER COLLECTION METHODS

The project utilized magnet moorings strategically positioned in the water column to intercept (sample) tracer travelling in suspension. Magnets were also used to sample tracer by dipping magnets into the suspended plume from a vessel; this is akin to lowering a conventional water sampler into the water and collecting a sample. Utilizing magnets in this fashion are a novel application of magnetic tracer and sampling techniques. The magnet sampling method was compared with the standard water sampler method under controlled conditions. Data requirements include laboratory and field tests and analyses on varying TSS concentrations to compare conventional and magnet methods, and assess the effectiveness of both. Success criteria will include maximum differences between conventional and magnet methods to be < 30%.

3.2.3 MAGNET RETENTION CAPACITY

In addition to understanding the efficacy of tracer capture (i.e. how well do suspended magnets capture suspended tracer), it is also important to know the magnet retention capacity of tracer particles under typical water column flow conditions. This assessment will be achieved through a series of staged laboratory flume experiments during which the flow conditions will be varied. This assessment will be quantitative. Data requirements include the expected flow speed magnitudes at the tracer dispersion study site. Success criteria will be retention capacity of magnet to be >90% for anticipated flow conditions.

3.2.4 MAGNET COLLECTION OF TRACER IN SEDIMENTS

A special frame equipped with magnets will be used to sample deposited sediments for recovery of deposited tracer. The effectiveness of this method will be evaluated by sampling a known mass of tracer deposited onto the sediment bed. This assessment will be quantitative. Data requirements include a controlled comparison of magnet frame and conventional sediment grab methods in the laboratory as well as field comparisons at selected sites. Success criteria will again be maximum difference between conventional and magnet sampling methods < 30%.

3.2.5 PERFORMANCE OF SPECTROFLUOROMETRIC ANALYSIS METHODS

The analytical method we propose to use for the enumeration of tracer (spectrofluorometric measurement) needs to be robust and fully characterized in terms of its utility and efficacy. A range of quality control tests will be performed to illustrate that the methodology is fit for purpose, including running of blanks and spiked samples, and assessments for accuracy, repeatability and bias. This assessment will be quantitative. Data requirements include the controlled laboratory based spectrofluorometric measurement and analysis of study specific tracer materials. Success criteria for accuracy will be differences within spikes and blanks to be < 25% of true value and bias data to be within 10%. Standard curve regression of tracer mass versus fluorescence intensity will show scatter to be within 40% of best fit line.

3.2.6 DEMONSTRATE MASS BALANCE

Although the tracer will only be collected at discrete locations over the study, a simple model to interpolate the mass of tracer across the site will be used to assess mass balance (material flux). Since we know the mass of tracer injected at the start of the study, we can compare this to the total interpolated mass suspended in the water column and deposited in the sediments. Many tracer studies typically report results as presence or absence, so this approach will attempt to provide a more quantitative map of where particles are present in the outfall area. Data requirements include the tracer mass at sampling locations, and interpolated masses for suspended and deposited tracer. Success criteria will be evaluated in a semi-quantitative manner with a closed mass balance >50% rated ‘fair’, >70% rated ‘good’, and >90% rated ‘excellent’.

3.2.7 EASE OF USE

A key performance objective is whether the technique is simple and effective to use. To evaluate ease of use feedback was collected from the project team undertaking field survey and laboratory analyses. This was a strictly qualitative assessment.

4. SITE DESCRIPTION

This section provides a concise summary of the demonstration sites and includes site information that is relevant to the technology. Specific subsections below are intended to capture relevant information that had bearing on the performance of the technology.

4.1 NAVAL BASE SAN DIEGO

4.1.1 INTRODUCTION

The first site selected for this demonstration project was Naval Base San Diego (NBSD) located in San Diego, California. At NBSD the tracer was released with pumped baywater at an outfall to simulate the release of contaminated particles from either a stormwater or dry dock discharge. Although the stormwater discharge would be freshwater and therefore more buoyant, the suspended tracer particles are expected to rapidly lose their momentum near the outfall and fall through the water column with particle dispersion dominantly occurring due to the tidal forcing at the time of release (see more discussion in Section 5.1.4). The buoyancy difference for particles with density ~2.5 g/cm^3 settling through freshwater (water density of 1.0 g/cm^3) versus baywater (water density of 1.07 g/cm^3) was therefore considered to be negligible (<5% in density difference). Using baywater as the discharge medium provided a reasonable approximation of the far-field transport of either the freshwater stormwater or salt water drydock release following the initial localized dispersion due to momentum and buoyancy driven transport.

4.1.2 SITE SELECTION

The selection criteria were also discussed in the Site Selection Memorandum developed for the site. In summary, NBSD was selected due to the presence of stormwater outfalls, drydock discharges, and urban creeks that discharge particles and may act as ongoing contaminant sources to the surrounding sediments. A large amount of pre-existing data was available for the site (Katz et al., 2006; 2011; 2014), and its proximity to the SPAWAR facilities makes logistics easier than other distant sites. The site also has a number of regulatory drivers including TMDL related actions that make the study highly relevant to DoD and regulatory decision making.

4.1.3 SITE LOCATION AND HISTORY

Figure 10 shows the location of the first demonstration site at NBSD. Sediments in the pier area contain elevated levels of metals and organic contaminants, and this area has been placed on the State of California 303D List requiring additional study under the TMDL program (see section 1.3 above; and Katz et al., 2011 for further discussion). The target outfall/discharge area for this ESTCP demonstration will be south of Pier 8 at Outfall 20 near Paleta Creek. The tracer was released as a simulated outfall discharge using pumped bay water from a vessel anchored along the quay wall in this area. Clearance for the 48 hour demonstration period was obtained so magnets could be deployed and recovered and a small boat could move within the pier area to collect samples.

San Diego Bay is a semi-enclosed, crescent-shaped bay opening to the Pacific Ocean and located in southern California. The bay is approximately 24 kilometers (km) in length and varies from about 0.4 to 5.8 km in width. Extensive dredging of channels and near-shore filling over time has significantly altered the bay in terms of depth and width. In the pier area demonstration site the dredged depth is fairly uniform at about 10 meters.

The climate in the region is generally mild with annual temperatures averaging around 65 degrees F near the coastal regions. Annual average rainfall ranges from 9 to 11 inches along the coast to more than 30 inches in the eastern mountains. There are two distinct climatic periods: a dry period from late April to mid-October and a wet period from mid-October through late April. Due to several drought years and the logistical difficulties of getting foreign personnel and equipment onsite at the time of a particular storm event, an outfall discharge was simulated with pumped water.

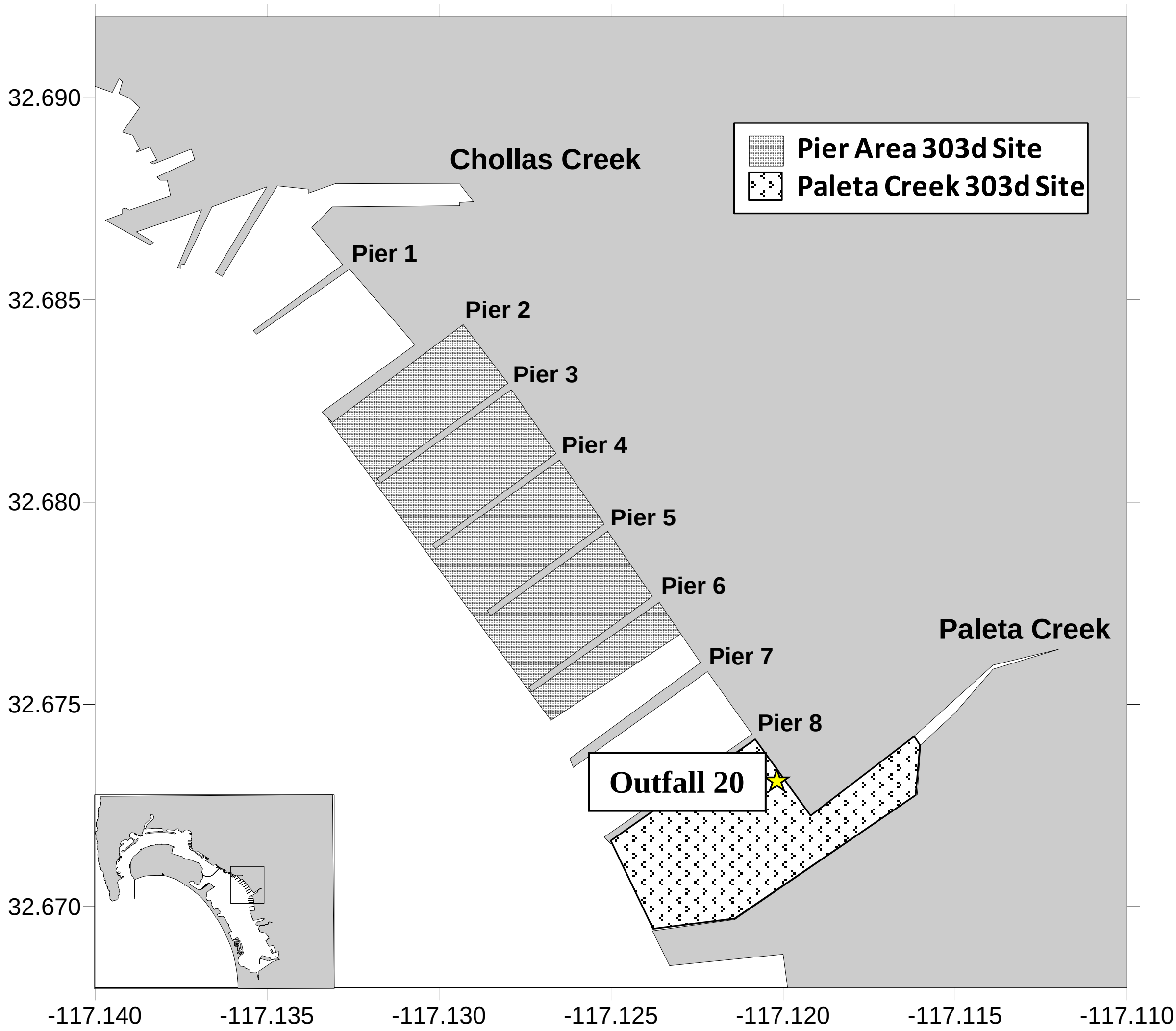


Figure 10. The Naval Base San Diego (NBSD) demonstration site is at Outfall 20 located between Pier 8 and Paleta Creek on the east side of San Diego Bay, CA (from Katz et al., 2011).

4.1.4 CONTAMINANT AND GRAIN SIZE DISTRIBUTION

The contaminated sediments of interest for this ESTCP project are adjacent to stormwater Outfall 20 at NBSD, noted in Figure 10 between Pier 8 and Paleta Creek (Katz et al., 2011). The Paleta and Chollas watershed areas located adjacent to NBSD are highly urbanized with commercial and industrial land uses dominating the shoreline around the bay. The sediment contamination around NBSD was from pollutant sources such as urban runoff/storm water conveyance systems, shipyards and ship activities, and other point and nonpoint sources of pollution. Sediment contamination includes metals such as copper, lead, mercury, and zinc as well as organic contaminants. Figure 11 shows a contour map of copper concentrations in the Paleta Creek area south of Pier 8, which was similar to the pattern seen in other contaminants. The higher contaminant concentrations tend to mirror the higher level of fines (silt and clay sized particles less than 0.0625 millimeters (mm) or 62.5 µm) shown in Figure 12. Table 2 shows the grain size data by site, with station P01 farthest to the west (left in Figure 12) and station P17 farthest to the east (right in Figure 12). Table 3 shows the average particle size distribution for the surface sediment compared to Paleta Creek stormwater, indicating that the surface sediments are very similar to the stormwater particles in terms of particle size distribution. Since we want to track the fine particles that tend to have higher contaminant concentrations, the tracer was manufactured with the particle size distribution centered in the silt range around 30-50 µm.

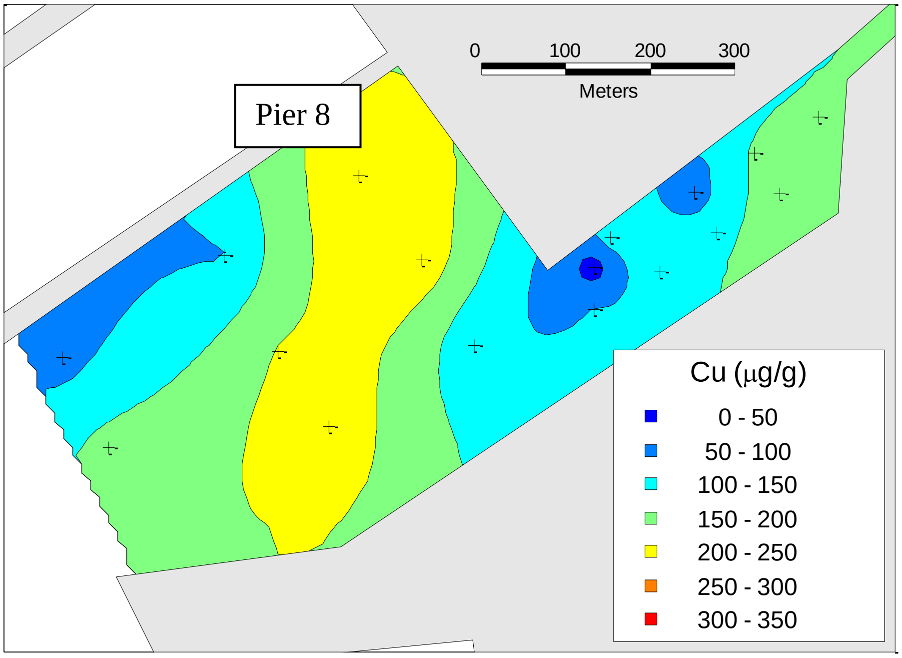


Figure 11. Spatial distribution of surface sediment copper in Paleta Creek area south of Pier 8 (from Katz et al., 2011). Copper (Cu) concentration units are in micrograms per gram.

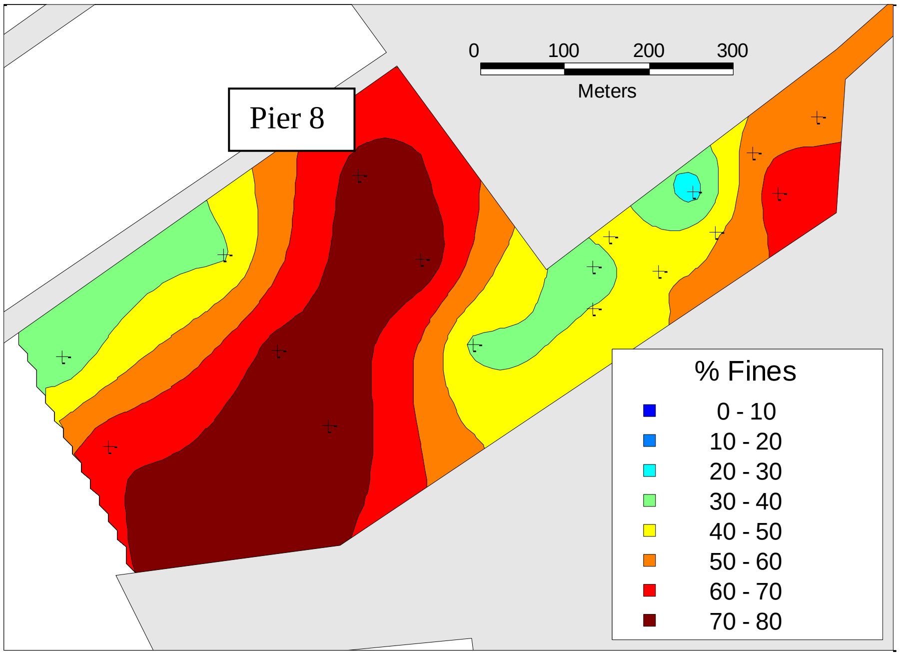


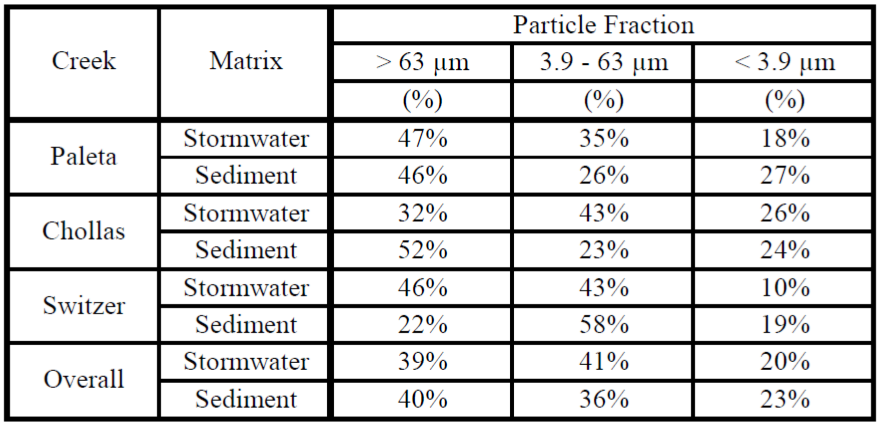
Figure 12. Spatial distribution of %Fines in the Paleta Creek area south of Pier 8 (from Katz et al., 2011). Sample P01 was farthest west along Pier 8 and Sample P17 was farthest east near mouth of Paleta Creek.

Table 2. Percent (%) Gravel, Sand, Silt, Clay, Fines, and Total Organic Carbon in sediments (from Katz et al., 2011).

Analyte	Size Range (mm)	P01*	P02	P03	P04	P05	P06
Gravel	>2	9.91	0.76	0.95	0.17	0	0.35
Sand	<2 to 0.0625	58.350	30.95	60.650	25.26	21.25	26.04
Silt	<0.0625 to 0.0039	15.70	29.8	15.63	33.5	34.7	32.9
Clay	<0.0039	16.04	38.52	22.77	41.07	44.06	40.72
Fines	<0.0625	31.740	68.300	38.400	74.560	78.750	73.600
TOC		0.420	1.290	0.9	1.4700	1.5900	1.540
Analyte	**Size Range (mm)**	**P07**	**P08**	**P09**	**P10**	**P11****	**P12**
Gravel	>2	0	0.92	7.77	2.35	1.435	0.48
Sand	<2 to 0.0625	20.85	61.56	60.61	56.92	53.54	50.37
Silt	<0.0625 to 0.0039	37.0	17.64	26.05	21.43	19.87	26.34
Clay	<0.0039	42.11	19.89	5.56	19.3	25.15	22.81
Fines	<0.0625	79.140	37.530	31.610	40.730	45.020	49.150
TOC		1.600	0.7000	0.09	0.830	1.12	1.240
Analyte	**Size Range (mm)**	**P13**	**P14**	**P15**	**P16**	**P17**	
Gravel	>2	2.76	0.07	0.57	0.25	1.07	
Sand	<2 to 0.0625	72.49	51.10	43.40	34.1	43.24	
Silt	<0.0625 to 0.0039	12.46	26.77	25.50	37.28	27.7	
Clay	<0.0039	12.29	22.06	30.52	28.36	27.99	
Fines	<0.0625	24.750	48.830	56.020	65.640	55.690	
TOC		0.620	1.320	1.47	2.110	2.00	

***first value of lab duplicates**
****mean of field duplicates**

Table 3. Comparison of particle size distributions in stormwater and surface sediments for creeks entering San Diego Bay (from Katz et al., 2006).



Creek	Matrix	Particle Fraction		
		> 63 µm (%)	3.9 - 63 µm (%)	< 3.9 µm (%)
Paleta	Stormwater	47%	35%	18%
	Sediment	46%	26%	27%
Chollas	Stormwater	32%	43%	26%
	Sediment	52%	23%	24%
Switzer	Stormwater	46%	43%	10%
	Sediment	22%	58%	19%
Overall	Stormwater	39%	41%	20%
	Sediment	40%	36%	23%

4.2 HUNTERS POINT SHIPYARD

4.2.1 INTRODUCTION

The second demonstration site that was selected for this project was Hunters Point Shipyard (HPS) located in San Francisco, California (Figures 13 and 14). At HPS two tracers were released (as opposed to the one tracer used at the first demonstration) to conduct a demonstration with two objectives:

1) To examine the potential for 'loss from source' of the activated carbon amendment material (as mimicked by a pink tracer), and to identify the subsequent transport pathway (and potential depositional zone) for this lost material; and
2) To examine if contaminated material (as mimicked by a green tracer) from the sediments upland of capped areas are being mobilized to the capped areas thus recontaminating the site.

4.2.2 SITE SELECTION

The selection criteria were also discussed in the Site Selection Memorandum developed for the site. In summary, HPS was selected due to this location having placement of an activated carbon cap in June 2015 over contaminated intertidal and subtidal sediment in the South Basin at HPS. A large amount of pre-existing data was available for the site (Battelle et al., 2006), and this site served as an early demonstration site for activated carbon used for sequestration of sediment contamination (ESTCP Project ER0510 (Luthy et al., 2009)). Luthy et al. (2009) speculated that the small plot size used for the early amendment studies allowed recontamination by the surrounding contaminated sediments to confound the later monitoring periods (one to two years following placement of activated carbon amendment). The Navy and regulators have recently (June 2015) placed a larger activated carbon cap in the South Basin to compare the efficacy of two different types of activated carbon cap materials (SediMite vs AquaGate). This ESTCP tracer study was leveraged with this recent capping project to provide site managers and regulators with additional data to help determine: 1) how much amendment material (activated carbon) is lost from the cap area; and 2) how much recontamination of the cap from the surrounding uncapped contaminated sediments occurs.

4.2.3 SITE LOCATION AND HISTORY

Figures 13 and 14 show the location of the second demonstration site at HPS. Sediments in the South Basin area contain elevated levels of multiple contaminants, and current plans include the potential use of amendment caps as part of the remedial options. Additional maps for the target area for this ESTCP demonstration will be provided in the next section (Section 5 Test Design). Detailed site history can be found in various references cited in this section, with the remaining text in this subsection taken from the regulatory documents (BAI, 2007; Battelle et al., 2006).

HPS is a former naval shipyard located on a peninsula in southeast San Francisco that extends east into San Francisco Bay (see Figure 13). In 1940, the Navy obtained ownership of HPS for shipbuilding, repair, and maintenance. After World War II, activities at HPS shifted to submarine maintenance and repair. HPS also was the site of the Naval Radiological Defense Laboratory. HPS was deactivated in 1974 and remained relatively unused until 1976. Between 1976 and 1986, the Navy leased most of HPS to Triple A Machine Shop, Inc., a private ship repair company. The Navy resumed occupancy of HPS in 1987.

HPS is 420 acres in size, with Parcel F comprising approximately 446 acres offshore of HPS. The Navy proposed dividing HPS into separate parcels to conduct Remedial Investigations (RI) and Feasibility Studies (FS) and to expedite remedial actions in support of transferring the property. As a result, the Navy divided the facility into seven contiguous parcels: A, B, C, D, E, E-2, and F. The Navy transferred Parcel A to the San Francisco Redevelopment Agency in December 2004; as a result, Parcel A is no longer Navy property and is not shown in Figure 13 (it contained the property between parcels B and D).

Past shipyard operations left hazardous materials on site so HPS was included on the National Priorities List in 1989 as a Superfund site pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as amended by the Superfund Amendments and Reauthorization Act of 1986. In 1991, HPS was designated for closure by the Defense Base Closure and Realignment Act of 1990. Closure at HPS involves conducting environmental remediation and making the property available for nondefense use. The main contaminants of concern in the Parcel F offshore sediments are PolyChlorinated Biphenyls (PCBs). Figure 14 shows a surface contour map with concentrations ranging from below detection limits to over 5000 micrograms per kilogram (µg/kg). Subsurface sediments contain higher concentrations, with the highest concentrations located in two separate areas, one to the northeast by the former landfill and one to the west by Yosemite Creek.

Between 1935 and 1975, soils from the hillside located on Parcel A and additional fill materials were placed on the outboard side of HPS levees in San Francisco Bay, thus increasing the land area of the HPS facility from less than 100 acres to the current size of approximately 420 acres. The artificial fill used may contain serpentinite bedrock, excavated Bay Mud, sands, gravels, construction debris, industrial debris, and sandblast waste. As a result, the subsurface stratigraphy at HPS includes three artificial fill units: (1) serpentinite bedrock-derived fill, primarily serpentine with chert, shale, and related materials; (2) industrial fill (including sandblast waste, construction debris, and dredged material); and (3) backfill consisting of poorly graded sands and gravel. Generally, these fill materials overlie Bay Mud deposits and, to a lesser extent, undifferentiated sedimentary deposits.

Based on cores collected along the shoreline at Parcels E and E-2 the (landmass upland to the South Basin), the shallow geology consists of artificial fill, similar to the adjacent upland areas. The fill left an inlet that extended from the South Basin to the northern corner of Parcel E-2. The inlet was later filled with shipyard wastes, including construction and industrial debris and waste, domestic refuse, sandblast waste, paint sludge, solvents, and waste oils. This inlet, referred to as the “former slough”, was filled to construct the landfill located in Parcel E-2 and may represent a potential source for the PCB contamination in South Basin shown in Figure 14 (in addition to potential sources up Yosemite Creek to the west).

The South Basin is a shallow embayment on the south side of HPS, with water depths ranging from 6 to less than 2 feet. Yosemite Creek enters the South Basin from the west and is characterized as a shallow, tidally influenced channel with no permanent flow. Circulation in South Basin is restricted and tidal currents are generally weak. The most significant sediment resuspension occurs as a result of storm waves that are generated from the southeast winds during the winter. Sediment stability was evaluated in the South Basin in Parcel F by analyzing site-specific critical shear stress and erosion rate data provided by Sedflume measurements in conjunction with hydrodynamic measurements conducted during the FS (Battelle et al., 2006). The data were used to assess the likelihood that sediment would erode under typical and extreme hydrodynamic conditions and to predict the maximum depth of erosion. Hydrodynamic measurements of waves and currents were conducted in the South Basin during a winter month and a summer month to characterize the seasonal hydrodynamic conditions. Radioisotope data from South Basin cores indicates that the net sediment accumulation rate is approximately 1 centimeter per year (cm/yr). Appendix F of the FS Technical Memorandum (Battelle et al., 2006) provides a detailed description of the investigation.

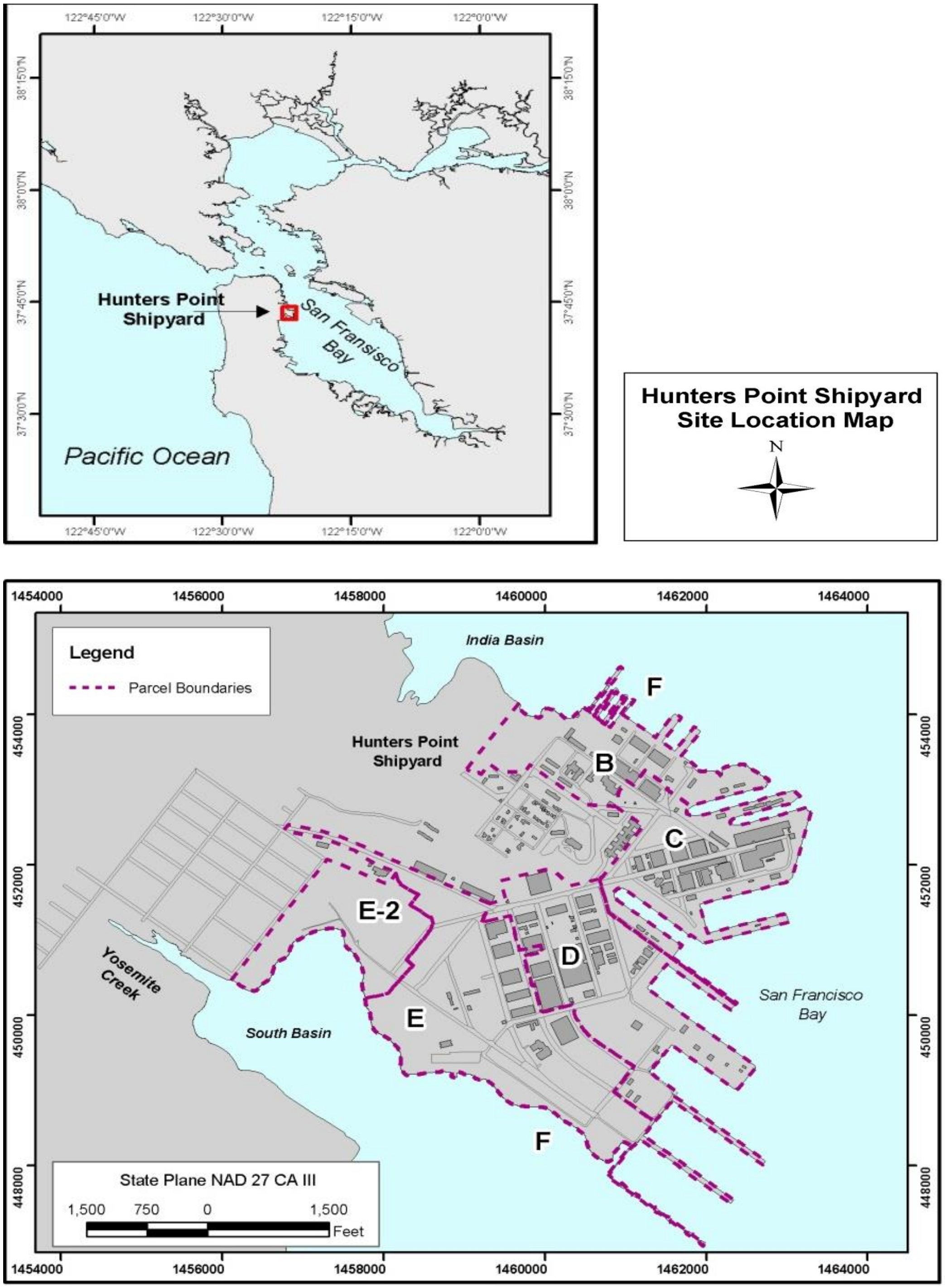


Figure 13. Map of HPS with Parcel Boundaries, including Parcel F with offshore sediments the South Basin where the second ESTCP Demonstration occurred (Battelle et al. 2006).

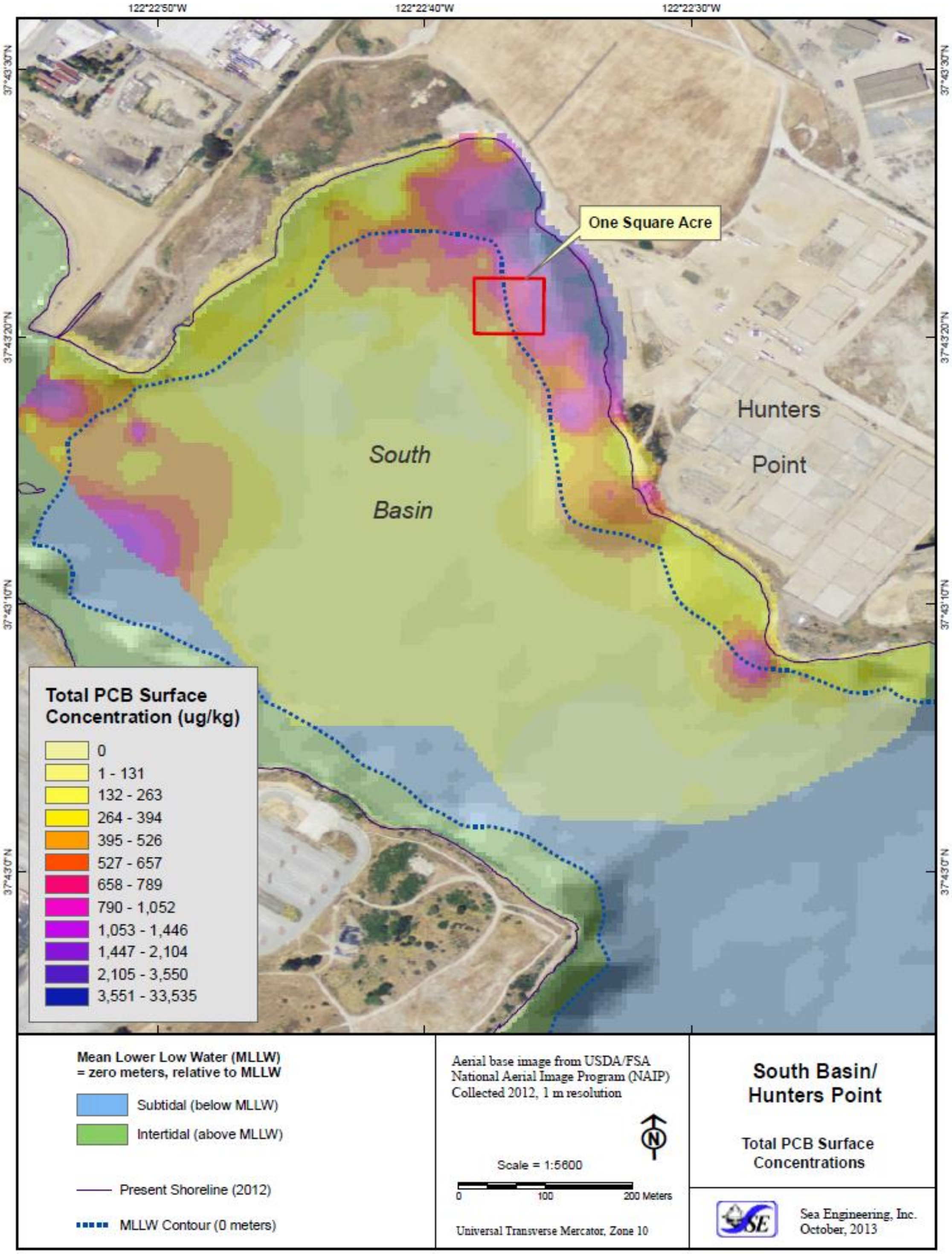


Figure 14. Location of one square acre amendment study site along the mean low low water (MLLW) contour in South Basin for the second ESTCP demonstration (modified from NAVFAC presentation for public review of cap design).

4.2.4 CONTAMINANT AND GRAIN SIZE DISTRIBUTION

The contaminated sediments of interest for this ESTCP project are shown in Figure 14 along with the location of the one acre pilot scale amendment cap placed in June 2015. A previous contour map done for the FS is shown in Figure 15, showing the sample locations that were discussed in the FS. Table 4 shows the range of grain size and total organic carbon (TOC) around the site, with the cap being placed between SB14 and SB15 in surface sediments with 1000 to 2000 µg/kg PCB concentrations. The offshore sediments are consistently fine grained, with most sites between 90 and 100% fines (particle sizes <63 µm containing silt and clay) and TOC levels near 1.5%. Only very near the beach (see for example SB-19, SB-21, SB-23) does the sediment composition shift to mainly sand, shell hash, and gravel (particle sizes >63 µm). The upland silt tracer discussed in Section 5 was released near FS site SB-11 (see green rectangle in Figure 15) which shows >90% (Table 4) of the native material grain sizes are less than sand size (particle sizes <63 µm).

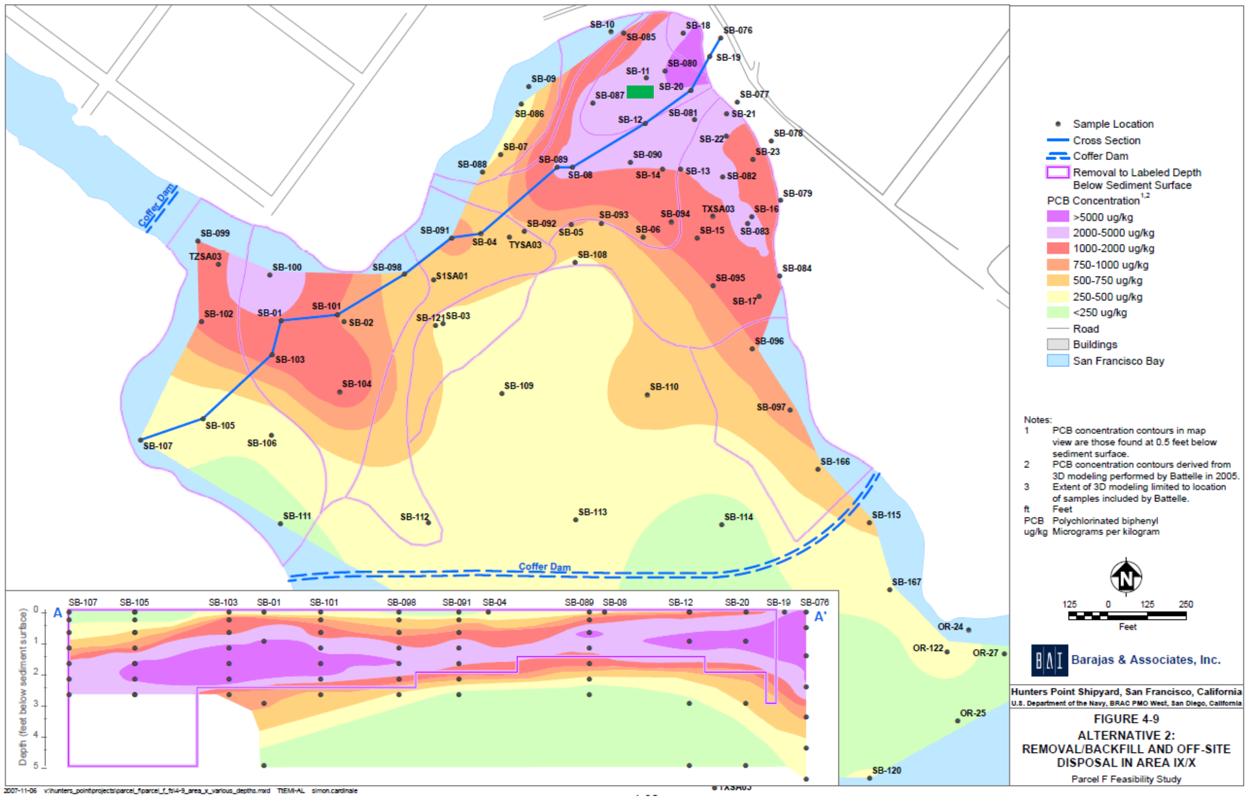


Figure 15. Contour Map with cross section showing PCB concentrations in offshore sediments (from BAI, 2007). PCB concentrations are in micrograms per kilogram or parts per billion. The green rectangle just below site SB-11 represents the approximate position of the green tracer release zone.

Table 4. Grain Size (percent of particles above and below 63 micrometers (um) which represents the silt to sand boundary) and Total Organic Carbon (TOC) in sediments (Battelle et al. 2006 Phase 1 sites from SB-01 to SB-23).

	Grain	Size (%)	TOC
Site	<63 um	>63 um	(%)
SB-01	64.3	35.7	1.35
SB-02	88.5	11.5	1.53
SB-03	99.6	0.4	1.87
SB-04	99.6	0.4	1.56
SB-05	98.6	1.4	1.52
SB-06	99.4	0.6	1.64
SB-07	93.7	6.3	1.38
SB-08	98.7	1.3	1.59
SB-09	40.7	59.3	0.786
SB-10	68.9	31.1	1.11
SB-11	95.1	4.9	1.7
SB-12	89.9	10.1	1.56
SB-12	97.2	2.8	1.68
SB-13	97.1	2.9	1.58
SB-14	97.4	2.6	1.52
SB-15	98.9	1.1	1.57
SB-16	47.4	52.6	1.36
SB-17	83.3	16.7	1.26
SB-18	15.8	84.2	0.434
SB-19	8.6	91.4	0.326
SB-20	92.7	7.3	1.63
SB-21	28.2	71.8	0.689
SB-22	87.4	12.6	1.7
SB-23	19.2	80.8	0.696

5. TEST DESIGN

This section of the report contains a detailed description of the testing conducted at each demonstration site. The testing conducted at NBSD is presented first followed by the testing done at HPS.

5.1 NAVAL BASE SAN DIEGO

5.1.1 CONCEPTUAL EXPERIMENTAL DESIGN

As discussed in Section 2.1.3, conducting the particle tracking demonstration and validation study involves a specific set of steps. These steps are:

1. Conducting pre-demonstration background studies which include: 1) Native material assessment (PSD and particle density (specific gravity) of typical sediment at NBSD) and manufacture of tracer to mimic natural particles; and 2) Background material sampling for the presence and quantification of native magnetic or fluorescent particulates.
2. Demonstration setup and introduction of tracer material at outfall site to simulate an outfall discharge. Setup will include fixed magnet arrays and equipment for collection of information of local tidal currents.
3. Magnetic collection period (up to 2 days) with sample collection from fixed magnet strings and mobile vessel point sampling for water column plume mapping, and seabed magnet and grab/core samples for deposited tracer on sediment surface.
4. Data analysis of samples in the laboratory and subsequent validation of the technology based on assessment of performance objectives.

The first three of these tasks were described below in Section 5.1.4 and the final analysis task was described in Section 5.1.6.

5.1.2 BASELINE CHARACTERIZATION ACTIVITIES

Baseline characterization information required for the demonstration includes (1) discharge particle size characteristics to allow robust tracer matching, (2) discharge volume, flow rate and particle concentration conditions, and (3) the abundance and characteristics (e.g. size) of any naturally occurring magnetic or fluorescent particles. Sufficient baseline characterization was conducted by previous studies to support development of the demonstration for items 1 and 2 above. Surface sediment data from Katz et al. (2011) and SCCWRP and SPAWAR (2005), and large volume samples collected by Chadwick et al. (2006) provided sediment contaminant concentrations and grain size distributions (see Section 4.1.4). Katz et al. (2006, 2014) also provided some general site information on outfall discharge rates and total suspended solids (TSS) levels that were matched during the simulated outfall discharge (see section 5.1.4). Based on these data, particle loading from drainage basins at the installation are generally on the order of ~4-6 g/m^2, and first-flush particle concentrations in discharges are typically in the range ~450 mg/L ranging as high as ~840 mg/L. A typical storm of 0.25-0.50 inches of rain is expected to generate an outfall discharge along the quay wall of 1000 liters/min with TSS of 75-500 mg/liter depending on the drainage area. Surface sediments in the general vicinity of the outfall indicated particle size distributions predominantly in the fines range (average 47%) with mean particle size in the silt range (Table 2). This is comparable to the particle size distribution observed on large volume water samples collected from the discharge of Paleta Creek itself (see Table 3).

5.1.3 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

The design of the dual signature tracer is provided in Section 2 and shown in Figures 1-4. Discussion of the magnet designs used for collection is provided in Section 2.2 and shown in Figures 5-8. Specifics of the field testing components are described in Section 5.1.4. Additional discussion of the laboratory analytical equipment and results is provided in Section 5.1.6.

5.1.4 FIELD TESTING

The field testing at NBSD occurred at Outfall 20 between Pier 8 and Paleta Creek (Figure 10) during the week of September 15, 2014. The demonstration site location was moved south from the previously discussed sites (during Nov 2013 IPR) to avoid potential ship operations and also to leverage with additional studies associated with the ongoing TMDL work around Paleta Creek. Several ship movements in the area delayed the start of field work until 9/17/14 and all field work was completed by 9/21/14.

BACKGROUND STUDIES

Prior to the introduction of tracer particles a background survey was conducted using a small survey vessel to survey the site and collect samples. Surface sediment samples were collected using a conventional grab and analyzed for native sediment characteristics and for the presence and abundance of magnetic fluorescent particles and samples of water from 2 depths were collected and analyzed for the same. In addition a single magnet string was left *in situ* for 24-48 hours to quantify the presence/absence of background magnetic in the system. A pole mounted fluorimeter survey was also performed. To do this, the sensor was secured at the aft of the survey vessel and turned on. Two transects were performed in the alongshore direction in the vicinity of the outfall (tracer deployment location) with the sensor sampling at a rate of 1 hertz.

SETUP AND INTRODUCTION OF TRACER

Typical stormwater discharges at NBSD are supplied by runoff from a drainage basin. Outfall 20 at NBSD is typical of outfalls at coastal DoD installations that drain highly developed industrial areas characterized by low permeability and high runoff coefficients. The drainage basin for Outfall 20 has a surface area of about 23,000 m^2 which is almost entirely covered by buildings and/or paved areas. Flow conditions from the basin are a function of the intensity and duration of a given storm event. As the demonstration goal was to use the particle tracking technology to demonstrate the linkage between stormwater particle discharges and adjacent sediments, we elected to simulate a relatively strong storm event with a relative magnitude of 1.0 inch of precipitation. To provide some background information on storm event frequency and magnitude of rainfall to help select this size storm, historical data on storm size and duration was reviewed (see website at http://hdsc.nws.noaa.gov/hdsc/pfds/index.html for historical data, select "Precipitation Intensity" for Data Type and "San Diego NWS" for station). Intensity-duration-frequency characteristics for the San Diego region indicate that a 0.5 inch/hour intensity storm with a duration of 2 hours occurs on average once every 5 years (Figure 16). So this storm event was considered as the model we tried to simulate with our pumped seawater system setup aboard the sampling vessel anchored in front of the outfall.

Assuming a storm event of this magnitude and a first-flush particle concentration of about 500 mg/L, then the resulting mass discharge would be on the order of 100 to 200 kg/hour (Katz et al., 2006; 2014 indicate this is typical in quay wall outfalls with a storm of this size). The scale of the discharge zone can therefore be estimated based on the assumption that it behaves as a simple jet flow (Fischer et al., 1979). In this case, we can estimate the length of the jet based on the distance at which the maximum jet velocity is reduced to less than the typical ambient tidal velocity in the area of the discharge (~ 5 cm/s; Wang et al., 1998). From Fischer et al. (1979) we have

$$V_{jet} = \frac{7\sqrt{M}}{x}$$

where V_{jet} is the maximum average velocity in the jet, M is the jet momentum given by

$$M = \frac{\pi D^2 V^2}{4}$$

where D is the jet diameter (~50 cm), V is the initial velocity of the jet (~12 cm/s), and x is the distance offshore along the axis of the jet. From this we find that the jet velocity drops to ~1 cm/s, well below the 5 cm/s ambient tidal current velocity at about x=60 m (Figure). The associated jet width at this distance is ~0.127x so that at x=60 m the width scale is ~ 8 m. Thus, the discharge can be represented by pumping the particles into the receiving water offshore from the outfall over an area of approximately 60 m by 8m. Because the outfall discharges near the water surface, the particles were released (pumped) sub-surface (<1m below the water surface) into the receiving water.

Figure 18 shows a conceptual representation of this discharge zone depicting the released tracer originating from the vicinity of Outfall 20 along the NBSD Quay wall. At the top of this figure the drainage area is depicted in yellow and consists of buildings and parking lots with the possibility of little or no infiltration. Stormwater would therefore be channeled through the subsurface pipes (depicted in white) and exit along the quay wall at Outfall 20. The lower picture in this figure depicts a 60 m by 8m discharge plume that places particles into the bay where tidal currents can then act to disperse the plume and allow particles to deposit onto the sediment surface. Figure 19 shows the positions of the magnet arrays, where collection magnets were floated 1 meter above the sediment surface using a subsurface pellet buoy to avoid any possible surface interference to ship

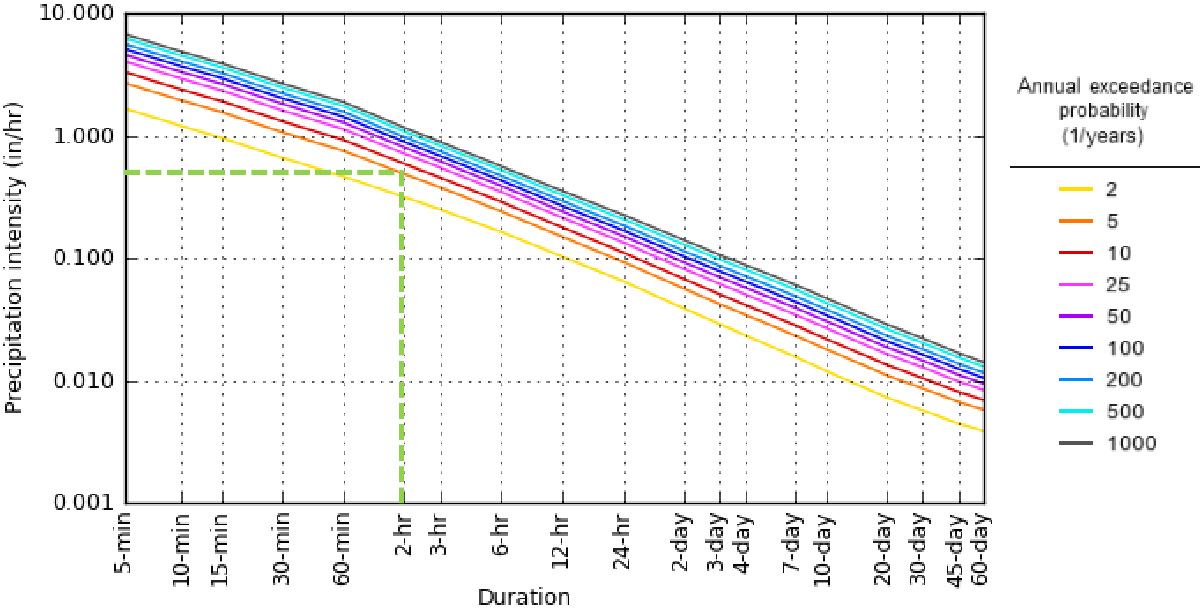


Figure 16. Precipitation intensity-duration-frequency curves for the San Diego region (from http://hdsc.nws.noaa.gov/hdsc/pfds/index.html).

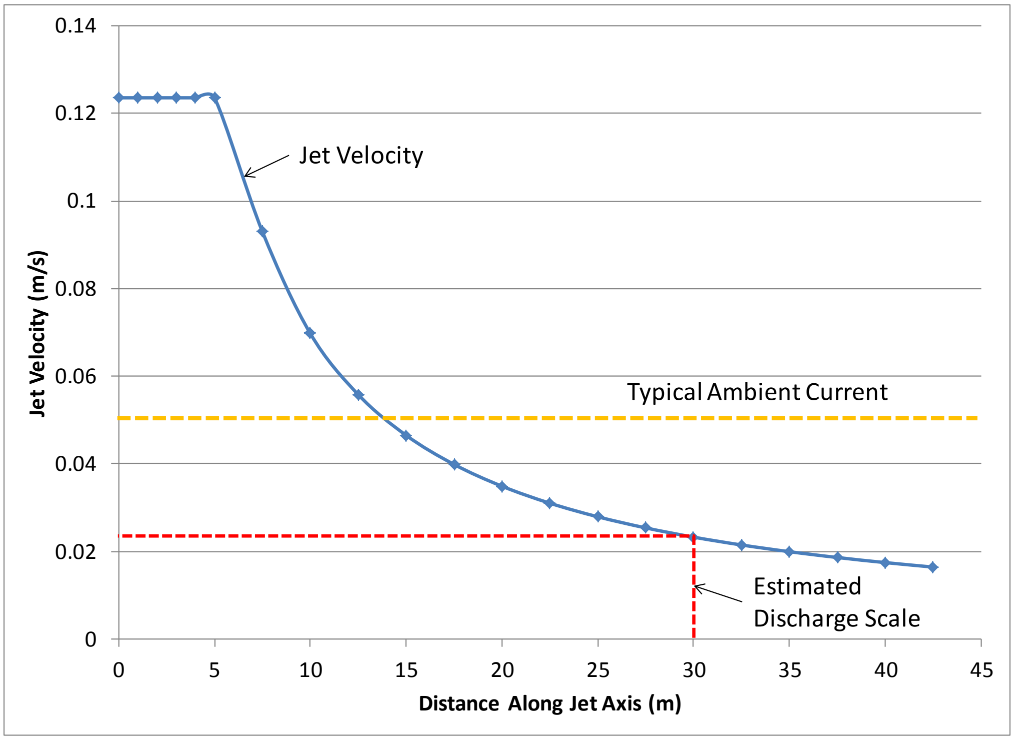


Figure 17. Estimated length scale for the dissipation of discharge jet velocity based on the discharge parameters for Outfall 20.

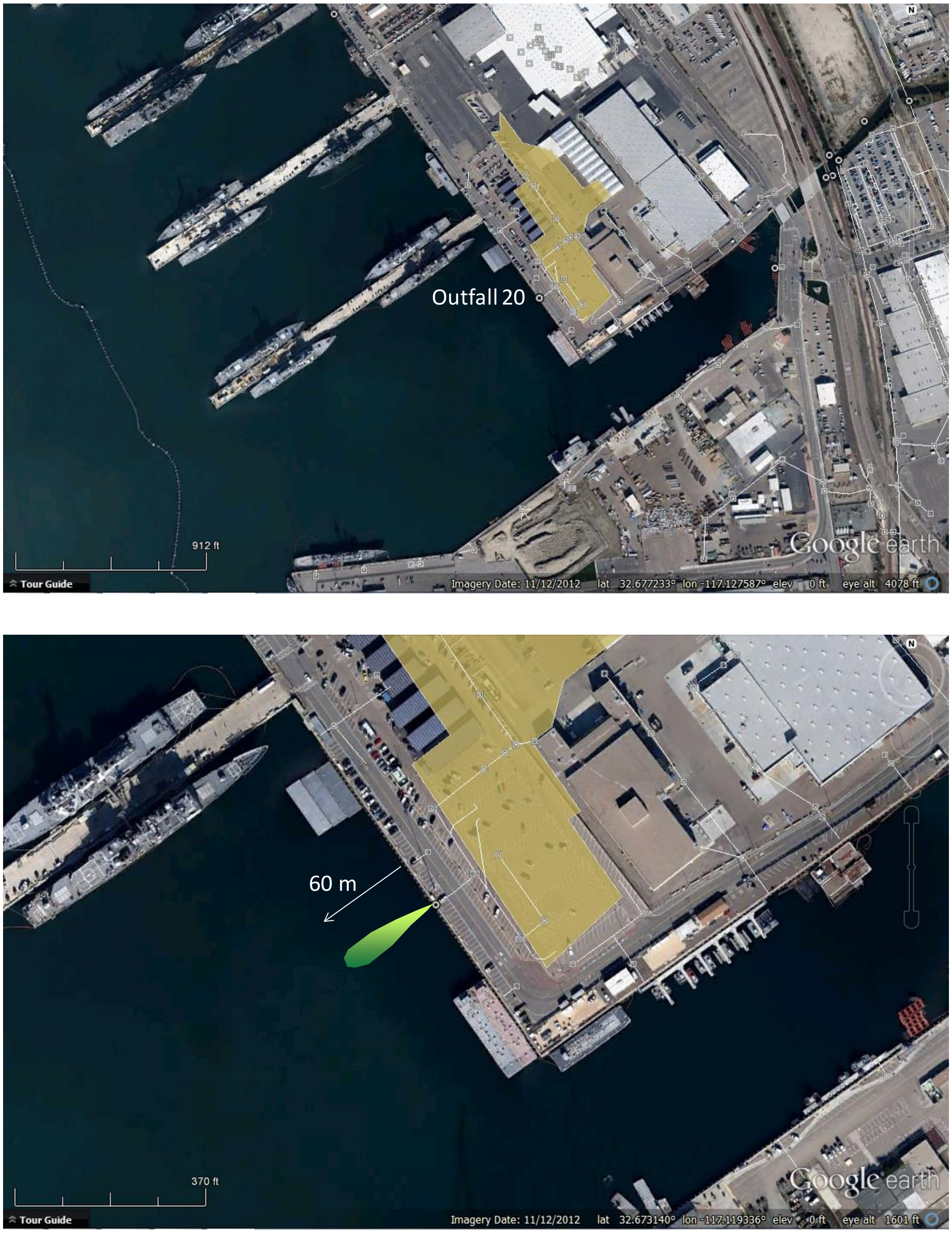


Figure 18. Proposed Outfall 20 location, with drainage basin (top, in yellow), and associated discharge zone plume depicted in the Paleta Creek area south of Pier 8 (bottom, in green).

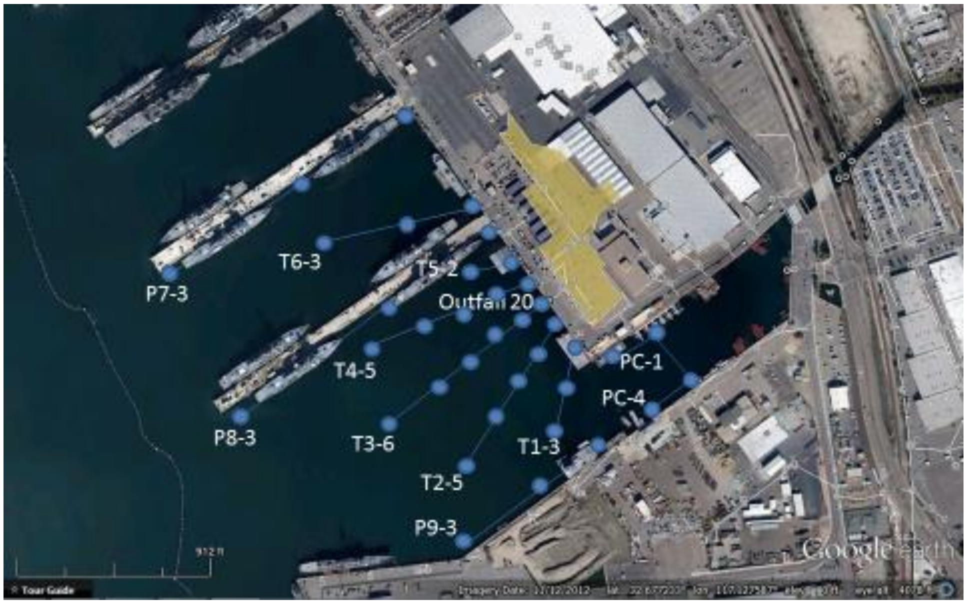


Figure 19. Grid of magnet positions around Outfall 20 located just south of Pier 8. Magnets are positioned along transects (T1 to T6) and piers (P7 to P9), with four additional positions inside Paleta Creek (PC1-4). The last sample along each transect or pier is labeled for reference.

movements. The grid of 37 magnet positions roughly approximated the concentric rings depicted in the Demo Plan, with spacing of the rings at 30, 60, 120, 180, and 300 meters from the outfall. For example, the 30 meter ring was formed by samples T2-1, T3-2, and T4-1; and the 60 meter ring by samples T1-1, T2-2, T3-3, T4-2, and T5-1.

These fixed magnets were deployed on Thursday 9/18/14, the day prior to introduction of the tracer. Due to navy ship movements not allowing any surface buoys, near surface magnet collections were only possible directly in front of Outfall 20 (at T3-2) and along the piers (P7-1 to P7-3, P8-1 to P8-3, and P9-1 to P9-3). At all sites magnets were deployed within a meter of the sediment surface. To obtain information on the tidal current velocities during the demonstration, we also deployed an acoustic sensor on a bedframe to measure tidal current variability. An Acoustic Doppler Current Profiler (ADCP) was placed in the middle of the site near magnet position T3-3 to provide current information, providing data which was subsequently used to explain the movement of the suspended tracer plume.

The tracer introduction took place over an 8 hour period (0900 to 1700 on Friday 9/19/14 with local low tide at 1300) to capture both ebb and flood tide conditions. The tracer release was done from a 40 foot vessel which was anchored in front of Outfall 20 with the vessel continuously moving from 10-50 meters in front of the outfall. The tracer was introduced with a pumped seawater system in the discharge zone outside the outfall location along the quay wall. Figure 20 shows the delivery system setup and a plume of the tracer near site T3-2 located 30 meters in front of the outfall. With a high pressure pump (flow of 3000 liters/min) the total tracer load of 800 kg was delivered in approximately 8 hours with an average TSS of 555 mg/L which was close to the modeled TSS value of 500 mg/L found in outfalls at the site (Katz et al., 2006; 2014).

Figure 20. (Left) Setup for tracer release done from stern swim platform from 32 gallon mixing container with overflow through 4 inch PVC pipe so tracer released just below the water surface. (Right) High flow pump with 2 inch fire hose (blue hose) mixes and disaggregates tracer to deliver tracer plume to surface waters 10-50 meters from outfall 20 (visible buoy at site T3-2).

MAGNET COLLECTIONS OF TRACER

For tracer particles in the silt range, the Stokes settling velocity is in the range of 0.01 – 0.1 cm/s. Given typical water depths in the area of ~10 m, this translates into settling times in the range of about 3-28 hours. Due to this, magnets located 1 meter from the sediment surface were sampled one day after release (Saturday 9/20/14) and sediment grabs were collected two days after release (Sunday 9/21/14). Rapid inspection of magnet sheaths using blue light torches (with wavelength ~395 nm) provided qualitative *in situ* tracer presence/absence assessment (‘none’, ‘little’, or ‘large’ quantities of particles) for determining tracer in the field.

Magnets were sampled by recovering transect lines T1 to T6, followed by piers P7 to P9, and finally the Paleta Creek (PC) sites. Since the magnets were covered by a clear acrylic sheath, it was removed from the magnet and the tracer was washed into collection jars (Figure 21). Sampling jars were held at SPAWAR until shipment back to Partrac during the following week.

To collect samples of the sediment surface a 0.1 m^2 Van Veen style sediment grab was utilized. Additional *in situ* fluorimeter measurements were captured to measure the concentration of tracer directly beneath the sensor head (see method and results in Appendix 1 NBSD Field Report).

Figure 21. (Left) Magnets deployed 1 meter above sediment surface with pellet buoy (just out of picture); (Center) Magnet recovered with green tracer; (Right) Removal of outer sheath by sliding off magnet and then washing tracer into sampling jar.

5.1.5 SAMPLING METHODS

In addition to emplacing a fixed point sampling grid of magnets in the vicinity of Outfall 20 on 9/18/14, an ADCP was also placed near site T3-3 to afford direct measurement of the tidal flows during tracer release (on 9/19/14), magnet sampling (9/20/14), and sediment grab collection (on 9/21/14). To ensure safe working practices the field work was undertaken during daylight hours during a full ebb-flood tidal cycle from 0900 to 1700 local time with low tide at 1300 (Figure 22).

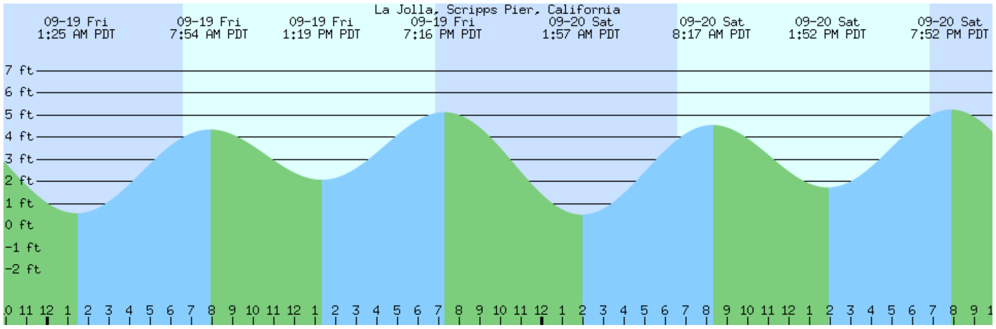


Figure 22. The tide curve for the tracer release from 0900 to 1700 on 9/19/14 (from website http://tides.mobilegeographics.com/locations/3220.html?y=2014&m=9&d=19).

5.1.6 SAMPLING RESULTS

Enumeration of tracer can be undertaken using a range of differing approaches. However, the end point was to ascertain the tracer dry mass (grams) within each sample. It was not possible generally to simply dry and weigh samples collected by the *in situ* magnets or recovered from the sediment grabs. This was because in natural systems, and especially in industrialized estuarine and port environments, there was inevitably a population of non-fluorescent, magnetic particles. These constitute noise within the samples, and it was the inclusion of the fluorescent signature on each tracer grain that aided enumeration at this point. A wider review of site conditions, tracer specification, source/introduction points (i.e. single vs multiple sources) and the characteristics of the receiving water and sediment environment (all information collected during the background survey) often dictate the specific analytical method used. There are a number of methods available for use in the laboratory:

1. Dissolution of the fluorescent coating, centrifugation and spectrofluorometric analysis;
2. Flow cytometry, or FlowCam™ analysis;
3. Filtration/sedimentation followed by digital image analysis.

For this demonstration, all analyses were conducted using spectrofluorometric analysis, as this was the simplest and most cost-effective of the options. Figure 23 shows examples of this technique, including the analysis of the green tracer used in the first demonstration. Once the sample container was received in the laboratory, tracer samples were collected and dried. The sample was then extracted in analytical grade acetone for 24 hours and centrifuged to separate the dissolved fluorescent coating from the mineral kernel. The resultant solution was then tested using a TriLux fluorimeter set for the specific excitation and emission wavelengths of the tracer (see Figure 2). To derive tracer mass (in grams) from the intensity of the fluorescence emission, standard curves were developed using site specific (i.e. manufactured tracer and native sediment) stock solutions (see additional discussion in Appendices). The resulting tracer mass data were displayed in Appendix 1 NBSD Field Report Table 12 (for 24 hour magnet data) and Table 13 (for 48 hour sediment grab data).

A full discussion of the results can be found in Appendix 1, so only an example of the types of results that were obtained will be repeated here. Figure 24 shows a map of the results for the 24 hour magnet collections located 1 meter above the sediment surface. The color coded site data indicate most of the tracer was found in the area in front of Outfall 20, with decreasing tracer mass recovered farther away from the release area. Based on each magnet representing the mass of tracer deposited below the magnet over one square foot of sediment area, we were able to interpolate between sites to determine an approximate mass balance. The 4 sites in Figure 24 inside the 60,000 ft^2 red highlighted area (T3-2, T3-3, T4-2, T4-3) average 8.6 $grams/ft^2$ which can be interpolated across this highlighted area (concentration of 8.6 times area or 60,000) to provide 516 kg. The 8 sites within the larger 400,000 ft^2 yellow highlighted area (T2-1, T2-2, T3-1, T3-4, T4-1, T4-4, T4-5, T5-2) averaged 0.38 $grams/ft^2$ which accounts for 152 kg of tracer in the yellow area. This total of 668 kilograms represented 84% of the total 800 kg of tracer that was released in front of outfall 20. The remaining 16% of the tracer was retained on the remaining magnets as well as some tracer that left the immediate sampling area. The grab data show similar patterns but with a lower mass balance.

Figure 25 shows modeled results for silt sized particles (10 to 60 microns) in a simulated stormwater release from Outfall 20. Results are similar to Figure 24, although there was more particle movement to the north along the quay wall and less to the west away from the outfall. Since the piers are on pilings and currents are free flowing beneath, piers were not included in these model runs. However, as shown in Figure 24 there were ships berthed at all piers during the demonstration period that block the top 20 to 30 feet of water so we would expect less movement of tracer to the north under Pier 8 along the quay wall and more movement out to the west away from the outfall. Additional model runs could be attempted with spatially varying currents in and around the pier structure to simulate the presence of large naval vessels which would likely improve the correlation between the modelled and measured datasets, but this was outside the scope of the project. However, the modeled results are consistent with the tracer results and indicate that the silt particles are mostly retained within the pier area out in front of the outfall. Additionally, concerns previously raised that the size distribution of tracer particles does not include clay size particles could be addressed with additional modeling results. If the results from modeling efforts are confirmed with silt tracer studies, then additional model runs could be done with other grain sizes (including clays) to show particle (and therefore sorbed contaminant) transport under many scenarios (different particle sizes, with and without ships at piers, different storm and stormwater release sizes, etc.). In fact since these types of tracer studies can only be done under a limited number of site conditions, it is typically expected that modeling will be performed in tandem to explore the various other possible scenarios that need to be addressed.

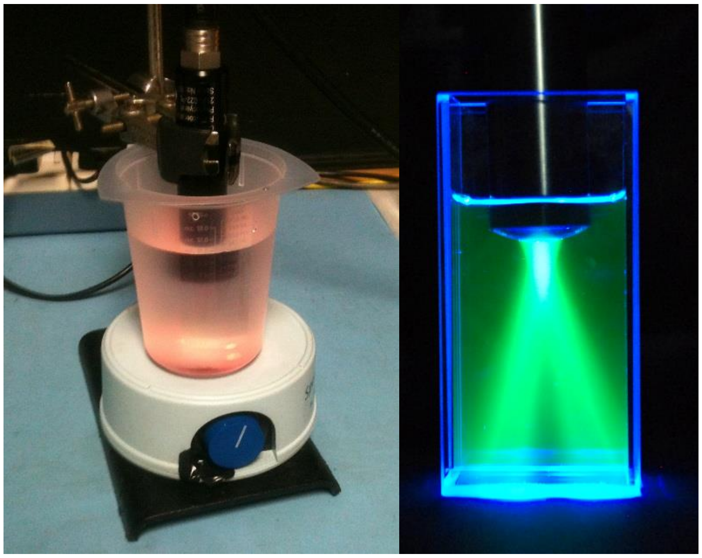


Figure 23. For Spectrofluorimetric analysis, the sample was extracted in analytical grade acetone for 24 hours then centrifuged (left). The resultant solution was then tested using a TriLux fluorimeter set for the specific excitation and emission wavelengths of the tracer (right). More than 1 color can be tested simultaneously (photos from Partrac files).

Figure 24. Colored post map of magnet results 24 hours after tracer release near Outfall 20.

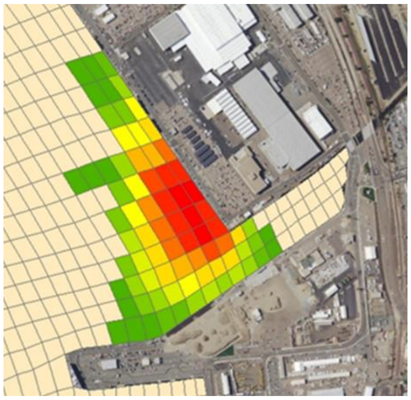


Figure 25. Modeled release of silt tracer from Outfall 20 (color scale same as previous figure with units of tracer as grams per ft^2).

Overall, the NBSD study demonstrated the following:

- Dual signature tracer proved to be an effective tracer able to be monitored effectively within, and recovered from, the environment following release.

- The designed tracer proved to be an effective analogue for fine sediment typically discharged from storm water outfalls.

- Following release transport was observed in the direction of the prevailing current. As distance increased from source the plume dispersed laterally and vertically within the water column due to advection and diffusion processes. The depositional footprint was characterized by the following:

    1. A high concentration deposition zone within 100 m of the release zone.
    2. Greater deposition to the South of the release zone, in the direction of the prevailing current flow.

- The data captured by the high field magnets, revealed the transport pathway of the particles which remained in suspension through the tide.

- The findings of the study demonstrate the potential of the technique to provide site specific data useful in terms of both site characterization and model validation.

The particle tracking study provided baseline data useful for future field studies and validation of modelling approaches. The study demonstrated a particle tracking methodology that can be used at the field-scale, within a complex, highly industrialized setting, to monitor the transport and deposition of fine sediments discharged from storm water outfalls at DoD sites.

5.2 HUNTERS POINT SHIPYARD

5.2.1 CONCEPTUAL EXPERIMENTAL DESIGN

As discussed in section 2.1.3, conducting a tracer study involves a specific set of steps. For our second demonstration at Hunters Point Shipyard (HPS) these steps are:

1) Conducting pre-demonstration background studies which include:
    - Native material assessment (Particle Size Distribution and particle density (specific gravity) of typical sediment of the ‘upland environment’ at HPS) and manufacture of tracer to mimic natural particles;
    - Manufacture of (a different color) tracer to mimic the physical (hydraulic) properties of the activated carbon amendment;
    - Background material sampling of both upland and amendment material for the presence and quantification of native magnetic and fluorescent particulates;
    - Collection of information of local tidal and wave induced currents, and turbidity.
2) Demonstration setup and introduction of tracer material at both the amendment and upland sites.
3) Magnetic collection period (here set at 1 day and 1 week) with sample collection from fixed magnet strings and grab/core samples for tracer deposited on the sediment surface proximal to the site.
4) Data analysis of samples in the laboratory and subsequent validation of the technology based on assessment of performance objectives.

The first three of these tasks are described below in Section 5.2.4 and the final analysis task is described in Section 5.2.6.

5.2.2 BASELINE CHARACTERIZATION ACTIVITIES

Baseline characterization information required for the demonstration includes (1) discharge particle size characteristics to allow tracer matching, (2) current flow rate and particle concentration conditions, and (3) the abundance and characteristics (e.g. size) of any naturally occurring magnetic or fluorescent particles. Sufficient baseline characterization was conducted by previous studies (Battelle et al., 2006) to support development of the demonstration for items 1 and 2 above. Additional field data collected as part of the field demonstration to address item 3 above resulted in no observable background fluorescent material being collected on the magnets.

5.2.3 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

The design of the dual signature tracer is provided in Section 2 and shown in Figures 1-4. Discussion of the magnet designs used for collection is provided in Section 2.2 and Figures 5-8. Specifics of the second demonstration field testing components are described in Section 5.2.4. Additional discussion of the laboratory analytical equipment is provided in Section 5.2.6.

5.2.4 FIELD TESTING

The field testing at HPS occurred over 2 weeks starting the week of September 12, 2016. Typical dry season weather conditions occurred during this entire period, with calm to light winds (<10 knots) in the morning and evening, with stronger winds (10 – 15 knots) during the afternoon hours. The objective was twofold: i) to assess the stability against wave and tidal erosion of AC cap amendment material and ii) to investigate natural deposition and recontamination from the surrounding sediments onto the cap surface. The use of multiple tracers (unlike the previous study which utilized only 1 tracer color) with different fluorescent color characteristics demonstrated the ability of the magnet collection techniques to differentiate and quantify multiple tracers during the same experiment. Caution should be used in offering any conclusions concerning the longer term movements of the tracer due to the short duration of the actual demonstration, which was designed to show the utility of using tracer studies to address site specific sediment transport questions. Additional longer term field studies under a range of weather conditions would be recommended to address longer term transport questions.

BACKGROUND STUDIES

Prior to the 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. Previous data were available for particle characteristics (Table 2) which were used for item (1) tracer manufacture. For item (2), surface sediment samples were collected prior to tracer release using a conventional sediment grab and analyzed for the presence and abundance of magnetic or fluorescent particles.

SETUP AND INTRODUCTION OF TRACER

Setup for the particle tracking demonstration is linked to the characteristics of local tidal and wave induced sediment transport at the site. As discussed previously the objectives of the study at the HPS location are twofold: 1) To examine the potential for ‘loss from source’ of the activated carbon amendment material (represented by a pink tracer), and to identify the subsequent transport pathway (and potential depositional zone) for this lost material; and 2) To examine if contaminated material (represented by a green tracer) from the local upland areas are being mobilized to the capped areas thus recontaminating the site.

On Wednesday 9/14/16, a fixed point sampling consisting of vertically oriented magnets were installed prior to the release of the two tracers. Figure 26 shows a view of the South Basin area where the amendment cap is located along with the labeled locations of the outboard (OB) sampling sites. Also shown is a green rectangle between sites OB06 and OB07 where the green tracer was released. Figure 27 provides a magnified schematic view of just the cap area to show the inner sampling locations and the red rectangle between the buffer zone (BZ) sites represents where the pink tracer was released. An Aquadopp current profiler was also placed near UP04 to record current direction and velocity during the demonstration period.

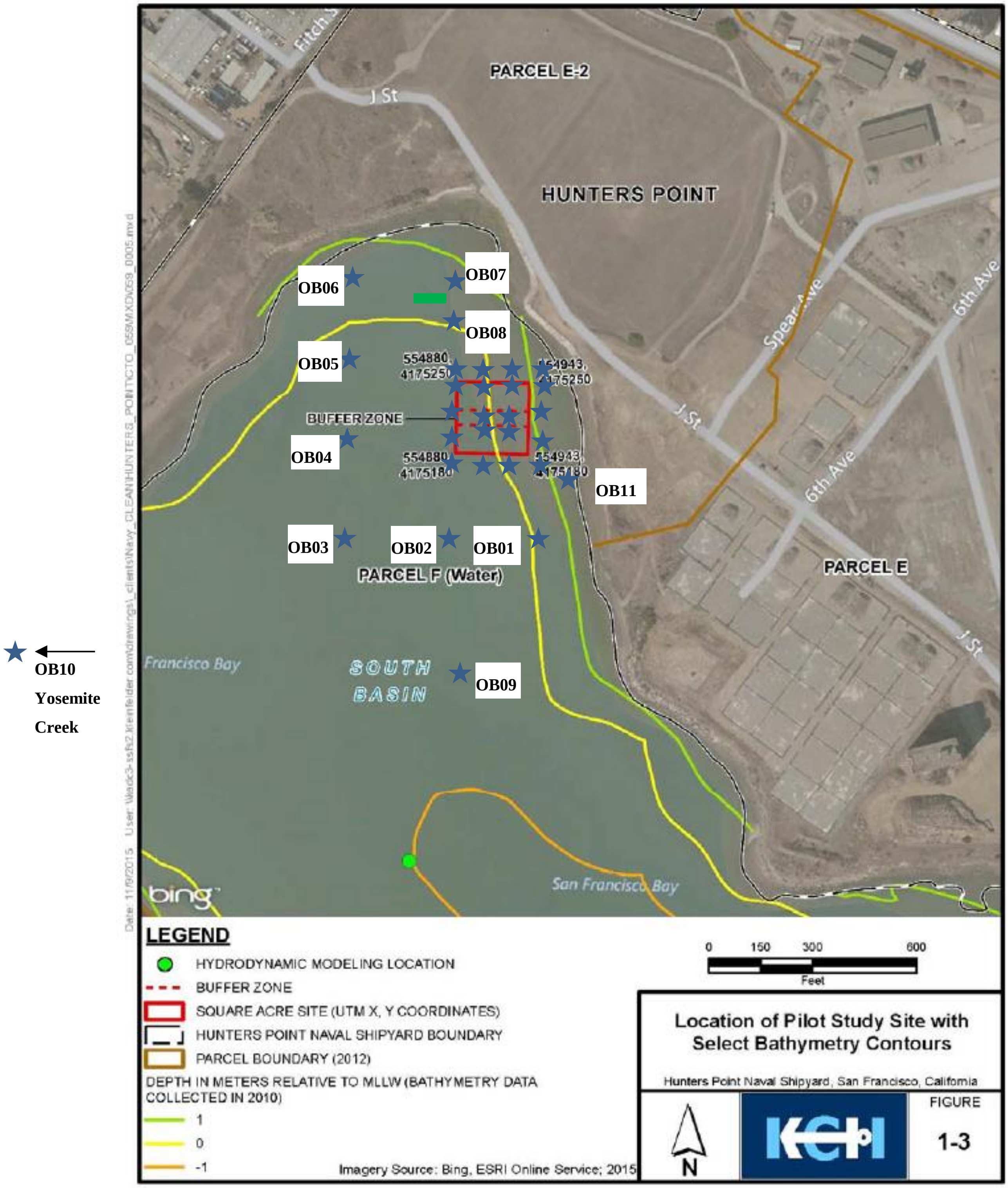


Figure 26. South Basin amendment cap area showing out-board (OB) locations and green tracer placement near OB07 location. Magnified view of Cap locations shown in next figure (modified from NAVFAC presentation for public review of cap design).

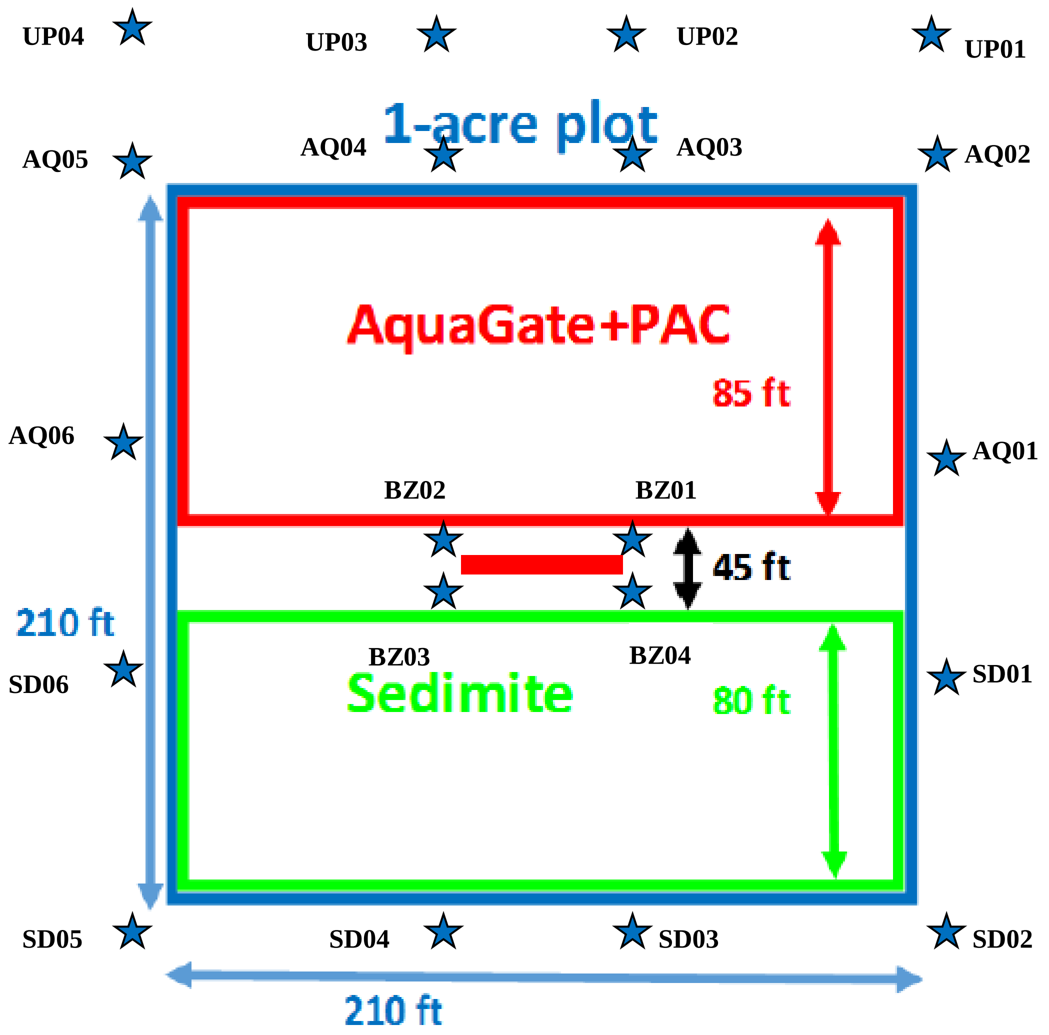


Figure 27. Magnified view of the one acre amendment cap site showing north AquaGate and south SediMite amendment areas, separated by 45 foot buffer zone with no cap materials. Blue stars show magnet and grab sampling locations for Sedimite (SD), Buffer Zone (BZ), AquaGate (AQ), and Upland (UP) areas. Red rectangle in middle of Buffer Zone represents pink tracer release area where AquaGate+Pink Tracer was dropped with 5 foot water depth (modified from NAVFAC presentation for public review of cap design).

Presented below are the procedures for the setup and introduction of the tracer material on Thursday 9/15/16 for each of the two objectives:

1) ‘Loss from source’ from the Activated Carbon Cap Site

Partrac tracer material was manufactured to mimic the physical properties (particle size and particle density (specific gravity)) of the activated carbon amendment. Table 1 in Appendix 2 shows activated carbon typically is < 200 microns with specific gravity between 1200-1400 kg/m3, so that was the target specification for the pink tracer. Partrac collaborated with the manufacturer of the AquaGate product used at the cap site during the 2015 cap placement so the tracer would be released to the sediment surface in the same manner as the activated carbon material. The pink Partrac tracer (100 kg) was substituted into the AquaGate product (see Appendix 2 HPS Field Report Section 2.1 for more discussion) for the activated carbon that was used in the original AquaGate formulation. The Aquagate formulation had 5% tracer by weight so 2000 kg of material were shipped to the site in 25 kg buckets. At high tide with 5 feet of water depth, the AquaGate with tracer was dropped in a small rectangular area (10 foot by 40 foot red rectangle in Figure 27) in the center of the cap (Figure 28).

Figure 28. Manual release of pink tracer in AquaGate formulation from the bow of the landing craft style vessel (looking west with BZ02 buoy at right of vessel). Note yellow pole which held an *in situ* fluorimeter sensor 0.5 meters below the surface to check for tracer release in the water column.

2) Recontamination from the Upland Sediments

In total, 200 kg of a green silt tracer was deployed in the intertidal zone upland of the cap near sampling site OB07 (see Figure 26). The objective was to demonstrate if contaminated sediments were being remobilized (principally by wave action) and transported towards the AC amendment cap. The original tracer deployment method from the Demo Plan was to walk out onto the site at low tide to place the upland tracer directly onto the sediment surface. But due to radiological concerns we were not allowed to walk onshore at the site so we were forced to bring the deployment vessel into 2 feet of water and drop the tracer through the water column onto the sediment surface. This resulted in some of the tracer being suspended in the water column during deployment. Though not ideal, this acted to better simulate the transport of re-suspended material that would occur in the one to two foot depths during larger storm induced wind wave events. This likely explains why material collected on the magnets after one day from deployment was 5x greater than after the longer six day collection period.

The following sections present the arrangement of sampling (using magnets and grabs) for initial (1 day) and subsequent (6 day) tracer collections. Inspection of previous data and reports show the site to be weakly tidal, with sediment transport driven largely by local wind wave events (Battelle et al. (2006) Appendix F Sediment Transport). Therefore we installed a spatial sampling grid comprising 31 sampling stations designed to assess the spatial distribution of tracer mobilized and transported in suspension and to document the length of the transport pathways, as well as to map deposition of green tracer released from upland areas of the cap and pink tracer from the center of the cap area.

MAGNET COLLECTION OF TRACER

The sampling of the magnets was conducted during the midday high tide on Friday 9/16/16, and a second collection on the afternoon high tide of Wednesday 9/21/16. Powerful (high field) cylindrical rare earth magnets were utilized in this experiment (Figure 29), each measuring 0.3 meter in length. These are encapsulated in plastic sheaths with end caps and attached to supporting plates (Figure 30 and Figure 31) for the purpose of deployment on the sediment bed. Each plate had a small float attached with an identifying location mark.

Figure 29. One of the magnets used in this study (top) and housed in the sheath with endcaps (bottom). For scale, the bar magnets are 30 cm in length.

Figure 30. The magnet and sheath assemblies attached to baseplates with identifying location floats prior to deployment.

Figure 31. The magnet and sheath assemblies attached to baseplates and placed on the seabed.

Since the magnets are covered by a clear acrylic sheath, it was a relatively fast change for the removal of the old covering (by sliding off once caps are removed) and replacement of a new covering sheath. A spare magnet with sheath set on a base plate was preset while motoring between stations so when the float was recovered at each station the line was unclipped from the recovered magnet and immediately attached to the spare magnet which was dropped back into the water. The process of magnet recovery, transferring the float to the spare magnet, and putting the spare magnet back into the water took only seconds. This could be done without the need for anchoring and any sediment disturbance at each site by a sampling team of two individuals in rapid fashion. The recovered magnet then had the top endcap removed so the sheath could be slid off and the tracer washed off the sheath into a sampling jar while motoring to the next site (Figure 32). While motoring to the next sampling site a clean acrylic sheath and top end cap was placed on the magnet and this magnet became the "new" spare magnet for the next site. A second sampling team of two individuals used a smaller Petite Ponar sediment grab to recover surface sediment at each site while the magnet was being recovered (see next section). This rapid sampling technique was repeated 6 days later, and could be repeated for as many sampling cycles as desired. However for this demonstration, once we had shown repeated sampling cycles were possible we decided to terminate the demonstration. It was decided that repeated night time thefts from various locations around this closed navy site (no navy security and limited contractor presence) did not warrant longer deployments with expensive current meters and magnets.

Figure 32. Tracer collection from magnets.

Seabed sampling using grabs

The bottom sediments were sampled at the same time as the magnets using a smaller Petite Ponar grab (Figure 33), which samples a smaller 6 inch square portion of sediment surface (as opposed to the larger Van Veen grab used at the first demo which samples about one square foot). Very fine grain silty sediment was recovered at all sites with no signs of visible tracer (except in the deployment zone shown in Figure 33). Since we were collecting grabs at the same time along with magnets, we did not have time to inspect the samples with a blue light or UV-A torch to look for surface tracer (as was done during the first demo when magnets and grabs were sampled on different days), so the top 5 cm of sediments were placed in jars for analysis back at the laboratory. This analysis included magnetic separation to remove tracer from the sediments followed by the same dissolution and spectrofluorometric detection process used for the magnet samples.

Figure 33. A sediment grab from the middle of AquaGate deployment zone (DZ1) 6 days following placement showing the pink tracer has been released from the white pea gravel at the sediment surface.

5.2.5 SAMPLING METHODS

Sampling methods were the same as those described earlier in the first demonstration.

5.2.6 SAMPLING RESULTS

Enumeration of tracer was discussed in Section 5.1.6 for this study where we used dissolution of the fluorescent coating, centrifugation and spectrofluorometric analysis. Once the sample container was sent back to the laboratory, tracer samples were collected and dried. The samples were extracted in analytical grade acetone to separate the dissolved fluorescent coating from the natural mineral kernel. The resultant solution was then tested using a TriLux fluorimeter set for the specific excitation and emission wavelengths of the tracer shown in Figure 2. Solutions of known tracer mass were run in the laboratory to develop standard curves of tracer dry mass versus fluorescence intensity, so that the obtained fluorescence intensity for each sample can be related to the original dry mass of tracer in the sample.

Appendix 2 HPS Field Report shows results from the field demonstration with tabled data in Appendix Table 10 along with multiple post maps for magnet and sediment grab samples, both 1 day and 6 days after tracer release. Figure 34 below shows an example post map for the green tracer on magnets and Figure 35 below shows an example post map for the pink tracer on magnets, both 6 days following release of the tracer. Both figures show tracers moved to the southeast, which is consistent with currents measured on an Aquadopp current meter during the release period (see additional discussion in Appendix 2 HPS Field Report). We chose in this section to show the magnet figures with tracer data after 6 days rather than after 1 day for several reasons. As previously discussed, due to radiological concerns we were not allowed onshore so placement of the green tracer in the intertidal areas during low tide (with access from the shore side as described in the Demonstration Plan) was not possible. So the green tracer was placed near site OB07 (see Figure 26) from a boat with 1 to 2 feet of water overlying the sediment. This resulted in additional tracer being suspended upon release in the 1 to 2 foot depth of water at the tracer deployment zone resulting in enhanced movement of tracer during the first day. This is shown by comparing the amount of green tracer collected on the closest magnet to the deployment zone at OB07 which was 2.321 grams after 1 day and 0.485 grams after 6 days (see Table 10 in Appendix 2). The presence of 5x as much tracer on magnets after 1 day might represent the levels of resuspension from larger storms, but this was not an intentional effort to represent larger storm events. It was a consequence of a deviation from the Demonstration Plan deployment due to not being able to access the intertidal area at low tide from the shore due to radiological concerns. We therefore chose here to show the results from the magnet collections after 6 days since they do not show the elevated tracer levels from the first day of sampling immediately following deployment of green tracer.

Green Tracer Results

Figure 34 shows the green tracer collected on magnets after 6 days and indicates most tracer moved to the southeast. The expected direction of tracer movement from the current data shown in the Demonstration Plan was toward the south southeast, but currents during our tracer study were more toward the east so the main plume of tracer only moved over the east side of the one acre amendment cap site and moved toward the beach. So rather than attempting a mass balance similar to what was done at the first demonstration site in Section 5.1.6 where the magnet sites fully bounded the tracer plume, we will attempt to approximate the amount of tracer that moved over the cap by looking at the data from only the east side of the cap site. This should represent the amount of tracer that would have moved over the entire site if the deployment zone had been placed farther west or the currents had moved the plume farther to the south as predicted in the Demonstration Plan. And since PCB contaminated silty sediments are present in all these shallow areas to the northwest of the cap site it is expected that these sediments would be resuspended and moved over the entire one acre cap site whether currents move to the southeast or the south southeast.

Tracer amounts on the magnets after 6 days decrease across the cap site from north to south, with an average of 0.17 grams for magnets on the east side of the cap (AQ02 0.304 g, AQ01 0.226 g, SD01 0.116 g, SD02 0.032 g from Table 10 in Appendix 2). One way to approximate the amount of upland material recontaminating the cap might be to take the difference between what enters on the north side (0.304 g at AQ02) and subtract what leaves at the south side (0.032 g at SD02), and multiply this by the 210 foot width of the cap along its north side, which results in 57 grams of tracer (or contaminated sediment) moving onto the cap area. But again the main plume of tracer did not move north to south but more to the southeast so the tracer amount leaving at SD02 might be less than if the plume had moved due south. However, during typical dry season current patterns such as those during this demonstration period, it might be expected that about 50-60 grams of contaminated sediments from northwest of the cap would be brought into the cap area over a 6 day period (roughly weekly). It is interesting to note that the average amount of tracer on magnets on the east side of the cap (AQ02, AQ01, SD01, SD02) after the 1 day collection was 1.1 grams, which is again about 5x the amount found after 6 days (0.17 g from above). So although there was no plan to simulate winter storm conditions, larger resuspension events that resuspend material over a full 2 foot water column might result in 5x as much material (250-300 g) transported onto the cap from the contaminated areas to the north. Another interesting note is that a small amount of green tracer made it all the way across South Basin to site OB10 after 6 days, probably from the large resuspension event occurring during initial tracer placement at the DZ during the first day although no tracer was detected at this site 1 day after release.

Pink Tracer Results

Figure 35 shows the pink tracer collected on magnets after 6 days, with some of the pink circles obscuring the 10 by 40 foot rectangular tracer deployment zone located in the middle of the BZ sites at the center of the cap (as shown in earlier figure 27). The tracer material appears mainly to the southeast of the deployment zone, although there are slight indications of some tracer moving toward the northwest also. As opposed to the green tracer, amounts of pink tracer on magnets from 1 and 6 days are roughly comparable. But as discussed in the Appendix 2 HPS field report some loose tracer material was released in the 5 foot water column during deployment which was identified by the *in situ* fluorimeter measurements in the top foot of the water column. Any tracer particles moving through the top several feet of the water column were not accessible to the magnets located from 0-1 foot above the sediment surface. So we again choose to discuss the 6 day magnet results which collect the tracer mass resuspended and moving near the sediment surface. To estimate how much tracer deployed in the center of the one acre cap site moved off the cap we can take the average of the 3 sites along the south side of the cap where tracer was collected (SD02 0.320 g, SD03 1.735 g, SD04 0.329, for average of 0.79 grams) and multiply by the distance between these sites (140 feet) to determine 111 grams of tracer left the cap after 6 days. Similar calculation shows 73 grams of tracer left the south side of the cap after 1 day, but this doesn’t include the tracer material released in the surface water during deployment. Since the tracer’s hydraulic behavior was similar to activated carbon (matched specific density and grain size to obtain similar settling velocity) this would indicate that a small amount of tracer could be expected to be transported away from the site during deployment and resuspension that will occur at the site until tracer is buried into the sediment. Given that 100 kg of tracer was deployed on the AquaGate formulation in the center of the cap, only 111 grams or about 0.1% left the one acre site after 6 days.

Sediment Grab Results

The grab data did not provide as consistent a picture of tracer movement as the magnets. This may be the result of tracer being more heterogeneously distributed in the sediments compared to the overlying water column where the magnets were placed. The smaller Petite Ponar also takes a smaller grab which may magnify any heterogeneity issues. Grabs also may create a bow wave which pushes tracer out of the way so it is not collected by the grab. Other options were to use sediment coring devices to reduce bow waves but the smaller area recovered may create more heterogeneity issues. We had originally planned to develop some additional magnet frame devices to collect sediment tracer (see lab development discussion in Section 6.2.4) but initial lab studies showed these early designs were not any more efficient at tracer recovery compared to grabs so only grabs were used during the demonstrations. Additional work will continue on these magnet frame designs because grab results alone still show more than expected heterogeneity when compared to magnet results.

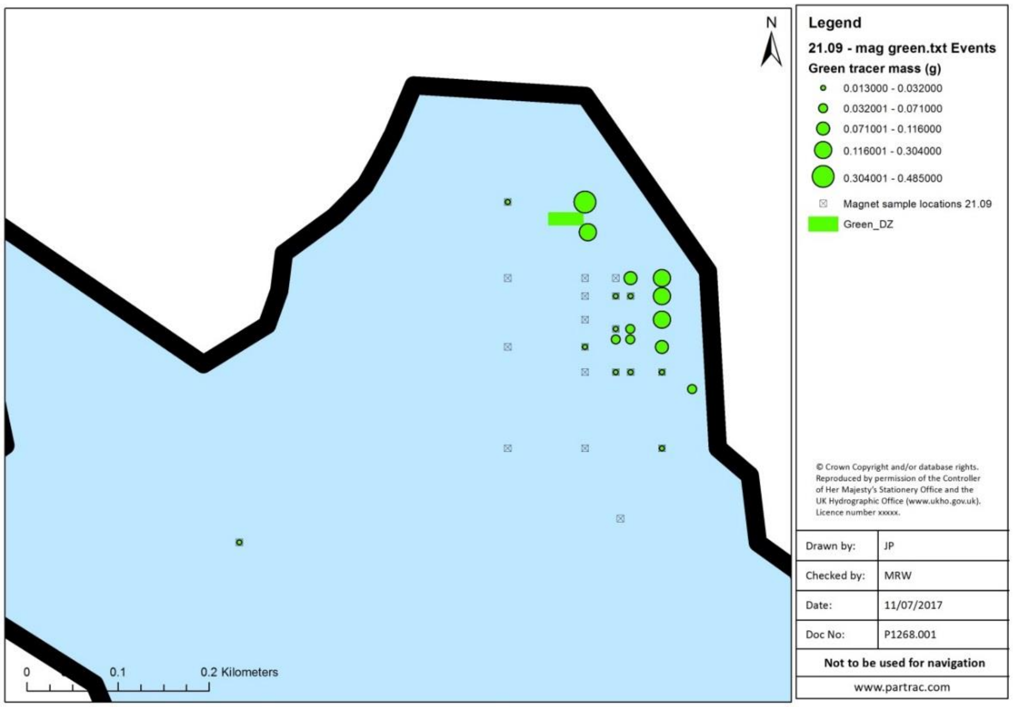


Figure 34. Green tracer results from magnets after 6 days.

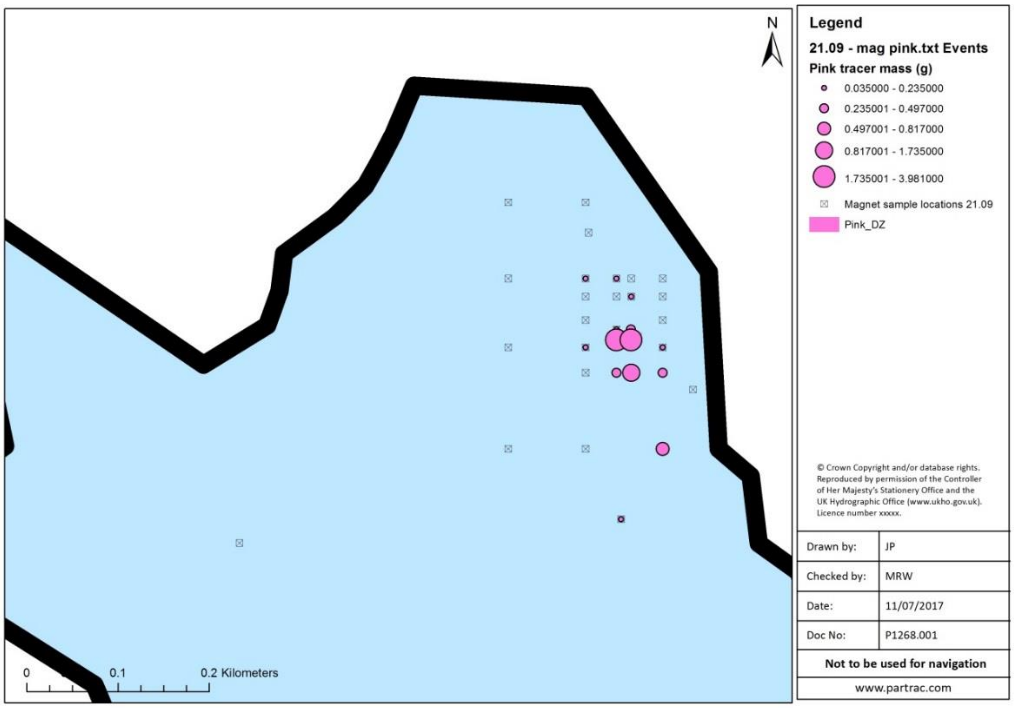


Figure 35. Pink tracer results from magnets after 6 days. Pink tracer deployment zone (Pink_DZ) covered by larger symbols in center of 1 acre cap.

Overall, the HPS study demonstrated the utility of tracer studies to address site specific sediment transport questions. However, caution should be used in offering any conclusions concerning the longer term movements of the tracer due to the fair weather conditions and short duration of the actual demonstration, which was designed to show the utility of using tracer studies to address site specific sediment transport questions. Additional longer term field studies would be recommended to address longer term transport questions under a range of weather conditions. Some specific conclusions from this demonstration include:

- Two tracers were able to be effectively designed (and manufactured) to provide suitable analogues for both native sediment and activated carbon amendment material.
- Partrac (using AquaGate formulation) were able to mimic the deployment methodology utilized during the emplacement of the carbon amendment cap.
- Dual signature tracer, and associated sampling tools including the use of submerged permanent magnets and underway *in situ* fluorimetry, proved to be an effective tool to elucidate local sediment transport pathways.
- The use of two tracer colors enabled investigation of two hydraulically different material types, and two differing source zones.
- Local sediment transport was observed to be multi-directional which is a function of wind and current direction; however, the following transport pathways were elucidated:

    1) transport of deployed amendment cap material across and away from the cap; and,

    2) transport of native sediments onto the cap.

- Meteorological effects on the current direction/velocity are pronounced and are likely a key driver of sediment transport at the site.
- Both tracers were found dispersed across the site highlighting potential processes which may limit the efficacy of the amendment cap.
- Native sediments, once mobilized, are observed depositing on the cap surface, constituting a form of re-contamination, and this may have mitigation / management implications.
- Dispersion (loss) of cap materials during deployment and following deployment was observed (or more specifically loss of the tracer material which mimics activated carbon was observed).
- The findings indicate that further study would be useful to better understand the transport of amendment cap material and the interaction of the cap with the surrounding sediments over longer timeframes.
- This study demonstrated the use of, and applied methodology, of deploying two types of dual signature tracer at the same site.

6. PERFORMANCE ASSESSMENT

6.1 INTRODUCTION

All the performance objectives to be evaluated by this project that are listed in Section 3 Table 1 have been judged as successfully passed. The first compares the physical characteristics of the manufactured tracer to the natural particles that are to be simulated so that the tracer will be hydraulically equivalent. The second through fourth objectives were various aspects of the magnet sampling technique. A combination of laboratory data collected during the first year of the project along with the field data collected during the demonstration studies were used to demonstrate the performance of the magnets within a tracer study. The fifth objective relates to the performance of the laboratory enumeration of tracer based primarily on laboratory quality assurance samples. The last quantitative objective was a mass balance determination based on the amount of tracer recovered compare to the amount released. From the tracer mass recovered at each station, we can interpolate across the site to obtain a total mass and compare with the known amount of tracer released. The last objective is a qualitative ease of use, with feedback from the project team undertaking the field survey and laboratory analyses used for comparing with conventional methods/techniques.

6.2 DATA ANALYSIS FOR EACH PERFORMANCE OBJECTIVE

6.2.1 HYDRAULIC MATCHING OF TRACER TO NATIVE PARTICLES

For the first performance objective at NBSD, we compared data from the physical properties listed in Table 2 (Section 4.1.4) for sediments collected at the site to the measured tracer characteristics given in Appendix 1 (Field Report for NBSD, Section 2.2 to 2.4). Although there is some variability in Table 2 grain size distributions, Sample P07 is located closest to Outfall 20 with 21% sand, 37% silt, and 42% clay (Table 2). The median grain size therefore falls within the silt range and compares well to the listed d_{50} of the tracer at 30 microns (Appendix 1 Section 2.2). Table 2 also lists 21% of the mass above 62.5 micron (sand fraction) so the d_{90} of the tracer listed at 79 micron (Appendix 1 Section 2.2) is also reasonable. In this case the objective was to manufacture a mainly silt sized tracer so although it is not possible to manufacture this tracer with clay sized particles to exactly match the sediment characteristics; we still consider this objective met. As previously discussed in Section 5.1.6, additional modeling results could be used to describe the behavior of clay sized particles that could not be manufactured for this study. The tracer grain density was measured at 2.2 g/cc (Appendix 1 Section 2.3) which compares closely to natural sediment grain density of 2.3 g/cc. An additional characteristic for the tracer to match is the settling velocity which was measured between 0.01 and 0.1 cm/sec for silt sized particles between 30 and 60 microns (Appendix 1 Section 2.4) which compares well to natural silt size particles at the site.

At HPS the same green tracer was used to simulate the PCB contaminated silt sized fraction of the native sediments. The second pink tracer was used at the site to simulate activated carbon that can be incorporated into an AquaGate formulation to deliver the tracer to the sediment surface just as the activated carbon was delivered during the 2015 cap construction. Appendix 2 Section 2.1.3 and Figure 4 show the grain size distribution for the d_{10}, d_{50}, and d_{90} fractions were 13, 51, and 149 microns, respectively. Appendix 2 Section 2.1.4 gives the density for the pink tracer of 1.3 g/cc. Both grain size distribution and density values match the targets provided in Appendix 2 Section 2.1.1, so the tracer was considered to match the targeted properties.

6.2.2 COMPARISON OF TRACER COLLECTION METHODS

For the second performance objective, data are presented from the laboratory testing conducted in the first year of the program. Table 5 shows the efficiency of high field magnets for sampling suspended sediment is > 90%. There is a slight reduction in the efficiency of the technique where higher concentrations of tracer material are in suspension, though generally the data reveals high efficiency in determining the concentration of suspended tracer material within a water sample (1 Litre). The efficiency of traditional water sampling techniques and analyses (i.e. via filtration and gravimetric analyses) to determine the concentration of total suspended solids (TSS), were correct procedures followed, can be considered to be > 90%. Thus, the two techniques can be considered comparable in terms of efficiency.

Table 5. Efficiency of magnet sampler for sampling suspended sediment. Please note the 'sampling window' afforded by each 30cm bar magnet is 1 Litre of water.

Mass of tracer in suspension (g)	Volume of water (l)	Concentration of tracer in suspension (g l^{-1})	Mass of tracer recovered (g)	Efficiency of magnet sampler (%)
1.0	20	0.05	0.05	100.0
2.0	20	0.1	0.089	89.0
5.0	20	0.25	0.234	93.6
Mean efficiency				94.2

It is of note that the aim during discrete water sampling within a particle tracking study is to determine the mass of tracer in suspension, rather than determine TSS. Where TSS is significant (the likelihood of which is greatly enhanced when conducting studies in highly industrialized environments, in the case of both demonstration studies), further analysis of the resolved sample would be required to determine the mass of tracer found in suspension. As such, despite both techniques showing high efficiency, the use of magnet sampling (in some cases), greatly assists with the determination of the mass of tracer within TSS.

6.2.3 MAGNET RETENTION CAPACITY

For the third performance objective, data are presented from the laboratory testing conducted in the first year of the program in conjunction with hydrodynamic data (measured current velocities) collected during the two demonstration studies at NBSD and HPS. At NBSD data collected using a bottom mounted ADCP sensor showed that current magnitudes were very low (mean current ~0.033 m s^{-1}, maximum 0.09 m s^{-1}; see Figure 21 in Appendix 1 NBSD study report). Similarly, at HPS, low current velocities were recorded at the site ranging from ~ 0.01 m s^{-1} – 0.1 m s^{-1} (see Figure 28, 29, 30 in Appendix 2 HPS study report).

Laboratory analyses conducted in the first year of the program investigated magnet retention efficiency in a series of flume tests where a magnet, with tracer retained, was exposed to incrementally increasing flow velocities (see Figure 36 for laboratory setup). The results of the foregoing analyses are presented in Table 6. The data shows that when exposed to current velocities of 0.1 m s^{-1} (equivalent to the greatest flow velocity observed during the two field studies) magnet retention capacity exceeded 90%. As the magnet was exposed to increasing flow velocities it is evident that retention capacity

Figure 36. The magnet secured in position within the flume, with tracer retained. At the time of the photo the flow velocity in the flume was ~0.1 ms^{-1}.

reduced significantly. Due to these data, for both tracer batches developed for use in the demonstration studies the quantity of magnetic mineral oxides per unit mass of tracer was increased which in turn increases the degree of magnetization of the sample (i.e. the tracer is ‘more’ magnetic).

Table 6. The magnet retention efficiency determined from experiments conducted in the flume.

Flow velocity (ms^{-1})	Initial Tracer on magnet (g)	Tracer retained on magnet after 1 min exposure to flow (g)	Retention capacity (%)
0.1	1.000	0.902	90.2
0.2	1.000	0.879	87.9
0.3	1.000	0.759	75.9
0.4	1.000	0.399	39.9
0.5	1.000	0.174	17.4

6.2.4 MAGNET COLLECTION OF TRACER IN SEDIMENTS

Within the HPS demonstration study magnet frames specifically designed to capture sediments as they deposit on the seabed were not used, instead bed frames with a single vertical magnet positioned in the center of the frame was utilized to capture tracer particles moving in suspension across the site to investigate near bed sediment transport. In essence, these frames are no different in regards to sample efficiency as discussed in our response to performance objectives 2 and 3.

However, in order to provide a response to Performance Objective 4 data are presented from the laboratory testing conducted in the first year of the program. Figure 37 shows schematic diagram of a proposed magnet frame used to sample, and retain tracer particles as they deposit on the seabed. Figure 38 is a schematic diagram showing the approximate magnetic field of bar magnets provided for ease of understanding for the reader.

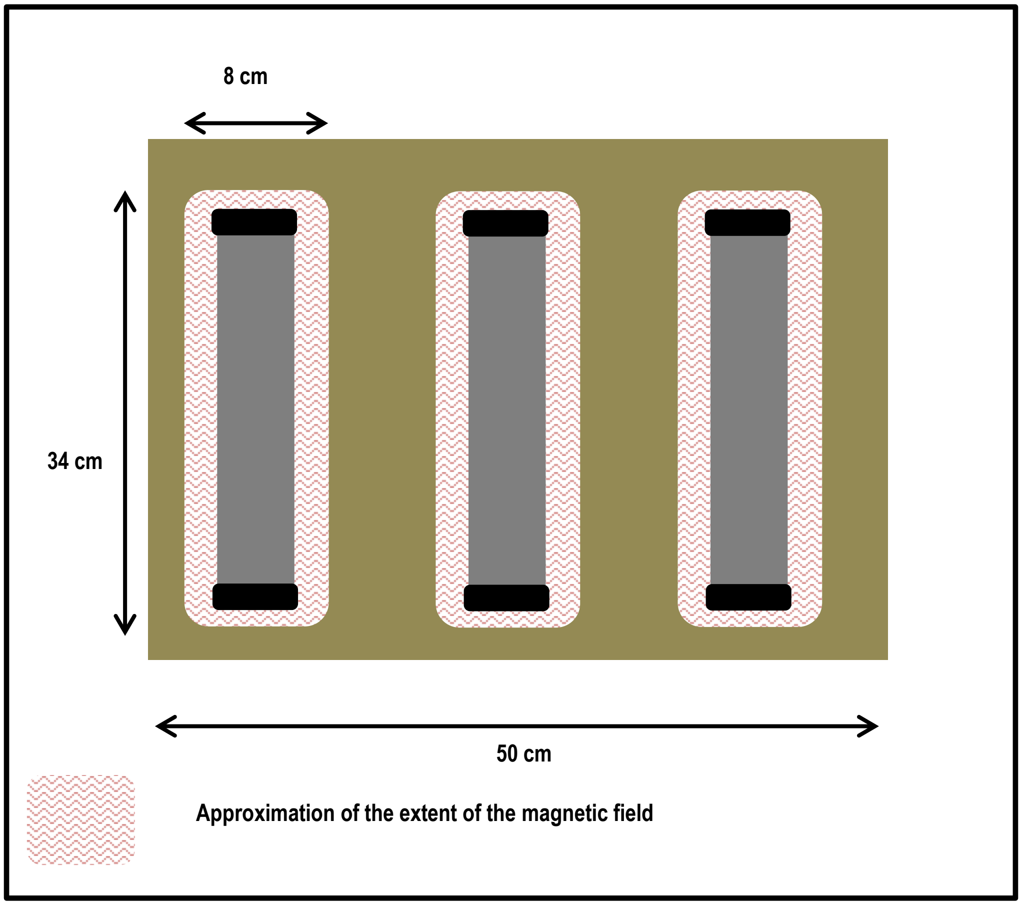


Figure 37. A schematic diagram showing the design of a magnetic bedframe designed to sample tracer particles as they deposit on the seafloor. A rough approximation of the extent of the magnetic field is provided. Please note this diagram is not to scale.

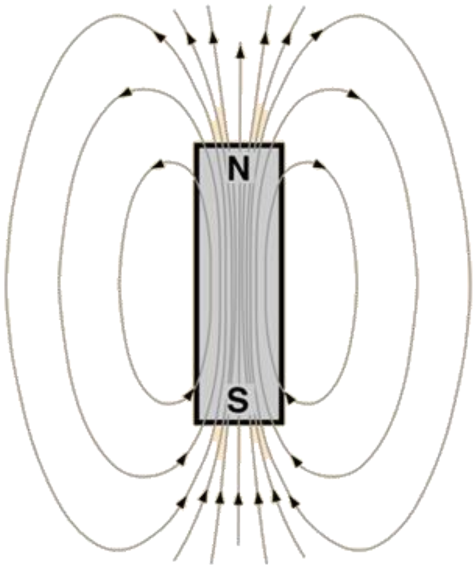


Figure 38. A schematic diagram showing the magnetic field associated with neodymium rare earth magnets. The permanent high field bar magnets utilized during the demonstration study consist of 10 neodymium rare earth magnets stacked vertically.

A sediment grab, in correct working order and properly deployed (slowly), will capture all deposited sediment (including tracer particles) within the ‘sampling window’ of the grab (i.e. a sampling efficiency of 100%). Comparatively, a magnet frame (e.g. 0.2 m^2) generally consists of 3 magnets equally separated across the frame. The resulting magnetic field (i.e. sampling window) of such a frame is ~ 0.082 m^2. Table 7 presents data from a laboratory experiment designed to determine the sampling efficiency of a magnet frame. The data indicates that the sampling efficiency of the magnet frame is within 30% of more traditional sampling methods such as the sediment grab. Again though, as described in the response to performance objective 2, where a sediment sample is collected (compared to a sample of the magnetic material in the system as afforded by the magnet frame), further analysis of the resolved sample would be required to determine the mass of tracer deposited.

Although Performance Objective 4 was passed (less than 30% difference between tracer collected on bedframe magnets compared to standard sediment grab), we still decided to use a standard grab to recover tracer from the sediment surface at both demonstration sites. This was based on the grab being able to recover >90% of the tracer released in laboratory settings compared to the various bedframe designs which never did better than recovering about 80%. Additional work is continuing to better design magnet bedframes to recover greater percentages of deposited tracer from the sediment surface because based on field performance the grabs were still not performing as well as expected. The grab data at both field sites provided lower mass balance values compared to magnet results.

Table 7. Example comparison of the sampling efficiency of traditional sampling methods (i.e. sediment grabs) and the magnet frame specifically designed to sample tracer particles as they deposit on the bed.

Sampling device	Instrument coverage (m^2)	Sampling window (m^2)	Tracer mass deployed (g)	Tracer mass recovered (g)	Capture efficiency (%)	Notes
Magnet frame	0.2	~ 0.82	10	3.214	79	Tracer deployed and left to settle for 1 hour, finest particles remained in suspension
Sediment grab	0.2	0.2	10	9.248	92	

6.2.5 PERFORMANCE OF SPECTROFLUOROMETRIC ANALYSIS METHODS

The spectrofluorometric analytical procedure was adapted and developed to exploit the fluorescent attribute of the tracer particles, to provide directly, the dry tracer mass (in grams). The technique has sufficient spectral resolution to distinguish low concentrations (< 0.01 g) of two spectrally unique tracer colors. The dye concentration was proportioned to dry mass of fluorescent tracer particles through the use of color specific reference standards. Consistently high coefficients of determination (r^2) were recorded throughout both demonstration studies (see Appendix 1 NBSD study report and Appendix 2 HPS study report). Table 8 presents the corresponding r^2 value for each reference standard developed (6 in total). Table 9 presents the percentage difference between each data point and the line of best fit. All scatter points were found to be within 40% of the line of best fit with the mean percentage difference found to be 4.9%.

Environmental samples spiked with varying quantities of both one and two tracer colors mixed with homogenous background material (silt and sand) were prepared to investigate the methodological accuracy (i.e. the difference between measured tracer content and known tracer content). The tracer content values of each spiked sample were unknown to the person who undertook the measurements and analysis. Calibration curves were developed empirically to account for the experimental and environmental conditions at the time of testing. Figure 39 presents data from the laboratory testing conducted in the first year of the program. Table 10 shows data from spiked sample analysis presented in the NBSD and HPS appendix study reports, the mean associated error between known and calculated tracer mass is 20%, falling within the 25% threshold defined as the success criteria for performance objective 5.

Table 8. The coefficient of determination (r^2 value) for the color specific reference standards developed during the study program.

Reference standard	Tracer color	r^2 Value
1	Green	0.99
2	Green	0.97
3	Green	0.98
4	Green	0.99
5	Green	0.92
6	Pink	0.95

Table 9. The percentage difference between each data point and the line of best fit. Data garnered from the 6 standard curves developed during the study program.

Data points (*N*)	Difference between scatter points and line of best fit (%)		
	Mean	Range	Std dev
54	4.6	0.0 – 29.5	7.1

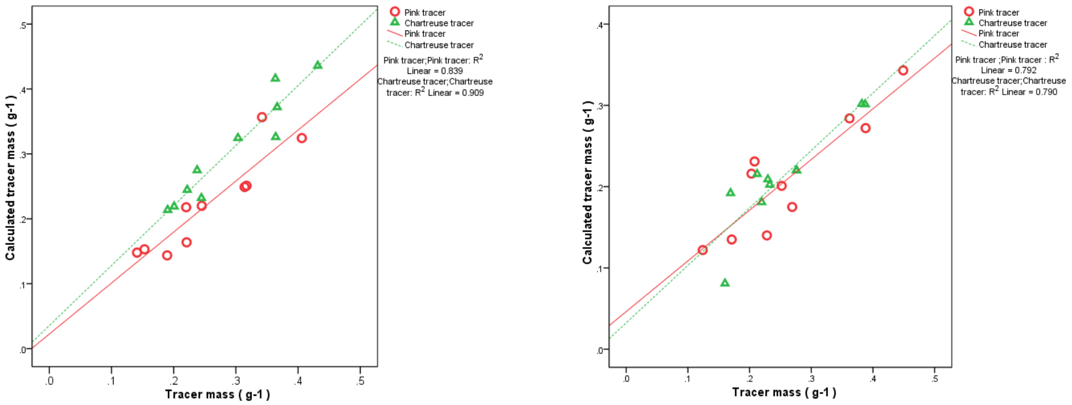


Figure 39. Tracer mass vs. calculated tracer mass for samples with one (left) and two (right) tracer colors in the sample (pink and green) variously mixed with homogenous background material (sediment).

Table 10. Results of blind testing of spiked samples containing various quantities of green and pink tracer mixed with low (< 0.5 g), moderate (0.5 - 2 g) and high (> 2 g) quantities of non-fluorescent sediment.

Actual tracer mass (g)		Added sediment volume (background non-fluorescent material)	Calculated tracer mass (g)		Difference (%)	
Green Tracer	Pink Tracer		Green tracer	Pink tracer	Green tracer	Pink tracer
0.346	0.269	Low	0.433	0.175	25	35
0.212	0.267	Low	0.216	0.150	2	44
0.230	0.438	Low	0.209	0.207	9	53
0.169	0.228	Low	0.192	0.140	14	38
0.382	0.203	Moderate	0.302	0.216	21	6
0.387	0.449	Moderate	0.301	0.343	22	24
0.220	0.362	Moderate	0.181	0.284	18	21
0.233	0.124	Moderate	0.202	0.122	13	2
0.276	0.388	High	0.220	0.272	20	30
0.276	0.171	High	0.220	0.135	20	21
0.585	0.252	High	0.475	0.201	19	20
0.160	0.208	High	0.081	0.231	49	11
0.231	-	Moderate	0.248	-	2	-
0.24	-	Moderate	0.289	-	5	-
0.2	-	Moderate	0.186	-	2	-

A methodological bias of ± 20% for single colour sample analysis, and ± 30% for two tracer colour sample analysis, was quantified. The observed increased error associated with the analysis of two colour spiked samples in comparison to single coloured spiked samples, indicated where high precision is required, the use of a single tracer colour is preferable. The methodological bias is considered tolerable within the sediment tracing methodology, due to the error associated with other enumeration techniques e.g. an error of 5 - 10 % was attributed by Carrasco et al. (2013) to counting fluorescent tracer grains by eye. Further, the error related to models of sediment transport are judged to be of the order of a factor of 10 (Eidsvik, 2004), reduced to a factor of 5 or better once validated (Soulsby, 1997).

Another useful metric for assessing the performance of the spectrofluorometric analytical procedure is made through periodic testing of blanks (solutions made up in entirely the same manner as samples but without inclusion of a sediment / tracer sample). As part of the two demonstration studies, during the sample analysis process periodic testing of blanks was conducted and reported (see Table 10 in the Appendix 1 NBSD study report and Table 7 in the Appendix 2 HPS study report). The data show that there is negligible variation in the blank sample signal throughout the two analysis campaigns.

Consequently, the performance of the spectrofluorometric analytical approach can be judged from the following key findings:

- During the analyses of spiked samples the mean associated error between known and calculated tracer mass, was 20%, falling within the 25% defined success criteria for Performance Objective 5;
- 100% of blank samples tested were within 10% of true value;
- Consistently high coefficients of determination were found for the 6 calibration standards developed throughout the program (100% of r^2 values exceeded 0.9); and,
- All scatter points were found to be within 40% of the line of best fit.

6.2.6 DEMONSTRATE MASS BALANCE

The evaluation of mass balance is based on the magnet data presented in Figure 24 and discussed in Section 5.1.6 for the first demonstration at NBSD. Assuming the tracer mass collected on each magnet represents collection of tracer over 1 square foot (ft^2) of the sediment surface, we interpolated the amounts of tracer that would be present on the sediment surface between the collection points and found that the red highlighted area representing 60,000 ft^2 (about 1.5 acre) would contain about 516 kg of tracer. The larger yellow shaded area representing 400,000 ft^2 (about 10 acres) contains another 152 kg of tracer. This total of 668 kg represents 84% of the total 800 kg of released tracer, so although we directly collected only a small fraction of the released tracer (<100 grams) on the magnets we are able to calculate a mass balance and pass this performance objective.

Although not listed as part of the performance objectives, mass balance can also be confirmed by comparison to modeled results. Figure 25 shows the predicted sediment deposition of silt sized particles released from Outfall 20. As discussed in Section 5.1.6, comparison between Figures 24 and 25 shows comparable results. Most of the silt and larger particles modeled in Figure 25 were deposited within the pier area out in front of Outfall 20, similar to the patterns seen in Figure 24. Additional model runs could be attempted to better match the pier flow conditions and therefore better match the tracer results. And since tracer studies can only be done under a limited number of scenarios (different particle sizes, with and without ships at piers, different storm and stormwater release sizes, etc.), it is typically expected that modeling will be done in tandem to run the various other possible scenarios that need to be addressed.

Unfortunately the tracer plume at the second demonstration site at HPS was forced onto the intertidal beach area on the east side of the site by prevailing wind driven currents. This resulted in the plume not being bounded by magnet collection sites so no full mass balance was calculated for this site. Some calculations were made in Section 5.2.6 to estimate the amounts of green tracer (representing upland contaminated sediments) redeposited over the cap area and amounts of pink tracer (representing cap materials) leaving the cap area.

6.2.7 EASE OF USE

The evaluation of ease of use was based on comparisons to previous SPAWAR experience with dye and particle tracer studies. The use of magnets for collection of particle tracers was easier and faster compared to collecting water samples with suspended tracers followed by filtration to collect solid tracer particles. And the use of laboratory spectrofluorometric techniques to quantify tracer levels was a distinct advantage over standard analysis techniques of counting fluorescent particles under a microscope. Overall the Partrac methodology and the dual-signature nature of their tracers proved “easier” to complete both field and laboratory aspects of a particle tracer study, in comparison to standard (mono-signature) tracer studies. This increased ease of use aspect propagates downwards enabling more samples for a given budget to be collected within a study, which increases the robustness and value of a study in comparison to standard methods and approaches.

7. COST ASSESSMENT

Cost issues are critical to the evaluation and acceptance of innovative technologies. Operational costs for the use of this particle tracking technology were developed and validated during this project. Relevant cost elements were tracked and documented during the demonstration to arrive at an estimate of operational costs for using the technology. The costs summarized below are largely based on data provided by Partrac as the commercial partner through their experience on this demonstration project and a number of additional efforts that have been completed during the duration of the demonstration project. The elements below will form the basis of the cost assessment.

7.1 COST COMPARISON

The cost of a particular Partrac tracer study will depend on many factors, including the objectives of the study, the size and duration of the study, and the amount of tracer that will be used. Based on the two demonstrations conducted for this project, some cost estimates can be made between smaller and larger sized studies with varying objectives. During the two demonstration studies the quantity of tracer introduced to the environment reflected the spatial scale of the study area of interest. As a comparison, Table 11 presents the size of the area of interest and the total tracer mass deployed at the two demonstrations.

Table 11. The site, size of area of interest, and mass of tracer deployed.

Site	Tracer color	Size of area of interest (acre)	Tracer mass deployed (kg)
NBSD	Green	10	800-1000
HPS	Pink	1	100-200

The amount of tracer introduced is critical – if too much material is deployed to the environment, sediment transport processes may be unduly affected. If too little is deployed, the subsequent recovery of tracer is compromised, potentially resulting in insufficient tracer recovery, and limiting the conclusions that can be drawn from the data. Pragmatically, the quantity of tracer that is introduced to the environment during a tracing study is dictated primarily by the project budget. In general, the more dynamic the environment and the less contrived the study, the greater quantity of tracer is required, as the resolution of the data obtained is dependent upon the measuring technique employed. This simple scaling up of tracer mass input to larger sites appeared to be effective with significant quantities of tracer recovered during both demonstration studies at NBSD and HPS. It is necessary however to also consider the hydrodynamic forcing (tidal flows and waves) at each site. Both demonstration studies were conducted in relatively quiescent, contained (sheltered) systems. If future studies were to be conducted in more dynamic systems (in terms of the hydrodynamic forcing observed) a greater mass input (of which could be afforded by the project budget) would be considered beneficial.

Table 12 provides an estimate of the likely costs of future particle tracking studies at DOD sites based on the two demonstrations conducted for this project. The "Study type" is intentionally general to address the variety of potential future study objectives, with standard linking of sources to sinks corresponding to the first demonstration at NBSD and the second cap assessment corresponding to the second demonstration at HPS. Costs under "Preparation and Field Survey" are about evenly split between costs of preparing the tracer and field work. The "Estimated Total" is provided as a range to reflect the reality that study objectives and study designs will vary so costs are only estimates.

Table 12. The estimated costs of similar future tracer studies at DoD sites derived from the two demonstration studies. Please note all future studies would be costed on a study by study basis.

Study type	Size of area of interest (acre)	Estimated study costs (USD)		
		Preparation and Field Survey	Analysis and Reporting	Estimated Total
Standard (e.g. linking sources to sinks, determination of sediment transport pathways, determination of depositional footprint)	1	36,000	10,000	40,000 – 60,000
Standard (e.g. linking sources to sinks, determination of sediment transport pathways, determination of depositional footprint)	10	54,000	20,000	70,000 – 120,000
Activated carbon cap assessment (combining tracers and cap materials)	1	46,000	10,000	50,000 – 70,000
Activated carbon cap assessment (combining tracers and cap materials)	10	81,000	20,000	90,000 – 140,000

Costs associated with a Partrac tracer study can be compared to costs associated with conducting particle tracking studies by traditional tracer methods (for example those using only fluorescent particles). Traditional tracer studies require significantly greater field efforts due to the need to recover tracer particles from the water through standard filtering techniques (due to the lack of a magnetic component that allows simple recovery in the field through the use of magnets). The laboratory analysis costs are also greater due to labor intensive methods including additional filtering and microscopic counting of tracer particles. Labor costs associated with conducting standard tracer studies are therefore estimated to be about double the labor costs of a Partrac study.

7.2 COST DRIVERS

Implementation costs for the tracer study will largely be driven by field survey activities (boat, materials handling, and associated labor), tracer manufacture, transportation, and laboratory analysis activities. Field survey costs will be driven by the desired sampling density; and during both ESTCP demonstrations we could probably have used more magnet sampling sites at both study sites. But the 30-40 magnet sites were what we calculated in the budget for one boat with four people to sample in a 10 hour workday. If the budget would have allowed, we could have used more magnets with higher sampling density near the release area at each demonstration to provide more detail near the tracer release locations.

Tracer manufacture costs are dependent on the amount of tracer to be deployed as shown in Table 12. Partrac was able to accommodate special order tracer development and worked with an AquaGate delivery method at the second demonstration site for the activated carbon cap assessment, but these types of special orders may impact development and shipment costs for the tracer. All post field work laboratory analyses were conducted by Partrac, with these types of services offered on their website. Although field work can be done independently (through purchase of tracer and purchase or lease of magnets), laboratory analysis for tracer results requires the expertise and equipment which Partrac offers as a commercial service.

8. IMPLEMENTATION ISSUES

As with many field studies, during the course of this ESTCP project some implementation issues arose which could be termed “lessons learned”. Many of these came to light after discussions with DoD and contractor personnel at the various demonstration sites, so we are grateful to all those un-named individuals who contributed to the project. At active DoD sites it is good to begin discussions of study design with site personnel as early as possible, but it is often only when the study schedule is posted in a weekly notice at the site that many implementation issues may arise so flexibility is usually required (at NBSD magnet positions needed to be shifted due to ship operations). At closed DoD sites the lack of activity and personnel may also lead to issues (at HPS the higher than usual rate of nightly thefts led to a shortened deployment period for expensive equipment). Working at sites under regulatory schedules may also require some flexibility in demonstration schedules (at HPS we needed to take a one year no cost extension in the project to wait for the amendment cap to be placed at the site). As part of the ESTCP project it was requested that a generic Standard Operating Procedure (SOP) be included, so a SOP is provided in Appendix 3. As a caveat it should be noted that all tracer studies are site and objective specific so any generic SOPs are just a starting point for a site specific study design. ESTCP also requested that additional toxicity studies be conducted to ensure any released tracer posed no adverse biological effects, so additional toxicity tests are reported in Appendix 4. All toxicity test results over a range of applicable tracer concentrations showed no effects compared to reference conditions for a range of common toxicity tests. Additional discussions of potential environmental effects of tracer studies are presented at the end of this chapter. The following sections contain some additional thoughts and discussion regarding key issues surrounding the implementation of tracer studies at DoD sites.

General Approach and Implementation of Tracer Studies

Particle tracking studies have the potential to improve upon the conceptual understanding of sediment transport regimes. They offer significant utility in this respect and they can be conducted to identify potential sediment source areas, transport pathways and specific areas of sediment deposition, accumulation and erosion and when applied correctly can be used to determine the sediment transport rate. These data are critical to developing robust sediment management plans, and implementing informed, remedial strategies to maintain and improve the marine and coastal environment. This ESTCP project has demonstrated that “dual signature” tracers and the associated methodology are an advance within the field of active sediment tracing. Having two signatures proved highly beneficial within both demonstration studies, facilitating the use of unique monitoring, recovery and enumeration methodologies which both simplified and accelerated a number of key stages of the methodology. The field methodologies employed during both demonstration studies were adaptive and in future studies could be specifically tailored to suit both the receiving environment, and study context. The use of a multistage sampling campaign enabled a greater wealth of information to be garnered from each field application. Further, the developed tracer enumeration methodology reduced both field and analytical timescales and associated costs, improving the cost/benefit ratio of the technique. The methodology is best utilized to: 1) improve our understanding of sediment transport processes; 2) provide field data to develop or validate existing sediment transport models; and 3) evaluate the effectiveness of sediment management techniques, preventive measures or management protocol to develop informed management or mitigation strategies. The technique is particularly useful in answering direct sediment transport questions – such as whether recontamination from a particular source is an issue. As sampling resources are never infinite, specific objectives need to be set and the limitation of the technique thoroughly understood at the study planning stage. Phrasing of appropriate research questions is key, so questions phrased in general terms (e.g. where does the sediment go?) are far less likely to achieve successful results compared with a specific hypothesis (such as does the sediment deposit within this specific area). This provides a far greater opportunity for the technique to provide useful study results.

This demonstration program linked SPAWAR with a commercial firm Partrac to demonstrate the potential utility of dual signature tracers to investigate contaminated sediment at DoD sites in the US. Having a commercial partner on the project provides a readily available technology transfer pathway for the technology. The commercial tracer technology product (specifically using dual signature tracers) proved to be an effective tool to monitor and map the transport pathways at two DoD sites improving the understanding of contaminant transport and efficacy of potential mitigation strategies. The development of a dual signature sediment tracer is considered to be an advancement within the field of active sediment tracing. This program explored the suitability and efficacy of the tracer material, as a tracer, and assessed the methodological benefits that the tracer provides through application to a series of relevant sediment management problems at DoD sites.

Having a single signature (such as only fluorescence which is common in most current tracer studies) by which to differentiate the sediment tracer from the native sediment restricts the sampling techniques available to monitor the sediment tracer. This often increases the resource intensive nature of active sediment tracing approaches by increasing the volume of samples collected in the field as the use of non-intrusive sampling approaches is finite. Dual signature tracers increase the variety of sampling techniques and non-intrusive *in situ* monitoring techniques that can be utilized. Dual signature tracers can replicate multiple tracer size fractions, from silts to cobbles, and marries the individual fields of fluorescent and magnetic sediment tracing. This improves the cost benefit ratio of sediment tracing studies. Thus, when deploying the same quantity (mass input) of tracer, studies which use the dual signature tracer method are more likely to collect more tracer and provide greater (and more robust) information. This is important as the cost of the tracing material often constitutes the principal cost within an active tracing study. Further, the presence of two tracer signals increases the flexibility of the technique and enables studies to be conducted within complex, industrial or anthropogenically altered settings. The passive and active sampling techniques described within this document and utilized throughout the program, detail a range of techniques available to monitor and recover silt and coarse sized tracer particles once deployed to the environment. In light of this, we find that the dual signature sediment tracer can be considered an advance over previously used mono-signature tracers.

There is a great need for field data relating to sediment transport processes for fine and cohesive sediments (Spanhoff and Suijlen, 1990). A pragmatic approach towards tracking the fine silts and clay fractions has been outlined, termed '*floc tagging'* (see appendix 3). Silt - sized sediment (20 - 63 micron in size) transported in suspension can be distributed over great distances before being deposited (Dyer, 1986; Dyer, 1995; Droppo and Ongley, 1994). Monitoring of sediment in suspension is required. The approach here utilized two approaches: 1) an *in situ* fluorimeter to monitor the cloud of tracer as it moved through the water column. The data generated highlights the potential of sensor based technologies to monitor tracer travelling in suspension, yet further development would be valuable (e.g. multi-sensor arrays); and, 2) *in situ* high field magnets which act as a time integrated samplers which samples only Fe or Fe bearing materials. The use of magnetic sampling approaches significantly reduces the volume of sediment collected, which is useful on a practical level. These tracer sampling tools enabled silt sized sediments to be monitored and sampled while in suspension.

Given the high spatial and temporal variability of particle movement, sediment tracing studies involve the collection of a substantial number (often >100) of environmental samples. This requires significant time and effort in the field and the laboratory, and often involves expensive, resource intensive methods of sample analysis. These factors act to reduce both the number of samples able to be collected in the field, and the number that can reasonably be analyzed in the laboratory. Historically, these limitations have formed a significant constraint on the tracing technique. Consequently, there has been a strong emphasis placed on developing simple, rapid and reliable analytical methods for enumeration of tracer (Guzman et al., 2013). The analytical method applied within this program can be considered an advance on previously used fluorescent (and magnetic) enumeration methodologies (e.g. Ciavola et al., 1997; Ciavola et al., 1998; Carrasco et al., 2013; Solan et al., 2004, Forsyth, 2000) as it reduces analytical timescales and associated costs. This increases the number of samples that can be reasonably analyzed within a tracing project. Simply, this increases the spatial and temporal resolution of active sediment tracing studies. Magnetic separation provides a quick and simple technique to determine the tracer dry mass content (mass per unit mass) within environmental samples.

Spectrofluorometric detection of fluorescent tracer particles is a method of broad applicability in the study of particle dynamics within marine, coastal and aquatic environments. The described analytical method provided a practical solution that was used to analyze a significant number of samples in a short period of time, at low cost. The spectrofluorometric analytical procedure was adapted and developed to exploit the fluorescent attribute of the tracer particles, to provide directly, the dry tracer mass. The technique has sufficient spectral resolution to distinguish low concentrations (< 0.01 g) of two spectrally unique tracer colors. The fluorescent excitation and emission wavelengths of fluorescent derivative are not common to materials commonly found in water (Stern et al., 2001, Wilson et al., 1986). This is strong evidence to suggest that this sample analysis technique will be applicable to analyze samples collected from a variety of environments with varying study designs.

This program has provided key ‘baseline’ data for future studies that utilize the dual signature tracer at DoD sites. Each field application highlighted the utility of sediment tracing studies to the wider scientific community providing information and data regarding real world, sediment management problems and the impact of contaminated sediment transport on the environment. Further, the field deployments of the tracer have demonstrated the effectiveness of the technique as the only direct field tool able to confirm the existence of sediment transport pathways and define source-sink relationships which provides important information to inform environmental management strategies. These tracer studies also provide direct field data to complement typical sediment transport modeling efforts.

The active sediment tracing approach does have inherent limitations that must be considered within each application of the active sediment tracing technique. It is critical to remember that sediment tracing studies only provide information regarding the forcing mechanisms observed during the study period and these conditions must be considered when interpreting the results. To improve any sediment tracing the availability or collection of longer term data regarding the forcing mechanisms at the site are beneficial (i.e. the collection of weather (wind) and hydrodynamic (current) data). And as discussed earlier, tracer studies are often run together with additional sediment transport modeling. When run together, tracer and modeling studies often overcome the limitations found in each technique, and undoubtedly form a powerful tool in combination. For example, tracer studies can validate the modeling efforts by providing direct input data or by providing field data to support modeling assumptions. And modeling efforts can run scenarios not covered in the limited number of tracer experiments that can be run in a costly manner (e.g., predicting 100 year storm events, or far field transport of very fine clay particles with size ranges below the current ability of tracers to reproduce, etc.).

Data Analysis and Interpretation

Tracer measurement or enumeration provides point-specific tracer mass/concentration data at a single instant in time. These data can be used to determine tracer presence/absence, map sediment transport pathways and deposition patterns and determine sediment transport rates and the volume of sediment in transit. As sediment tracing is fundamentally an empirical, evidence-based approach, it is important to consider all lines of evidence gathered during sampling (e.g., both qualitative and quantitative data sets).

The direction of transport is determined via the quantity of tracer recovered from the sampling grid, best described as a percentage of the total tracer mass recovered, not the total tracer mass deployed (e.g., > 50 % of tracer recovered was found to the south of position X). As transport of sediment is often multidirectional, the dominant transport pathway, and receptor area, is determined by the presence of the greatest quantity of tracer. However, care must be exercised, as these results only reflect the conditions observed within the study.

A principle of tracing studies is normalization of the data to represent tracer mass/concentration within the surrounding area (White, 1998; Vila-Concejo et al., 2004a; Black et al., 2007). This was first described by Inman and Chamberlain (1959) who concluded that the mass of tracer recovered from a sample point (S_x) is representative of the mass of tracer in a rectangular shape around the point of the sample, with the boundaries of the rectangle being midway between sample points. To compute the tracer content within each area of the sample grid, the volume (V_{ri}) of the area (A_{ri}) represented by each core sample can be calculated:

$$V_{ri} = A_{ri}h \tag{2}$$

Where h is the height of the tagged layer.

A multiplying factor (T_{mi}) used to extrapolate the tracer concentration of the core (C) to the entire represented area can then be calculated by dividing C by the volume of the core (C_{vol}).

$$T_{mi} = \frac{C}{C_{vol}} \tag{3}$$

The tracer concentration of the represented area (M_i) is then calculated by multiplying the T_{mi} by the representative volume.

$$M_i = T_{mi} V_{ri} \tag{4}$$

The transport rate of tracer through the environment can be described through the advance of the tracer front (Madsen, 1987; Black et al., 2007) and determination and tracing of the mass center of tracer distribution (e.g., White and Inman,1989; Vila-Concejo et al., 2004; Carrasco et al., 2013). In this approach the average transport velocity is calculated from the distance moved by the mass centroid of tracer divided by the time between introduction and sampling (White, 1998). Assuming that all samples collected have been sampled throughout the active transport layer, following the enumeration of tracer content from each sampling point, the location *(Y)* of the mass centre of the tracer distribution can be determined:

$$y = \sum M_i D_i / \sum M_i \tag{5}$$

Where M_i is the mass of tracer at each grid node and the average grain mass (usually obtained using mean grain size values from the area of interest), and D_i is the distance from the introduction point.

Determination of sediment flux (i.e. through a mass-balance approach) has proved useful in the analysis and interpretation of the sediment grab data within this study at both the HPS and NBSD sites. Using a mass balance approach to interpret the data collected using the magnets has been less successful and it has proved difficult to directly compare between the two datasets (sediment grabs and magnets) when utilizing a mass balance approach. High-field permanent bar magnets deployed directly in the water column on float moorings, and attached to infrastructure capture passing tracer, providing a time integrated sampler of Fe bearing material. Whereas a grab sample captures a snapshot in time of tracer deposition on the seabed, magnets capture tracer variously throughout the period of deployment. Thus the magnets are able to sample tracer that ultimately is transported beyond the limit of detection (i.e. outside of the sampling boundary) or, particles that remain in suspension and are transported back and forth with the tide. A limitation of the magnets is that there is an upper limit to the amount of tracer that can be retained on the magnet. This was evident at the sampling station (T3-2) located directly in front of the discharge zone at the NBSD site, where tracer concentrations on the sea bed, significantly exceeded those observed in the water column. This limitation prevented the reliable determination of tracer concentration values. The combinations of these factors provides an explanation of the difficulties of direct comparison of magnet and grab sample data, and the challenges of using time integrated data to determine sediment flux across the site. In general, extrapolation must be used with caution and the sampling frequency (i.e. distance between sample points) must be appropriate (Black et al., 2007). Given these concerns the mass balance calculations provided in Sections 5.1.6 and 5.2.6 must be considered approximate and some level of expected error should be included (but this would require additional study outside the scope of this project).

Environmental Considerations

Sediment tracing is a useful tool capable of providing information which aids in the protection of ecological habitats, supports the development of sediment management plans, and provide baseline data to inform sediment transport models, important for long term planning and development at the coastal scale. Continued development of sediment tracing techniques will inevitably increase application. However, there is a general concern regarding the introduction of microplastics and toxic fluorescent dyes to the environment, which are released to the environment within particle tracking studies, and these should be considered.

Firstly, crucially, particle tracking is principally an environmental monitoring tool that is useful in assisting in the assessment, clean-up and mitigation of heavily contaminated sediments; this is a positive aspect of the method. Secondly, due to the inherent hydraulic properties of sediments tracking the movement of sediments using biological tracers (e.g. biological spores, fruit, seeds) which may be generally considered beneficial in an ecological sense is fundamentally unachievable. Where possible a robust coated mineral particle is considered preferable to a polymer tracer, though in certain circumstances low density polymer tracers must be utilized to match the hydraulic properties of the target sediment (e.g. the HPS study). Degradation of tracer, through time, will inevitably lead to the breakdown of the fluorescent complex, introducing fluorescent dye to the environment. Fluorescent dyes, regularly utilized in dye dispersion studies, are known to have deleterious environmental impacts when used in higher concentrations. The toxicity of fluorescent dyes used within water tracing studies such as fluorescein, rhodamine B and rhodamine WT have been assessed in terms of their effects on aquatic organisms and marine life (Smart and Laidlaw, 1977). At low concentrations (typical of most tracing studies), no deleterious effects on ecology were recorded (Bandt, 1957; Sowards, 1958). However, as organisms were exposed to greater dye concentrations, over longer periods of time, deleterious effects (Akamatsu and Matsuo, 1973; Keplinger et al., 1974; Sturn and Williams, 1975; Ganz and Stensby, 1975), and mortality (Marking, 1969; Parker, 1973) are observed. The toxicity of these dyes can be assumed to be similar to other fluorescent dyes available (Smart and Laidlaw, 1977). The results of survivability/degradation testing indicate dual signature tracer is robust enough to withstand exposure, across research and industry relevant, temporal scales. The toxicity data of regularly used fluorescent dyes and the robustness / survivability of the dual-signature tracer coating indicates that following the culmination of a tracing study, the environmental impact of the dual-signature tracer remaining in the environment will be negligible. As the tracer is able to withstand extensive exposure without significant degradation and loss of fluorescent dye, at the stage where fluorescent dye is released, the particulate tracer is likely to be sufficiently dispersed and diluted. At this point, dye concentrations should be reduced to less than that of dye tracing studies, which input a dye solution directly into the environment at a concentration of ten-parts per 1000 (Stern et al., 2001) which is insufficient to create deleterious effects on the environment, ecology and human population (Smart and Laidlaw, 1977). Due to the initial concerns of tracer ecological effects raised by ESTCP at the start of the project, additional biological effects studies were added during the first year of the project and are reported in Appendix 4. These biological effects studies consisted of a number of elutriate bioassay tests that all showed no adverse biological effects under a range of typical tracer exposure levels. Finally, where polymer tracers must be used for scientific reasons, Partrac added a commercially available molecule to the tracers which enables bacterial breakdown over timeframes of 1-2 years, thereby mitigating environmental concerns associated with this particular tracer type.

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APPENDICES

Appendix 1 – NBSD FIELD REPORT (Study 1 Naval Base San Diego)

Appendix 2 – HPS FIELD REPORT (Study 2 Hunters Point San Francisco)

Appendix 3 – PARTRAC TRACER STUDY SOP

Appendix 4 – PARTRAC TRACER BIOLOGICAL EFFECTS WHITE PAPER

ESTCP Project ER201214 Appendix 1

NBSD FIELD REPORT (Study 1 Naval Base San Diego)

Demonstration of Fluorescent Magnetic Particles for Linking Sources to Sediments at DoD Sites

Study 1 Naval Base San Diego

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EXECUTIVE SUMMARY

Transport Pathway Evaluation (TPE) is a method in which a sediment transport pathway is visualised using a mass of uniquely labelled fluoro-magnetic (tracer) particles. Tracer particles are released into the environment and subsequent capture of these particles in space and/or time provides information on the localised transport direction and rate.

Partrac Ltd were contracted within a contract vehicle created by the US Navy to undertake a TPE study and provide sediment tracking services at the San Diego Naval Base in the Port of San Diego, California, to assess the fate of silt sediments flushed into military waters by a simulated storm event with outfall discharge. This report represents a site field report required by the US Navy.

The particle tracking study was conducted from 19th – 21st September 2014. The tracer was released as a continuous discharge on the 19th September. In total, 800 kg of tracer material were deployed from the SPAWAR vessel Ecos. The tracer was mixed in a chamber and introduced sub-sea surface (~1m below the surface) through 2 continuous flow stations established at the rear of the vessel. Due to site restrictions deployment of tracer through a storm water outfall was not possible. Thus, during deployment, the vessel was moved back and forth along a transect at 90° from the quay wall to 50m offshore at the location of the storm water outfall. This movement of the vessel was undertaken so as to (as best as possible) mimic and replicate the sort of sediment plume discharge that would arise as a result of storm water runoff from the storm water outfall. To sample tracer following release a multi-tool approach was adopted. To assess the depositional footprint a fixed point, spatial sampling grid was installed (prior to release), consisting of magnet moorings deployed in open water with a sinker weight at the bed and a surface buoy. Additional magnets were also hung from quay wall infrastructure. To investigate the depositional footprint of the tracer particles, at each mooring location a seabed sediment grab sample was collected. During tracer deployment an *in situ* fluorometer, targeted at the peak excitation and emission wavelengths of the tracer, was deployed sub-surface continuously sampling, to measure tracer concentration within the water column. Alongside the particle tracking study *in situ* current measurements were recorded to contextualize the study findings.

Inspection of the data revealed that the sediment plume created during tracer deployment dispersed both vertically through the water column, and laterally in both a northerly and southerly direction due to advection and diffusion. Tracer was transported in the direction of the prevailing current flow (South). During high water slack, near field transport to the North was observed, driven by the jet flow. The observed sedimentation patterns show a high deposition zone, elongated significantly in the mean flow direction. Extensive deposition of tracer within 100 m of the discharge zone is attributed to reduced current velocity at high water slack, and the general low ambient current velocities observed at the site. The data revealed the critical role of tide and current flow in driving transport and deposition of fine sediment discharged from storm water outfalls at DoD sites.

Dual signature tracer proved to be an effective tracer able to be monitored effectively within, and recovered from, the environment following release. The study demonstrated a practical particle tracking methodology which can be utilised to monitor fine sediment transport at the field-scale, within complex, highly industrialised settings. Further, the findings of the study confirmed the potential of the technique to provide site specific data useful in terms of both site characterisation and model validation.

CONTENTS

1. INTRODUCTION

1.1 Background

Contaminated sediments are found in numerous ports and harbour environments world-wide, where they comprise legacy deposits from historical industrial activities as well as more recent deposits from on-going contamination. Management approaches directed towards decontamination of contaminated seabed sediments require information on the range of processes governing the transport and fate of the contamination.

Partrac Ltd were contracted within a contract vehicle created by the US Navy to undertake a TPE study and provide sediment tracking services at the San Diego Naval Base in the Port of San Diego, California, to assess the fate of silt sediments flushed into military waters by a simulated storm event with outfall discharge. This report represents a site field report required by the US Navy.

Assessment of the mobilisation and transport was achieved through the use of powerful*, in situ* moorings of permanent magnets and through collection of sediment grabs. This methodology is otherwise known as ‘Transport Pathway Evaluation’ (TPE).

1.2 Transport Pathway Evaluation (TPE) Using Sediment Tracers

Transport Pathway Evaluation (TPE) is a method in which a sediment transport pathway is visualised using a mass of uniquely labelled fluoro-magnetic (tracer) particles (White, 1998). Tracer particles are released into the environment and subsequent capture of these particles in space and/or time provides information on the localised transport direction and rate (Black *et al*., 2007). TPE experiments require the manufacture of sediment analogues called ‘tracers’; these are particles highly similar to those wishing to be tracked and which therefore behave in a highly similar way as native sediment. Partrac manufacture tracer with two unique signatures associated with every tracer grain – fluorescent colour and magnetic character – in order that they may be both extracted from environmental samples, with the use of powerful (11,000 Gauss) bar type magnets, and identified unequivocally using their fluorescent colour. Rarely are environmental particles found which are both fluorescent in colour *and* magnetic, and this thereby provides a firm foundation for the use of ‘dual signature’ tracers in tracking the movement of sediments.

The benefits of using powerful *[in situ]* magnets to capture the tracers include:

- Magnets can be left in the field to accumulate tracer (passive sampling);
- Magnets can be used to extract tracer from within a (bottom) sediment sample, thus concentrating tracer for ensuing analysis;
- They are simple to use and require minimal operator time;
- They can encompass a large area very easily thereby allowing a large area to be monitored;
- They immediately indicate the presence/absence of tracer, and can therefore be used to inform adaptive sampling; and
- They generally enable subsequent analysis of tracer particles by mass.

2. TRACER DESIGN, MANUFACTURE AND TESTING

2.1 Introduction

Discussions with Dr Jim Leather (at SPAWAR) distilled a tracer specification for use in the studies that matched native sediments in the area of the stormwater outfall. This was:

- Size range: coarse-medium silt tracer (ca. ~20 – 70 μm).
- Density: mineral density (~2300 – 2900 kg m^{-3}).
- Colour; 1 fluorescent colour (green; code: BSR-CH227).
- Ferri-magnetic attribute; yes.
- Quantity (kg): 800 kg x 1 (chartreuse green).

Partrac manufactured 800kg of green, fluorescent-magnetic silt tracer.

To ensure that the use of sediment analogues to track sediment movement in aquatic systems is valid the tracer material employed should, as best as possible, meet a series of underlying assumptions (see Foster, 2000). These are:

1. The tracer's hydraulic and bio-organic properties mimic those of the sediment of interest, and therefore the tracer is transported in the same way as the native sediment.
2. The tracer material does not change properties through time (at least over the timescales of interest) and can be monitored/detected.
3. The tracer does not manifestly change the transporting system in any way.

The following sections summarise characterisation tests performed on the tracer and are written in relation to [1] and [2].

2.2 Size Spectra

The particle size distribution of the tracer material was matched to the known characteristics of the native stormwater and deposited sediments at the site. In this case approximately 40% of the measured grain size distribution is in the >63 micron sand fraction and another 60% is in the 10-63 micron fraction that represents the silt range. The approximately 20% of material in the average native clay fraction is below the size range that the current technology can produce so our focus was aimed at producing a mostly silt size fraction tracer product.

Size spectra measurements were made on a small sub-sample of the bulk tracer batch using the *Mastersizer 2000* Laser Diffraction instrument. Figure 1 presents data from this analysis. d_{10}, d_{50} and d_{90} values for this distribution, respectively, are 13 μm, 30 μm and 79 μm.

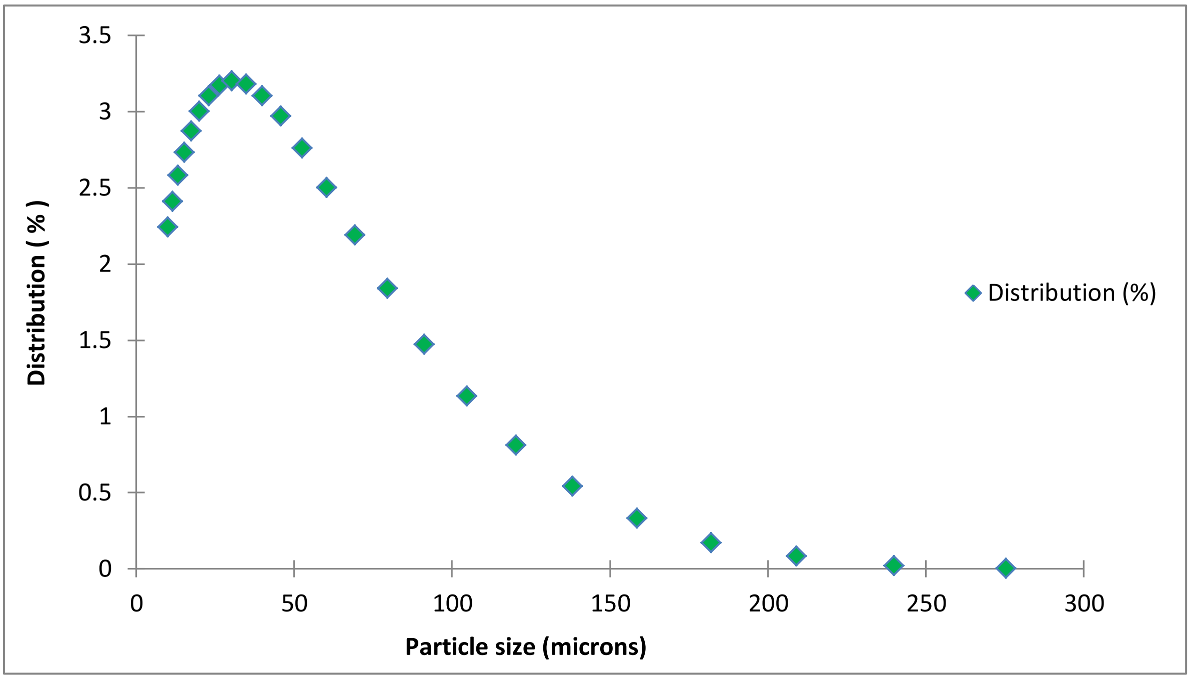

Figure 1. Particle size spectrum of the green silt tracer material (3 replicate runs on a Mastersizer 2000 Particle Size Analyser).

2.3 Particle Density

There was no contractual necessity to measure density of the native sediments as the tracer particles are coated, quartzitic mineral particles and understood to be of a sufficiently similar density. However, direct measures of the density were made using a standard volumetric methodology (BS 1377: 1990 Part 2: 8.2). This gave a density of 2182 kg m^{-3} ± 115 kg m^{-3} @ 20^0C for the tracer material.

2.4 Settling (Fall) Velocity

The settling (fall) velocity of tracer particles was measured using the low intrusive LabSFLOC (Laboratory Spectral Flocculation Characteristics) system of Manning and Dyer (2002). LabSFLOC utilises a video camera to observe flocs as they settle in a 190mm high by 100mm square Perspex settling column. The video camera views all particles in the centre of the column that pass within a 1 mm depth of field, 45mm from the lens. The complete LabSFLOC configuration is illustrated in Figure 2. By measuring a floc population within a controlled volume, floc properties such as porosity, dry mass and mass settling flux can be calculated

The results indicate tracer material particle sizes of between 30 μm and ~200 μm. Corresponding settling velocities range from ~0.1 to ~5 mm s^{-1} (

Figure 3).

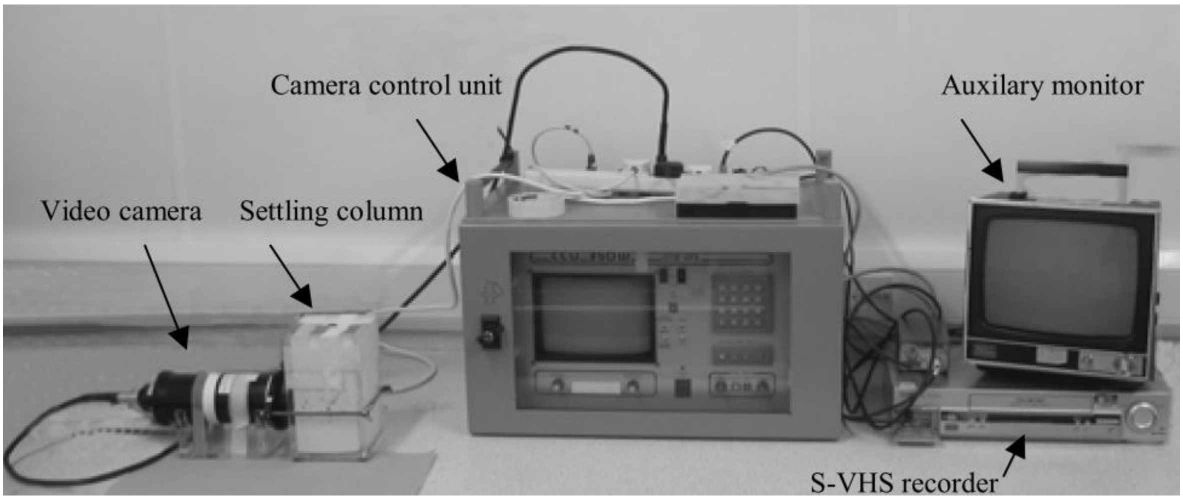

Figure 2. LabsFLoc setup.

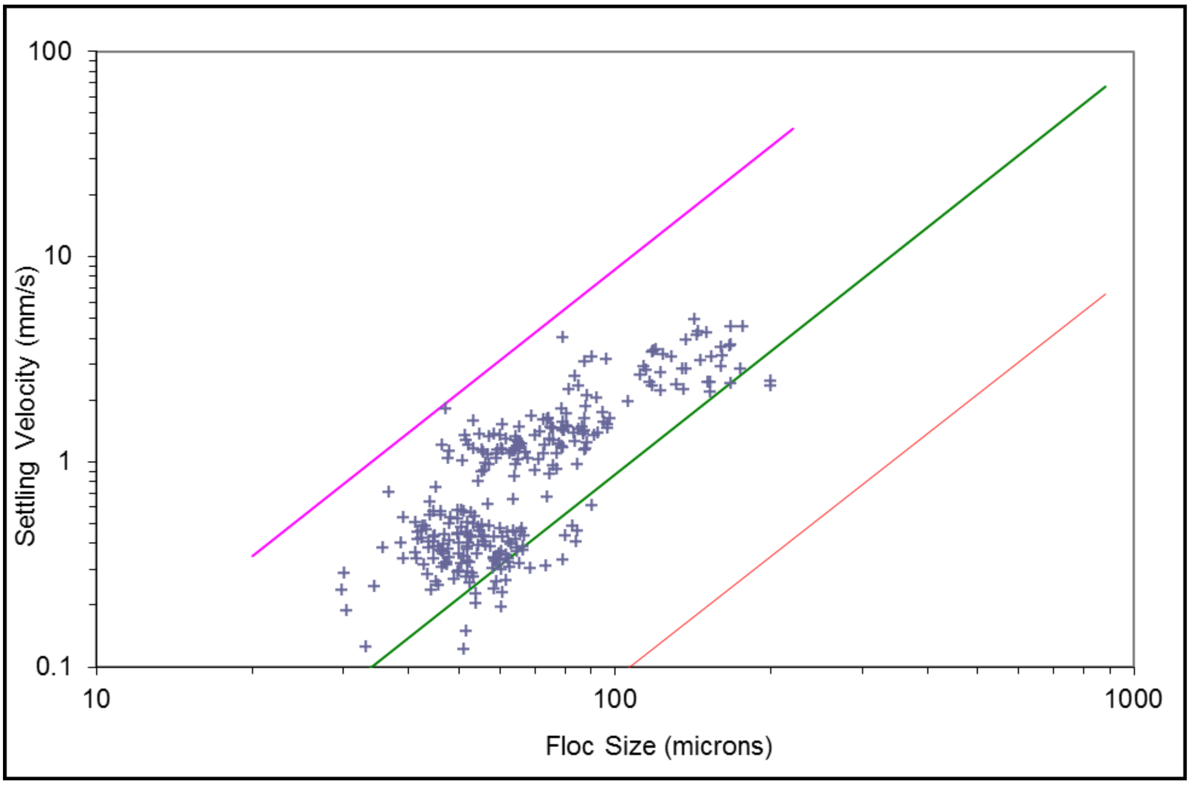

Figure 3. Settling velocity – tracer (floc) size relationship for a sample of the green tracer.

2.5 Ferrimagnetic Attribute

Particles with ferrimagnetic attributes were required, in order that magnets could be used both within field sampling and to achieve magnetic separation (i.e. separation of magnetic particles [including tracer]) from non-magnetic sediments). Magnetism is controlled by the forces created by the spin and orbital angular states of the electrons within atoms (Dearing, 1994). The manner in which these motions are aligned, the number of electrons and the type of motions determine the magnetic moment of the atoms. Ferrimagnetic materials have populations of atoms which are strongly aligned, but exist as two sets of opposing forces. These materials display high susceptibility and are considered highly 'magnetic' materials. The tracer 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., 2010).

The degree of magnetisation 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 provides a comparative measure of the relative ease with which a material can acquire a magnetic field when exposed to a low frequency, low intensity alternating magnetic field; Fe or Fe bearing materials acquire a magnetic field far more easily than non Fe bearing materials (Oldfield, 1999), hence they can be detected using this technique. The low frequency magnetic susceptibility was determined using a Bartington MS2B susceptibility sensor for 3 sub samples of tracer and 3 sub samples of a quartzitic beach sand sourced from South Bay, Scarborough, Yorkshire, UK to provide a comparison between a coated material (tracer) and an uncoated material. The results (Table 1) show the tracer to be ~128 times 'more magnetic' than common beach sand.

Also, a simple test was designed to establish the percentage (%) of particles that are magnetic. To do this, a high field bar magnet (~11,000 gauss) was held in suspension just above the sample and carefully passed over the sample three times. The magnetic material recovered was then weighed and compared to the known mass (g) of tracer particles present within the sample. This test was repeated 3 times. The results (Table 2) show that **100% of tracer particles were magnetic**.

Table 1. Low frequency mass specific magnetic susceptibility (χ_{LF}) of the tracer and a quartzitic beach sand provided as a comparison.

Sample (material)	Mass (g)	Air 1	Sample 1	Sample 2	Air 2	*K* corrected	*Mass specific* χ_{LF} (kg m^{-3})
Tracer	0.48	- 0.04	310.7	310.7	- 0.06	310.75	647.396
Tracer	0.502	- 0.06	313.7	312.5	- 0.06	313.16	623.824
Tracer	0.794	- 0.06	519.3	519.3	- 0.09	519.375	654.125
Mean (χ_{LF})							**641.782**
Quartzitic sand	0.669	0.3	2.4	2.3	0.1	2.55	3.812
Quartzitic sand	0.518	0.1	1.9	1.9	0	2.35	4.537
Quartzitic sand	0.570	0.5	3.0	3.0	0.3	3.8	6.666
Mean (χ_{LF})							**5.005**

Table 2. The percentage of tracer particles that are magnetic.

Sample	Tracer mass (g)	Tracer mass recovered (g)	Percentage of tracer particles recovered (%)
1	0.764	0.764	100
2	0.561	0.561	100
3	1.097	1.097	100

2.6 Fluorescent Colour

A sub-sample of the tracer was inspected under blue light illumination (UV- A~395 nm) using a high power photomicroscope to determine the integrity of the fluorescent-magnetic coating and the quantitative % of coated particles. These tests (Figure 4) indicated **100% of particles are coated**.

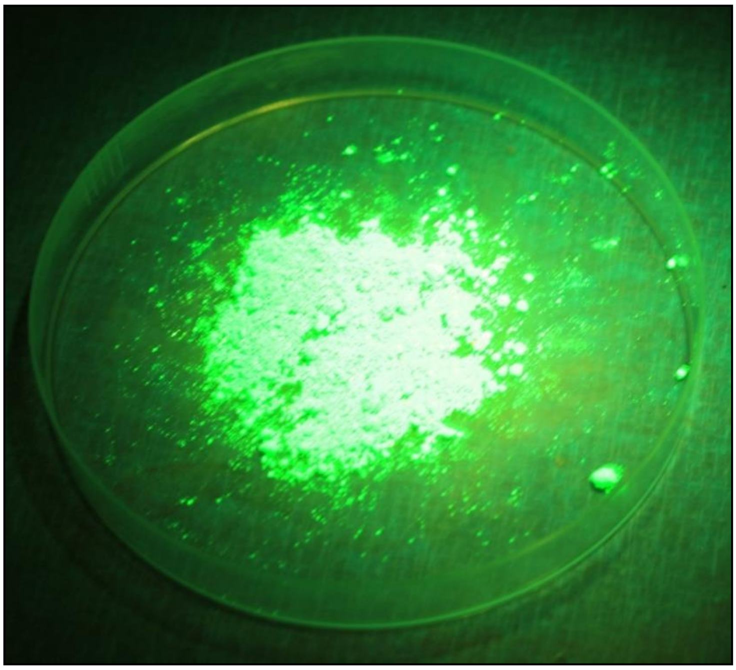

Figure 4. Photograph of the green tracer under blue light illumination (UV-A~395 nm).

2.6.1 Spectral Characteristics

Each tracer colour possesses spectral characteristics which are a function of the dye incorporated onto particle surfaces during the coating process. The analysis of dye concentration during the tracer enumeration procedure relies upon transmission of light of a specific wavelength - which optimally stimulates the dye to fluoresce (known as the 'excitation' wavelength, λ_{ex}) – and measurement of the intensity of light emitted specifically at the wavelength at which the dye is known to fluoresce (known as the 'emission' wavelength, λ_{em}). If these values are known then the measurement of dye concentration (and hence in this context tracer dry mass, *M*) is also optimised.

Figure 5 displays the excitation and emission spectra of the chartreuse green tracer material utilised in this study. The fluorescence excitation spectrum (dark blue line) is obtained by fixing the fluorescence detector wavelength at 523 nm and then scanning the excitation wavelengths. This provides a fluorescence induction spectrum, which is, in effect, an absorption spectrum of the particles. Inversely, the fluorescence emission spectrum was obtained by fixing the excitation wavelength at 485nm and then scanning the emission wavelengths.

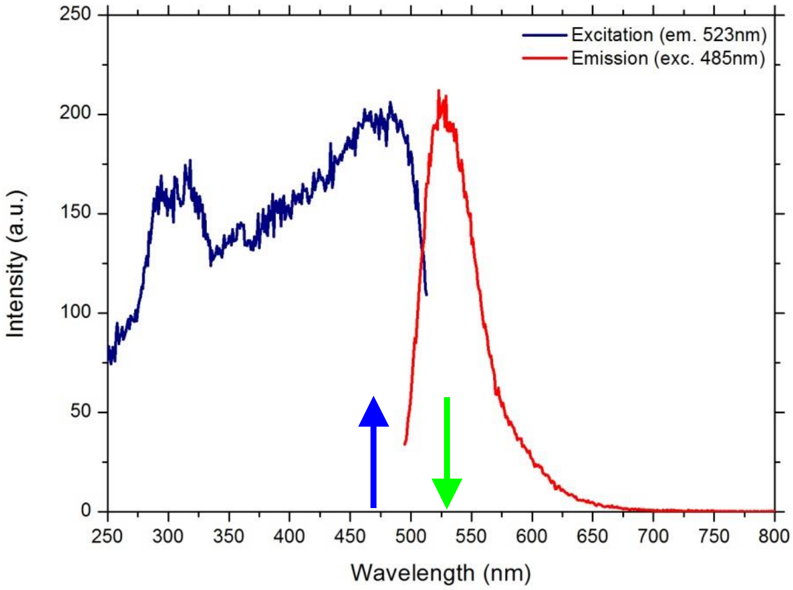

Figure 5. Emission – excitation spectra for the green tracer pigment. The blue and green lines indicate the peak dye excitation and emission wavelengths.

The peak excitation and emission wavelengths for chartreuse green tracer colour are given in Table 3.

Table 3. Peak excitation and emission wavelengths for each tracer colour.

Tracer Colour	Excitation Wavelength λ_{ex} (μm)	Emission Wavelength λ_{ex} (μm)
Green	470	530

2.7 Summary

Table 4. Summary of the characteristics of the tracer.

Colour	Quantity (kg)	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	Particle Density kg m^{-3}	Settling velocity (cm s^{-1})		Particles Para-Magnetic %	K_{LF}	Particles Fluorescent %
						<100 microns	**>100 microns**			
Green	800	13	30	79	2,182	0.009	0.195	100	642	100

Note: d_{10} = 10% of particles by weight are smaller than this figure; d_{50} = 50% of particles by weight are smaller than this figure; d_{90} = 90% of particles by weight are smaller than this figure

3. PREPARATORY WORK

3.1 Archive Sample

A sub-sample of the tracer was collected during manufacture which acts as a material archive sample for the project.

3.2 Tracer Mixing

The tracer was delivered to SPAWAR's offices in 25 kg batches in moist form. During manufacture ~10-15% by mass seawater was added to each batch; this is principally to reduce in advance surface active effects associated with the tracer, and this substantially simplifies tracer deployment. However, the presence of water promotes consolidation of the tracer mass, and therefore upon opening each drum a blade was used to agitate and soften the tracer so it more resembled a slurry.

3.3 Background Data Collection

3.3.1 Magnet Deployment and Bottom Grab Sampling

A 'background' site survey is undertaken as part of the TPE/sediment tracking methodology. The purpose of the background survey is to establish several issues:

- The nature, and typical mass, of naturally magnetic (but non-fluorescent) particulates in the water column; this information is of generic use in regard to the use of suspended magnets to collect magnetic tracer material naturally magnetic (but non-fluorescent) particulates in the receiving environment.
- The nature, and typical mass, of naturally magnetic (but non-fluorescent) particulates in the bed sediments; this information is of generic use in regard to the analytical methodology used to determine tracer dry mass in sediment samples.
- The abundance, if any, of naturally occurring magnetic *and/or* fluorescent particulates at the site.
- The need to collect sediment material for use in preparation of standard curves within the analytical methodology.

In order to support this a magnet mooring line with two suspended magnets was deployed close to the quay wall on the afternoon of Friday 12th September 2014, (see Figure 8) and 2 bottom sediment grab samples G05 and G06 (1 upstream of the tracer drop zone, 1 downstream) were obtained prior to deployment of tracer on 18th September.

3.3.2 *In Situ* Fluorimetry

As part of the Demonstration of the tools and techniques associated with the TPE approach, *in situ* fluorimetry using submersible fluorimeters was explored as a potential means of verifying the presence of tracer in suspension. This is akin to the use of fluorimeters for dissolved dye dispersion studies, but modified in context for particulates.

Using the foregoing rationale for magnet and grab sampling, a background moving vessel fluorimetry survey across the tracer material injection site was also completed on the 18th September.

4. ON SITE SURVEY WORK

4.1 GPS Position Recording

All positional detail was recorded by onboard DGPS system on the SPAWAR vessel *"Ecos"*. This included fixes for:

- each magnet mooring, including the background magnet mooring;
- the location of the zone from which the tracer material was deployed, and
- all of the sediment grabs collected, i.e. background samples, post-deployment QA samples, and sampling interval samples.

4.2 Deployment of Magnets

Powerful(high field) cylindrical rare earth element (REE) magnets 0.3 m (1 foot) in length, were utilised for this study (Figure 6). These were encapsulated in plastic sheaths with end caps and **either** i) integrated into a "mooring line" which were suspended in the water from infrastructure such as the quay wall bumpers or the edge of the ship mooring piers of the NBSD, **or** ii) suspended above the seabed from a "magnet mooring". Figure 7 shows schematic examples of how these two magnet configurations may be set up.

Figure 6. One of the powerful, permanent REE magnets used in this study (top) and housed in the sheath with endcaps (bottom).

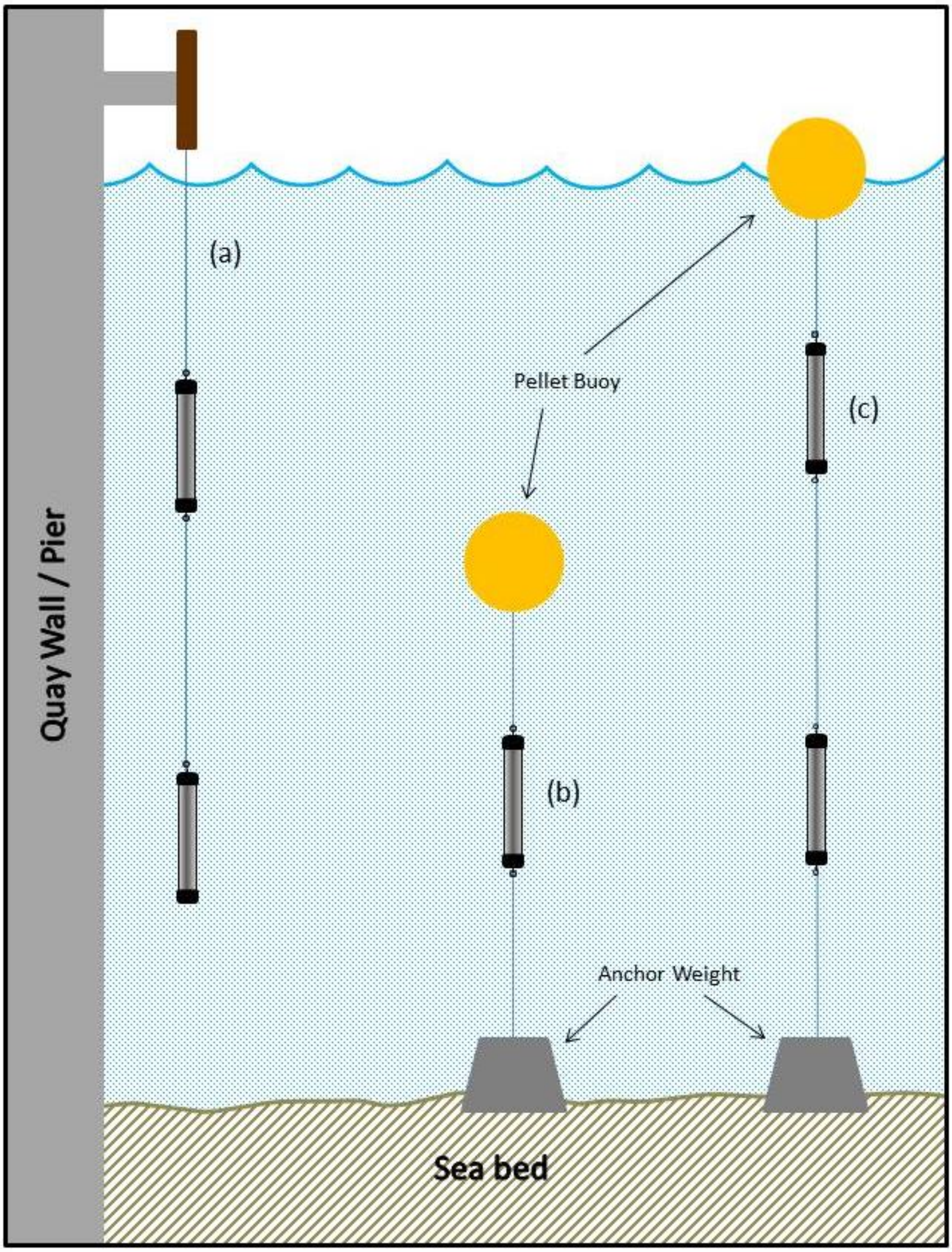

Figure 7. Examples of how magnets may be set up and deployed for magnet sampling of tracer material in the water column; (a) mooring line; (b) sea bed mounted magnet mooring with subsurface pellet buoy; (c) sea bed mounted magnet mooring with surface pellet buoy.

4.2.1 Magnet Mooring Lines

Following plumbing of the depth of the bed, at each of the magnet mooring locations, the moorings were positioned so that they would sample ~1 m above the bed and also at mid-depth[1]. A total of 6 magnet mooring lines (Figure 7) were deployed from Piers 7, 8 and 9 of NBSD (3 on each pier) around the periphery of the Paletta Creek / Pier 7 Study area (locations shown in Figure 8). The peripheral locations of the magnet moorings, while not preferred from a sampling standpoint, were necessitated so as to not interfere with Navy vessel movements during the study. Table 5 gives the locations of the mooring lines.

Table 5. Mooring line locations.

Pier No	Mooring Line No	GPS Location	
		Latitude	Longitude
7	**1***	**32.67589**	**117.12212**
7	**2***	**32.67503**	**117.12365**
7	**3***	**32.67379**	**117.12568**
8	**1***	**32.67416**	**117.12058**
8	**2***	**32.67326**	**117.12234**
8	**3***	**32.67211**	**117.12431**
9	**1**	**32.67128**	**117.11871**
9	**2**	**32.67083**	**117.11944**
9	**3**	**32.66997**	**117.12083**
Palletta Creek (PC)	**1**	**32.67248**	**117.11895**
Palletta Creek (PC)	**2**	**32.67277**	**117.11829**
Palletta Creek (PC)	**3**	**32.67207**	**117.11739**
Palletta Creek (PC)	**4**	**32.67171**	**117.11818**

- **The magnet mooring lines in these locations had 32 magnets at mid and bottom depths**

4.2.2 Magnet Moorings

A magnet mooring (Figure 10) is similar to the mooring line as described above however these moorings are deployed in open water with a sinker weight at the bed and rather than being tied onto infrastructure they are held up (in the water) by pellet buoys

NBSD stipulated that there should be minimum potential disturbance to Navy vessel movements and operations as a result of the study and as such advised that the study should minimise surface buoys in the study area. As a result a series of 6 transects of near bed only magnet moorings were deployed across the study area (Figure 8). Each transect was a length of coloured line that was tied off at the quay wall and slowly let out as the vessel moved away (see Figure 9). Magnet moorings were then connected to the lines at predetermined distances along the transects (Table 6) and lowered carefully to the seabed. This elegant system of deploying the magnet moorings ensured that there was no surface representation (i.e buoys on the surface) to concern NBSD and the transect lines connected to the quay wall enabled easy and swift relocation and retrieval of the magnet samples following tracer material deployment.

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[1] The Moorings along Pier 9 and Palleta Creek only had bottom magnets.

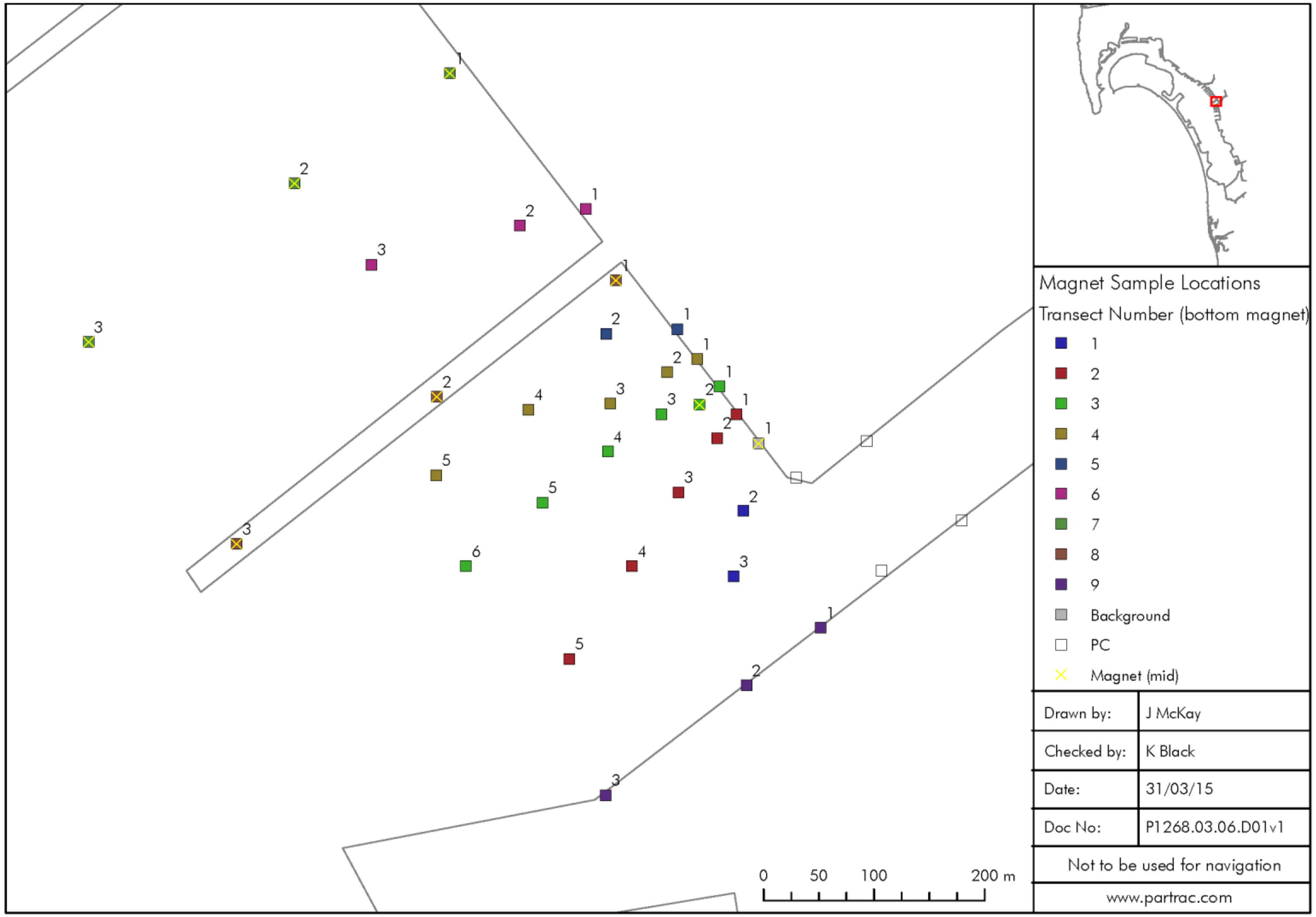

Figure 8. Locations of all mooring lines and magnet moorings. Pier mounted mooring lines comprise bottom magnets only except where indicated by a 'x'. The location of the background magnets is also shown.

Figure 9. Deployment of the magnet mooring transect lines from the *Ecos*.

Figure 10 shows the lowermost part of a magnet mooring *in situ*.

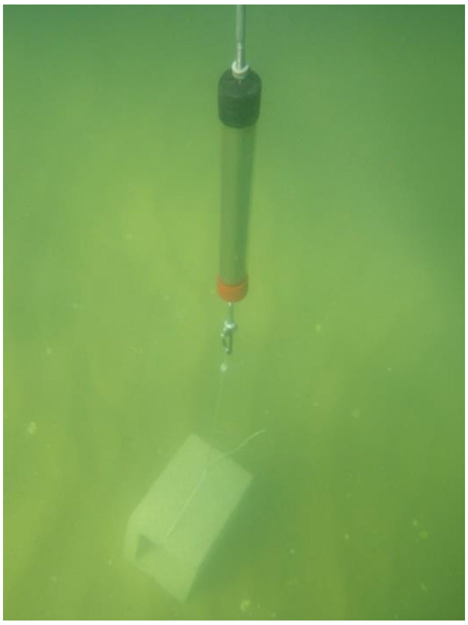

Figure 10. Deployed 'near bed' magnet mooring. Shown is the sinker weight on the bed and the magnet suspended ~1m above which is being held up in the water by a pellet buoy (attached ~1m above the magnet).

Table 6. Transect lines and magnet mooring locations.

Transect No	Magnet Mooring No	Approximate Distance Along Transect (feet)	GPS Location	
			Latitude	Longitude
1	1	0	32.67280	117.11925
1	2	207	32.67225	117.11942
1	3	402	32.67172	117.11953
2	1	0	32.67304	117.11946
2	2	91	32.67285	117.11965
2	3	288	32.67242	117.12004
2	4	456	32.67183	117.12051
2	5	877	32.67109	117.12114
3	1	0	32.67327	117.11961
3	2	80	32.67313	117.11981
3	3	192	32.67306	117.12018
3	4	385	32.67277	117.12071
3	5	628	32.67237	117.12135
3	6	923	32.67187	117.12211
4	1	0	32.67350	117.11982
4	2	96	32.67340	117.12011
4	3	290	32.67316	117.12067
4	4	523	32.67313	117.12146
4	5	848	32.67262	117.12237
5	1	0	32.67375	117.12000
5	2	213	32.67373	117.12069
6	1	0	32.67475	117.12085
6	2	202	32.67463	117.12149
6	3	657	32.67435	117.12293

4.3 Deployment of ADCP

An acoustic Doppler current profiler (ADCP) to measure *in situ* currents during the tracer study was deployed within a bottom frame at N 32.67296 W 117.12011 on 18th September 2014.

4.4 Deployment of Tracer Material

On 19th September 2014, 800 kg of the tracer material were deployed from the SPAWAR vessel *Ecos*. 32 buckets, each containing 25kg of pre-wetted tracer material, was mixed in a chamber and introduced sub-sea surface (~1m below the surface) through 2 continuous flow stations (see Figure 11) established at the rear of the vessel. The vessel was moved back and forth along a transect at 90° from the quay wall to 50m offshore at the location of the storm water outfall. This was movement of the vessel undertaken so as to (as best as possible) mimic and replicate the sort of sediment plume discharge that would arise as a result of storm water runoff from the storm water outfall. The location of transect over which the tracer material was deployed is displayed in Figure 8, and a photograph of the resulting plume is presented in Figure 12.

Figure 11. Continuous flow stations developed for the tracer material deployment on the swim platform of the Ecos.

Figure 12. Deployment of the tracer material through the continuous flow stations. The plume of tracer material in the sea is clearly visible.

4.5 Sampling

Post tracer introduction (19th September 2014) sampling was undertaken in the following order:

- 20th September 2014 (t=~24 hours after tracer introduction) retrieval of the magnet samples; and,
- 21st September 2014 (*t*=~48 hours after tracer introduction); grab sampling of bed sediment across the study area.

Magnet sampling (20th September): recovery of the of the magnets involved retrieval of the mooring line, careful removal of the sheath of each magnet and immediate washing of the sheath to remove the material which was retained into a pre-labelled sample bottle. Figure 13 shows a magnet immediately following sampling of the plume.

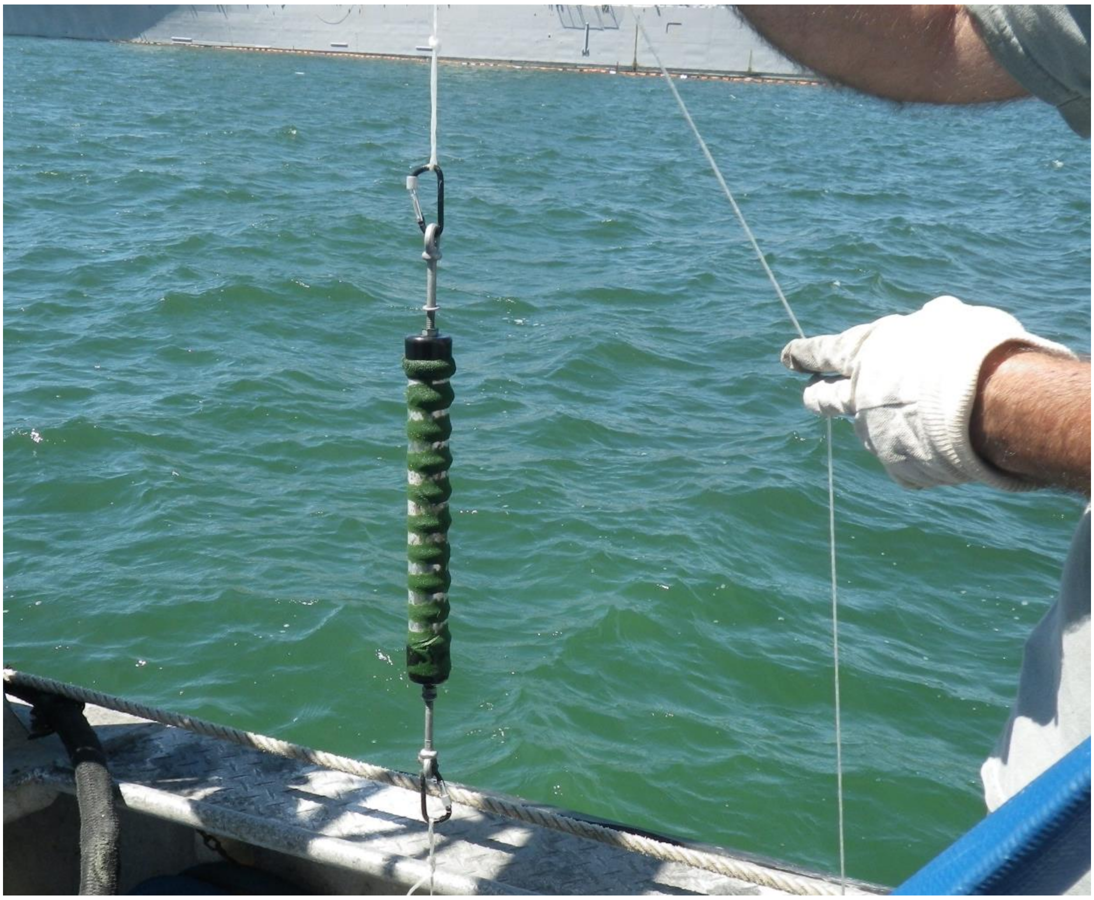

Figure 13. Recovered magnet showing tracer material that has been collected while submerged.

Grab sampling (21st September): Grab samples of bed sediment were collected with a van Veen style grab (size 0.1 m^2; see Figure 15) deployed from an over the side winch on the Ecos. Upon recovery each sample was inspected to assess that a suitable sample had been retrieved and the surface material [of the grab sampler] to a depth of 1-2 cm was scooped off with a stainless steel spoon or spatula, and transferred to a pre-labelled sample bag. Figure 14 shows the location of the sediment grab samples collected.

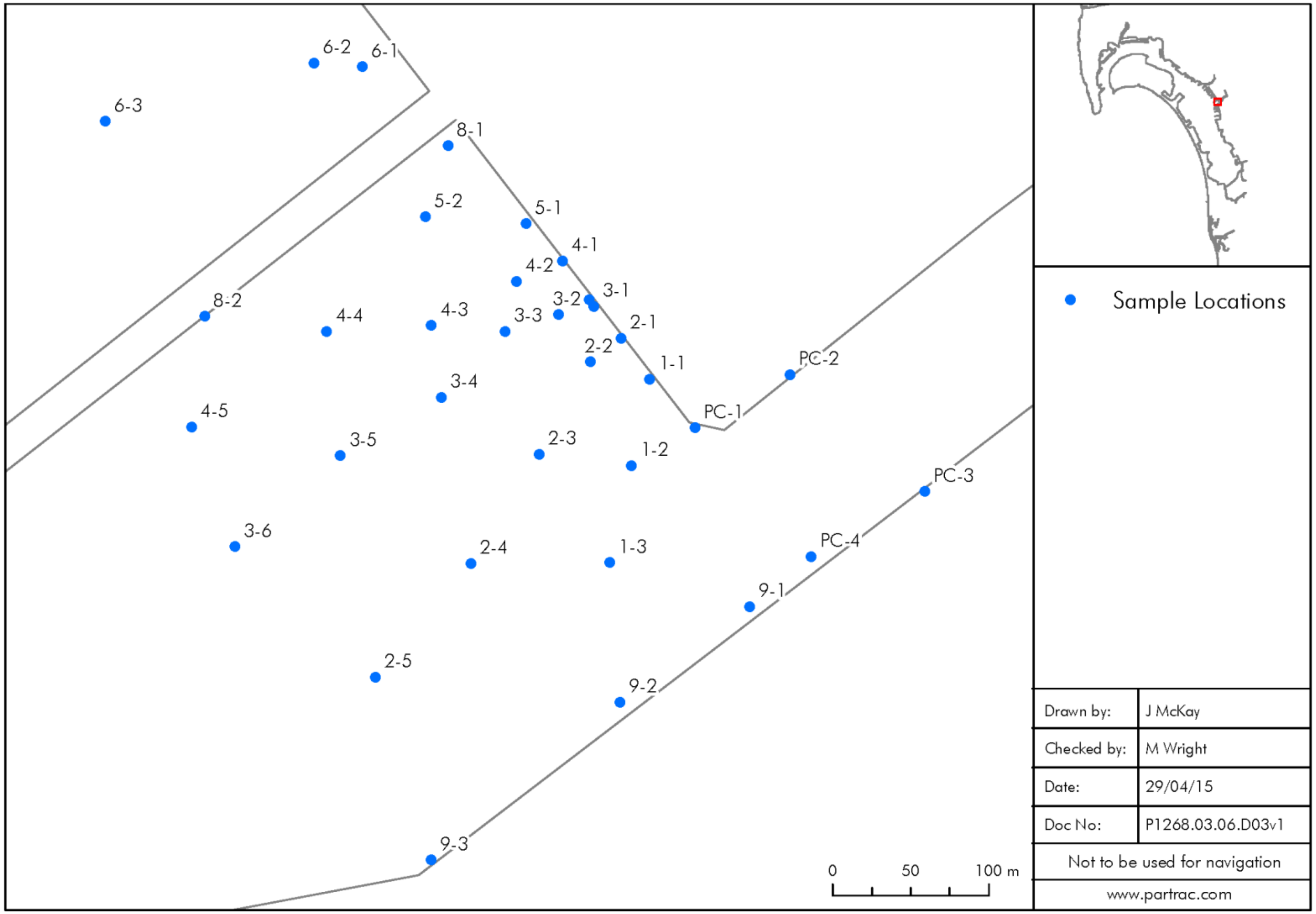

Figure 14. Location of the seabed sediment grab samples collected on Day 4 following tracer deployment

Figure 15. Sediment grab sampler (Van Veen) deployed from the Ecos's over the side winch.

4.5.1 Day 2 Work (19th September 2014)

Magnet Sampling

Location 3-2 was the only location near the outfall that NBSD permitted a mid-water magnet and surface buoy to be present. We were limited to this so as to avoid interference with ship movements (other mid water magnets hung from locations along piers where they would not interfere with ship movements). We collected this magnet several times to avoid over saturating the magnet and losing tracer material.

***In Situ* Fluorimetry**

To sample fluorescent material travelling in suspension Partrac's portable fluorimeter was used. A fluorimeter is a device used to measure parameters of fluorescence i.e. its intensity and emission wavelength spectrum after excitation by a certain spectrum of light. The sensor comprises a small (26.5 mm) diameter housing with single window geometry providing a sampling window of 9 cm^2 beneath the probe. The analysis of fluorescent particles relies upon transmission of light of a specific wavelength - which optimally stimulates the dye to fluoresce (known as the 'excitation' wavelength, λ_{ex}) and measurement of the intensity of light emitted specifically at the wavelength at which the dye is known to fluoresce (known as the 'emission' wavelength, λ_{em}). The fluorescein probe, employed to detect chartreuse tracer particles is configured to excite fluorescence at 470 nm and collect emission at 530 nm (see Figure 5). The probe sensor was attached to an aluminium pole and secured to the starboard side of the vessel – mid ship and secured at a depth of 5 m. The fluorimeter once turned on continuously records data at a 1 Hz sampling rate.

4.5.2 Day 3 Work (+24 hours after tracer deployment)

All of the magnet samples were collected on Day 1 (20th September 2014).

4.5.3 Day 4 Work (+48 hours after tracer deployment)

Table 7 shows the order and timing of the sediment grab samples collected on Day 2 (21st September 2014).

Table 7. Order and timing of grab sample collection on Day 2, 21st September 2014.

Sample Number	Sample Location		Time Sampled
	Latitude	Longitude	
1-1	32.67277	117.11925	10:48
1-2	32.67227	117.11939	10:34
1-3	32.67171	117.11956	10:26
2-1	32.67301	117.11944	11:00
2-2	32.67288	117.11965	11:08
2-3	32.67235	117.12002	11:16
2-4	32.67173	117.12051	11:24
2-5	32.67109	117.12119	11:31
3-1	32.67324	117.11965	12:52
3-1dup	32.67320	117.11962	12:56
3-2	32.67316	117.11986	12:43
3-2.5	32.67307	117.11996	14:55
3-3.5	32.67292	117.12036	15:03
3-2dup	32.67312	117.11975	12:48
3-3	32.67307	117.12023	12:23
3-3dup	32.67299	117.12016	12:30
3-4	32.67270	117.12068	11:59
3-5	32.67238	117.12138	11:49
3-6	32.67187	117.12212	11:40
4-1	32.67347	117.11982	13:26
4-2	32.67336	117.12014	13:32
4-3	32.67312	117.12073	13:40
4-4	32.67310	117.12145	13:51
4-5	32.67257	117.12239	13:59
5-1	32.67369	117.12006	14:28
5-2	32.67375	117.12075	14:37
6-1	32.67463	117.12115	15:45
6-2	32.67466	117.12148	15:32

Sample Number	Sample Location		Time Sampled
	Latitude	Longitude	
6-3	32.67436	117.12292	15:25
8-1	32.67416	117.12058	14:15
8-2	32.67321	117.12228	14:08
9-1	32.67143	117.11861	16:07
9-2	32.67090	117.11952	15:57
9-3	32.67002	117.12084	15:50
PC-1	32.67248	117.11895	10:09
PC-2	32.67277	117.11829	09:38
PC-3	32.67207	117.11739	09:44
PC-4	32.67171	117.11818	10:00

5. TRACER ENUMERATION

5.1 Introduction

Spectrofluorimetry was the method employed to determine the dry mass of tracer (in grammes) within a sample. A fluorimeter is a device used to measure parameters of fluorescence: its intensity and wavelength distribution of emission spectrum after excitation by a certain spectrum of light. These parameters can be used to identify the presence and the amount of specific dye molecules in a fluid medium. Modern fluorimeter's are capable of detecting fluorescent molecule concentrations as low as 1 part per trillion. This approach offers a means with which to obviate the additional mass due to the presence of magnetic but non-fluorescent particulates[2] simply and directly. It also provided a very high analytic resolution which would facilitate detection of very low (mg quantities) tracer mass. The fluorimeter signal output can be empirically related to tracer mass (kg or g) through a series of tracer (colour) specific, reference standards.

Prior to use of the spectrofluorimetric method environmental samples (grabs, magnet samples) are pre-processed. The chief aim of pre-processing is to remove all native non-fluorescent, non-magnetic particles.

5.2 Sample Preparation

For magnet samples, each sample is dried in an oven at 80°C until no further change in mass is observed. The pellet is then ready for fluorimetric analysis.

For grab samples, each sample is sieved at 300 microns to reduce volume, and then dried in an oven at 80°C until no further change in mass is observed. The magnetic and non-magnetic fractions are then separated using a Franz Vertical Isodynamic Separator[3]. This is a device used in commercial mining to separate out magnetic residues in granular substances. The device comprises a narrow (1 cm) funnel arrangement created between the discs of 2 powerful electromagnets. A small quantity of dry sample is introduced into the top of the funnel; a small boat at the funnel base captures and retains all non-magnetic material. A second boat is positioned, the electromagnet switched off and any adhering magnetic particles fall under gravity into this boat. The magnet surface is thoroughly cleaned to ensure capture of all magnetic particles. A sample is processed by repeating this procedure.

The magnetic fraction is then ready for fluorimetric analysis.

5.3 Gilden Photonics™ Fluorimeters

The analyses were carried out using a Gilden Photonics Fluorosens fluorimeter. The Fluorosens fluorimeter incorporates single photon counting sensitivity into a fully computer controlled spectrometer (Figure 16). As the peak excitation and emission wavelengths of the dye coating is known (peak excitation 470 nm, peak emission 530 nm) an emission scan across the emission wavelengths (500 – 600 nm) provides fluorescent intensity (V) readings at the chosen emission wavelength (530 nm). Each sample was run in triplicate and the mean value determined.

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[2] Magnetic (but non-fluorescent) particles would be expected in relatively high abundance in an industrialised port environment.

[3] In laboratory tests this methodology has been proven to be 91% efficient at extracting neat tracer material and 71% for a tracer and natural sediment admixture. Reported tracer dry mass values are all corrected by the factor 100/71=1.4.

Figure 16. The Fluorosens laboratory fluorimeter.

The Fluorosens fluorimeter is especially suited to the present task as measurement is recorded in a highly stable controlled environment. The general technical specification of the Fluorosens instrument is provided in Appendix I.

5.4 Methodology

A detailed **Standard Operating Procedure** for the analysis is commercially sensitive. The method in general terms involves a series of common steps:

1. drying and weighing of the sample (sieving if necessary);
2. dissolution of the fluorescent pigment into a special solvent for a period of 168 hours (7 days);
3. centrifugation if necessary (to remove all particulates);
4. dilution to a known level using analytical grade solvent;
5. analysis of the fluorescence intensity of the dye solution using a Fluorsens fluorimeter; and then
6. derivation of tracer particle dry mass (M_g) using calibration functions (dose response curves).

5.4.1 Standard (Dose Response) Curves

Eluted dye solutions for the green tracer are prepared by adding a known dry mass of tracer particles to a known volume of analytical grade solvent. The solution is then left to equilibrate for 168 hours (7 days). This time period has been established as optimal for maximal extraction of the pigment into the solvent. Dose response curves were obtained by filling the calibration cell with 3 ml of analytical grade solvent, recording a baseline reading and then adding sequential 20 μl aliquots of the stock solution, mixing and recording further readings. Due to the (significant) non-fluorescent magnetic background material present at the project site, dose response curves were prepared with both tracer and native material to account for the quenching effects of the native material. Consequently 4 individually tailored dose response curves were prepared to enumerate the tracer mass from the samples collected, 2 dose response curves representing samples of high sediment load and 2 representing samples of low sediment load for samples collected using *in situ* magnets and grabs respectively. Dose response curves were prepared as follows:

Grab Samples

1. Low sediment volume - 0.1g tracer; 10 g background native material (average background material concentration following magnetic separation), sequential readings through to 1g; and
2. High sediment volume - 5 g tracer; 25 g background native material (average background material concentration following magnetic separation), sequential readings through to 50 g.

Magnet Samples

1. Low sediment volume - 0.1g tracer; 1 g background native material (average background material concentration for samples with a low sediment load), sequential readings through to 1g; and
2. High sediment volume - 1 g tracer; 10 g background native material (average background material concentration for samples with a high sediment load), sequential readings through to 10 g.

Least-squares regression analysis (Fowler *et al.*, 1998) was performed on the data to generate calibration functions.

5.3.2 **Tracer Enumeration**

To determine the dry mass (M, g) of tracer in a in a sample containing 1 tracer colour, the respective regression equation is used to determine dye concentration from probe response. To derive dye concentration the regression equation must be inverted to enable determination of dye concentration (DC) from the fluorimeter signal. Tracer dry mass (TDM) is then calculated using the following equation;

$$TDM = \left(\frac{DC}{DC_{max}}\right) \times TDM_{max} \qquad 1.$$

Where, DC_{max} is the maximum assumed dye concentration (ug L^{-1}) and TDM_{max} is the equivalent tracer dry mass value.

5.4.2 Quality Assurance

An analytical quality control/assurance methodology was developed in tandem with development with the fluorimetric method. This involved inclusion of the following within the laboratory testing strategy:

1. Periodic testing of blanks
    a. 15 samples tested in total;
2. Periodic testing of blind samples (i.e. tracer masses unknown to the technician);
    a. 3 samples tested.

5.4.3 Visual Observations

Prior to fluorimetric analysis all samples were routinely visually inspected under UV illumination to assess tracer presence. Qualitative descriptions were developed as follows:

Magnet samples;

- Trace -~< 10^{-3}g
- Low -~10^{-3}g

- Intermediate -~10^{-2}g
- High -~10^{-1}g
- Very high –~10^{0}g

Grab samples;

- Trace -~< 10^{-2}g
- Low -~10^{-1}g
- Intermediate -~1g
- High -~10 g
- Very high – ~> 10 g

Note:- Due to quenching effects[4] of the background non-fluorescent, magnetic material and the low wavelength of a standard UV-A inspection lamp (~400nm), and since not all the sample is examined in depth, the probability exists *of a negative visual inspection and a positive fluorimetric result*. Cross-comparison of qualitative descriptions with fluorimetric data should accordingly be undertaken with caution.

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[4] Quenching is any process that decreases the fluorescent intensity of a sample (Lakowicz, 2006).

6. CALIBRATION AND QUALITY CONTROL

6.1 Dose Response Curves

Standard (dose response) curves were developed to relate fluorimetric measurements (probe reading in volts) to tracer dye concentration over the range of dry masses (0 – 1 g, 0 - 10 g and 5 – 50 g) (Figure 17). Consistently high coefficients of determination (r^2) are found (Table 8).

Table 8 Summary of r^2 values of the dose response curves for differing background sediment loadings.

Sample type	Sediment load	r^2
Magnet	High	0.99
Magnet	Low	0.97
Grab	High	0.98
Grab	Low	0.99

6.2 Minimum Resolvable Mass (MRM)

The MRM is derived from the lowest possible fluorimeter response (which is 1 volt). This value is then propagated through the regression equations of each dose response curve to determine the MRM, which is given by the intercept of the regression line on the y-axis. MRM values are summarized in Table 9 for both high and low background sediment loads.

Table 9. Summary of MRM values for each dose response curve.

Sample type	Sediment load	MRM (g)
Magnet	High	0.036
Magnet	Low	0.006
Grab	High	0.278
Grab	Low	0.038

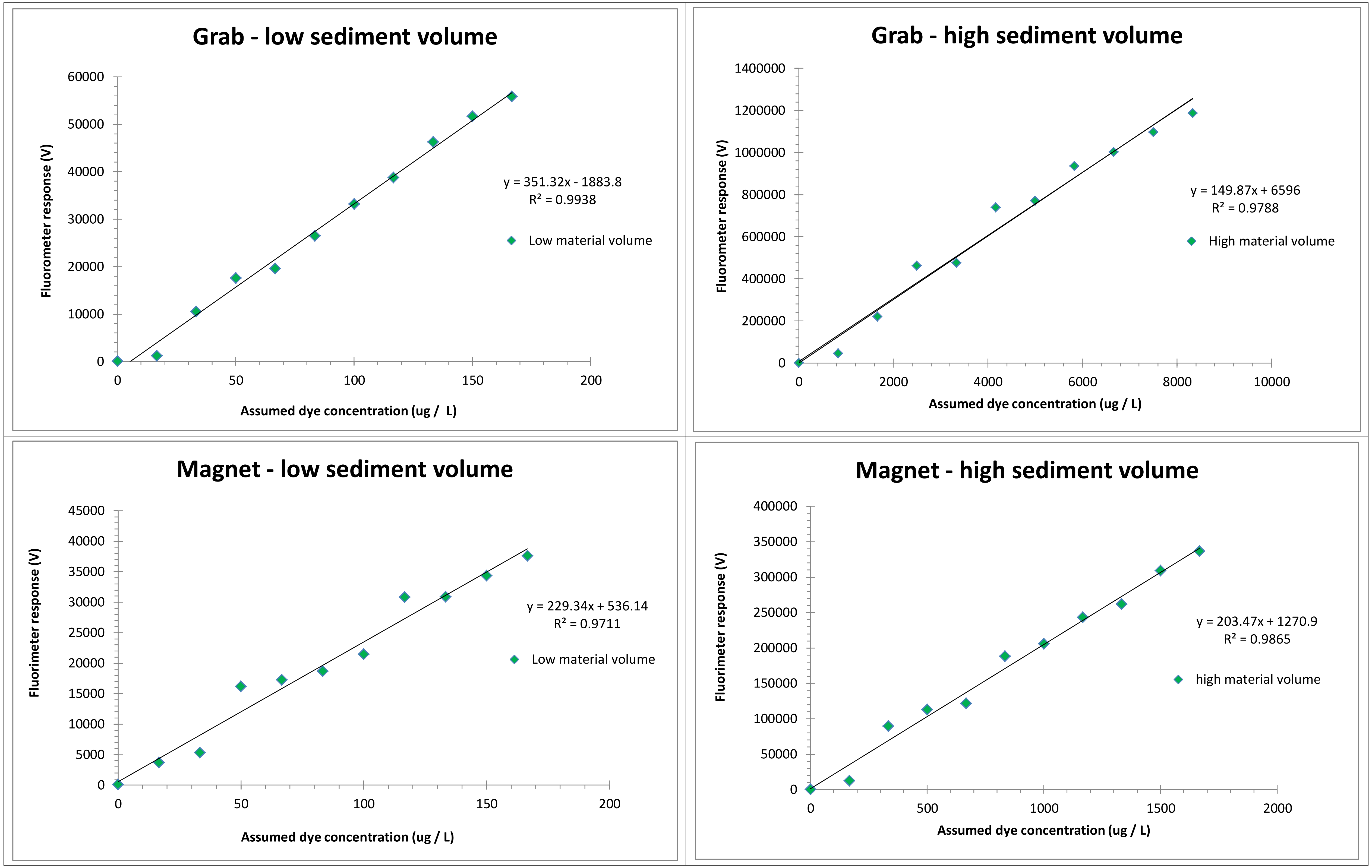


Figure 17. Dose response curves – High sediment volume and low sediment volume for both the magnet and grab samples. In practise the point concentration values on the x-axis are interchangeable with the corresponding tracer dry mass of each curve.

6.3 QC Data – Periodic Testing of Blanks

A check on the performance of the fluorimetric analytical procedure is made through periodic testing of blanks. Blanks are solutions made up in entirely the same manner as samples but without inclusion of a sediment/tracer sample. Note due to the use of a solvent zero values were not recorded (the Fluorosens returns raw values ~ 105.67; these are the y-axis intercepts in Figure 17). However, a value of zero for the *derived* tracer mass (Table 10) confirms proper functioning of the fluorimeters.

Table 10. Periodic testing of laboratory blanks for mono-colour (green) tracer dye.

Sample #	Blank Tracer Mass M_{blank} g
1	0.000
2	0.000
3	0.000
4	0.000
5	0.000
6	0.000
7	0.000
8	0.000
9	0.000
10	0.000
11	0.000
12	0.000
13	0.000
14	0.000
15	0.000

6.4 Testing of Blind Samples

In order to establish the fluorimetric analytical procedure together with operator efficiency function as desired, periodic blind samples were submitted for testing to the laboratory. Blind samples are prefabricated mono-colour sediment samples within which the tracer dry mass is unknown to the analyst. Table 11 summarises results from testing of three samples. The results are good (within 5% of true value) in terms of analytical accuracy.

Table 11. Periodic testing of blind samples (green tracer).

Sample #	Native sediment mass (g)	Doped Tracer Mass M_{dop} (g)	Measured Tracer Mass M (g)	Mean Error (%)
1	2.86	0.231	0.248	1.775
2	2.98	0.24	0.289	4.631
3	2.09	0.2	0.186	1.938

7. RESULTS

7.1 Magnet Data

Table 12 presents results for the suspended magnets, including the background magnets. Magnet values represent the neat mass (g) of tracer found on each magnet. Background samples (i.e. collected before any tracer was deployed) are found at the top of the table. Qualitative visual descriptions (inspection under blue light) are given for every sample (note the general use of caution in Section 6.3.3 if cross-referencing these to fluorimetric data is undertaken). A reference number is also given for a digital photograph for each sample which was taken.

7.1.1 Quality Control

No Quality Control issues existed in relation to the magnet samples, and a full set of samples was analysed for tracer mass.

Figure 18 shows the magnet data plotted as discrete values for individual mooring locations.

Table 12. Summary of tracer dry mass (g) for all magnet samples.

Magnet samples Sample Number	Magnet position	Visual Description under Blue Light illumination	Photo Number	Mass of Green Tracer (g)
T1-1	1 m above bed	Intermediate	3175	0.114
T1-2	1 m above bed	Intermediate	3176	0.053
T1-3	1 m above bed	Low	3177	0.010
T2-1	1 m above bed	High	3131	0.133
T2-2	1 m above bed	High	3133	0.587
T2-3	1 m above bed	Intermediate	3135	0.018
T2-4	1 m above bed	Low	3136	0.022
T2-5	1 m above bed	Intermediate	3137	0.021
T3-1	1 m above bed	High	3171	0.986
T3-2	1 m above bed	Very high	3161	22.894
T3-3	1 m above bed	High	3153	5.377
T3-4	1 m above bed	High	3172	0.292
T3-5	1 m above bed	Intermediate	3173	0.060
T3-6	1 m above bed	Intermediate	3174	0.030
T4-1	1 m above bed	High	3138	0.366
T4-2	1 m above bed	Very high	3139	5.311
T4-3	1 m above bed	Very high	3140	2.407
T4-4	1 m above bed	High	3141	0.332
T4-5	1 m above bed	High	3142	0.149
T5-1	1 m above bed	High	3156	0.000
T5-2	1 m above bed	High	3157	0.534

Magnet samples	Magnet position	Visual Description under Blue Light illumination	Photo Number	Mass of Green Tracer (g)
Sample Number				
T6-1	1 m above bed	Low	3168	0.012
T6-2	1 m above bed	Low	3169	0.000
T6-3	1 m above bed	Low	3170	0.033
T7-1 (P7-1)	1 m above bed	No tracer present	3147	0.008
T7-2 (P7-2)	1 m above bed	Low	3148	0.000
T7-3 (P7-3)	1 m above bed	Low	3149	0.000
T8-1 (P8-1)	1 m above bed	Intermediate	3165	0.138
T8-2 (P8-2)	1 m above bed	Low	3166	0.017
T8-3 (P8-3)	1 m above bed	Low	3167	0.014
T9-1 (P9-1)	1 m above bed	Low	3178	0.008
T9-2 (P9-2)	1 m above bed	Low	3179	0.008
T9-3 (P9-3)	1 m above bed	Low	3180	0.008
PC-1	1 m above bed	Low	3143	0.023
PC-2	1 m above bed	Trace	3144	0.011
PC-3	1 m above bed	No tracer present	3145	0.000
PC-4	1 m above bed	Low	3146	0.000
T3-2	Mid depth	Very high	3126	14.595
T7-1 (P7-1)	Mid depth	Low	3150	0.011
T7-2 (P7-2)	Mid depth	Low	3151	0.000
T7-3 (P7-3)	Mid depth	Low	3152	0.011
T8-1(P8-1)	Mid depth	Low	3158	0.055
T8-2(P8-2)	Mid depth	Low	3159	0.028
T8-3(P8-3)	Mid depth	Low	3160	0.016

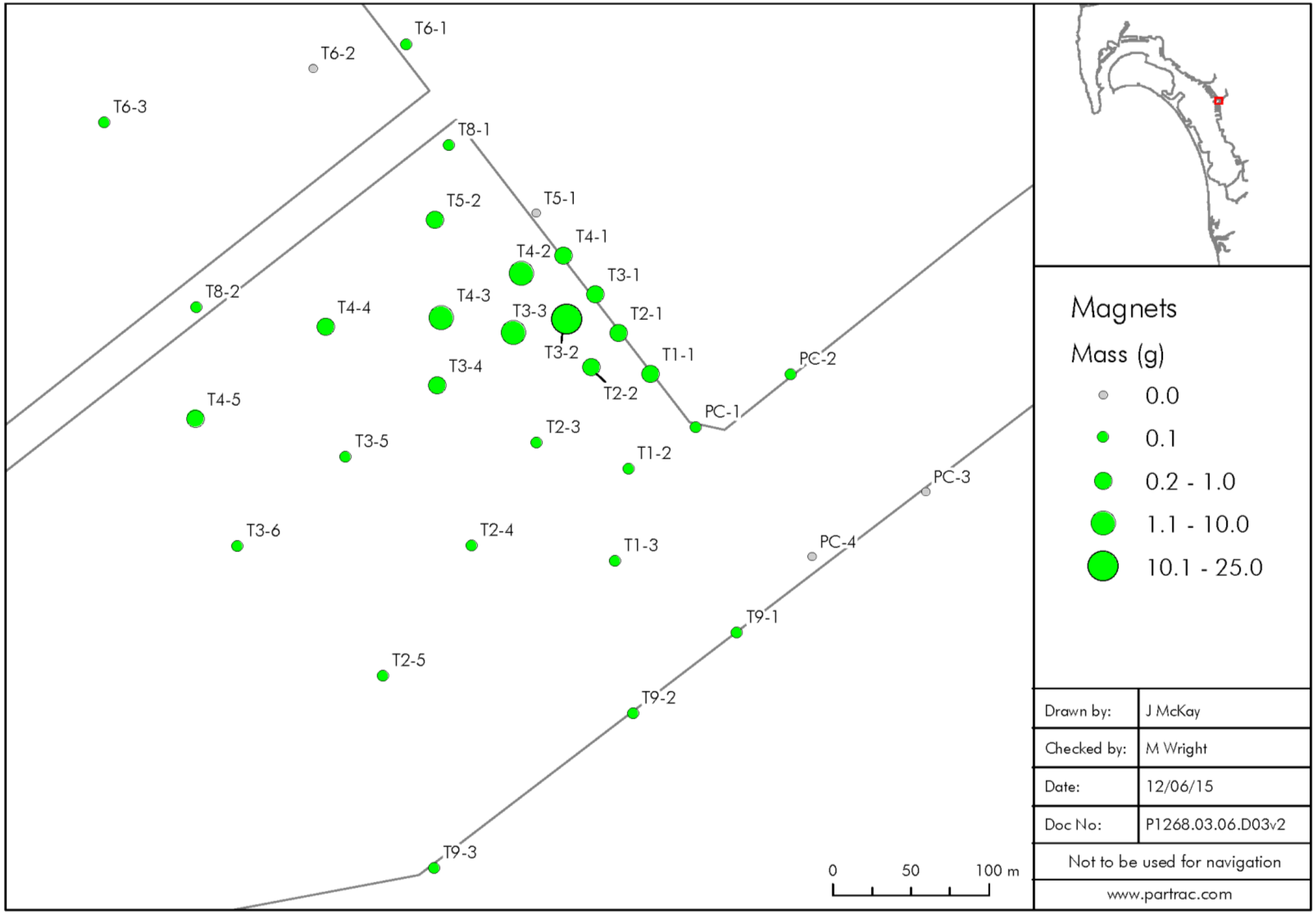


Figure 18. Discrete value (Classed Post) plot of tracer dry mass collected on magnet moorings.

7.2 Grab Data

Table 13 presents results for all sea bed grab samples analysed expressed as an area density metric (g m^{-2}). Qualitative visual descriptions (inspection under blue light) are given for every sample. A reference number is also given for a digital photograph for each sample which was taken.

7.2.1 Quality Control

No Quality Control issues existed in relation to the magnet samples, and a full set of samples was analysed for tracer mass.

Figure 19 shows the seabed grab data plotted as an area density metric for individual locations.

Table 13. Summary of tracer dry mass (g m^{-2}) derived from seabed grab samples.

Grab samples	Visual Description under Blue Light illumination	Mass of Green Tracer per m^2
Sample Number		(g)
T1-1	No tracer present	0.000
T1-2	No tracer present	0.000
T1-3	No tracer present	0.000
T2-1	Trace	0.470
T2-2	Trace	0.431
T2-3	No tracer present	0.000
T2-4	Trace	0.418
T2-5	No tracer present	0.000
T3-1	Trace	0.669
T3-1-DUP	Trace	0.622
T3-2	High	78.850
T3-2-DUP	High	27.420
T3-2.5	Very high	114.850
T3-3	High	20.000
T3-3-DUP	Very high	62.320
T3-3.5	Trace	0.405
T3-4	Trace	0.420
T3-4-DUP	Intermediate	0.584
T3-5	Trace	0.436
T3-6	No tracer present	0.000
T4-1	Trace	0.495
T4-2	Intermediate	18.040

Grab samples Sample Number	Visual Description under Blue Light illumination	Mass of Green Tracer per m^2 (g)
T4-3	Trace	0.430
T4-4	Trace	0.423
T4-5	Trace	0.421
T5-1	Trace	0.462
T5-2	No tracer present	0.000
T6-1	No tracer present	0.000
T6-2	No tracer present	0.000
T6-3	Trace	0.466
P8-1	Trace	0.437
P8-2	No tracer present	0.000
P9-1	No tracer present	0.000
P9-2	Trace	0.502
P9-3	Trace	0.579
PC-1	No tracer present	0.000
PC-2	No tracer present	0.000
PC-3	No tracer present	0.000
PC-4	No tracer present	0.000

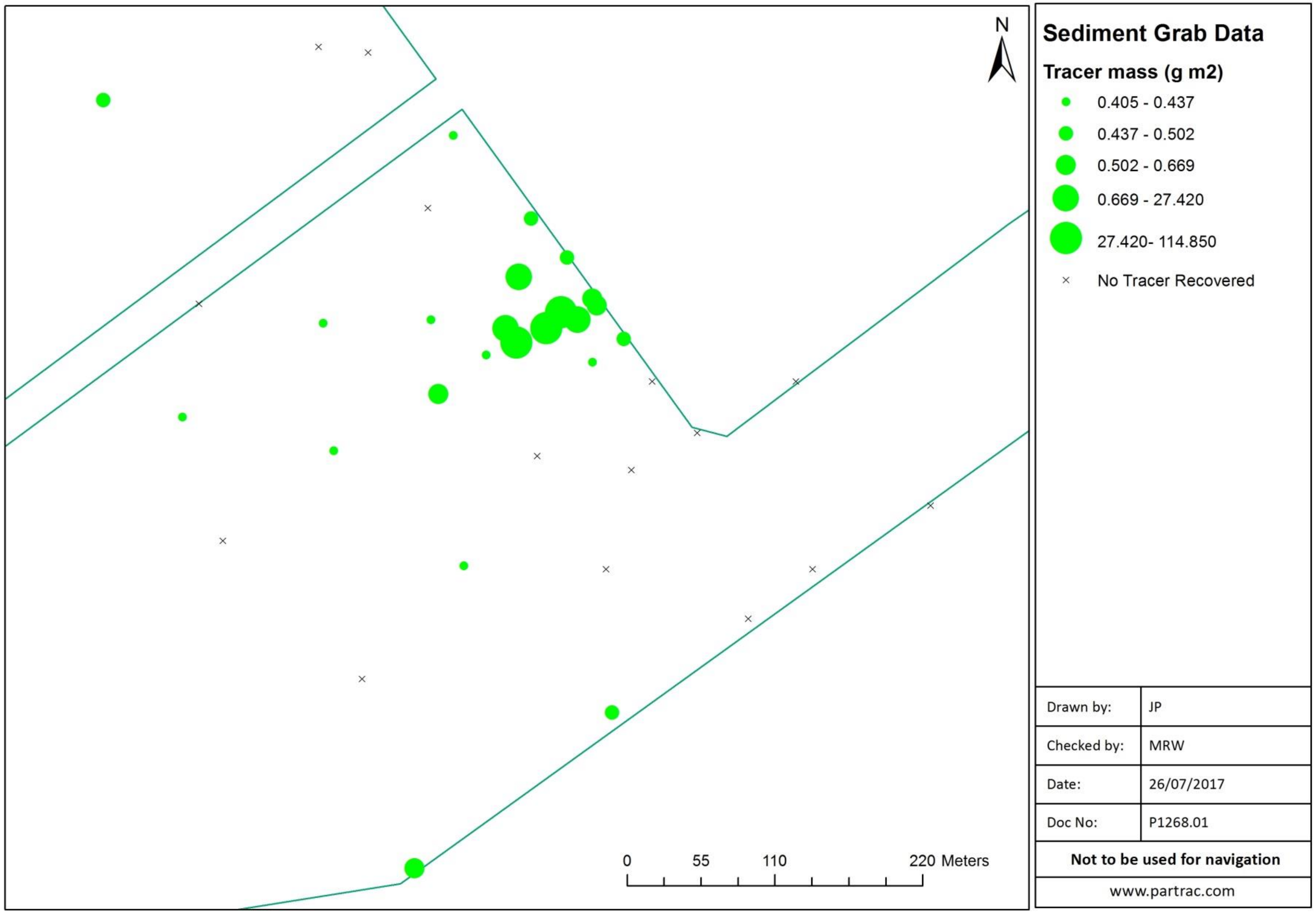


Figure 19. Geospatial distribution of tracer derived from seabed grab sample data. The tracer mass data has been normalised and is presented as a density area metric. Note: The duplicate samples collected are not presented in this figure.

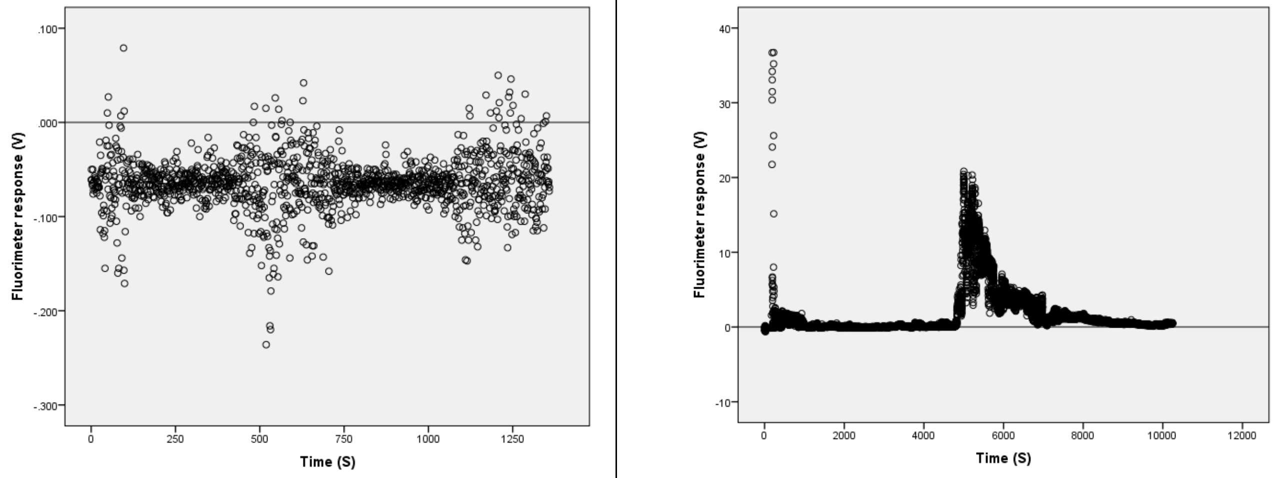
7.3 *In situ* Fluorimetry

The results from deployment of the *in situ* fluorimeter are presented in Figure 20. The background survey data (i.e. prior to introduction of tracer) shows a dominantly negative voltage output, centred on ~-0.5v. This corresponds to the natural dye/tracer free situation for the local ocean water. Data were subsequently recorded not via sailed transect but through time at a single point (5 m depth, midship vessel starboard) during tracer introduction. Excellent quality data were collected as the generated tracer plume (see Figure 20) was advected through previously clear water and past the sensor over the period of about an hour. The sensor records a peak in fluorescence intensity (corresponding to an output voltage of ~22 v), which is statistically significant (t (1359) = -37.376, p = <0.001), followed by an approximately exponential decay in the signal.

Two subsequent transects were undertaken, one following the tracer deployment and one following collection of the suspended magnets. Within each of these, sensor output voltages are much lower than in the above example, typically up to about 3 volts maximum; this reflects far lower concentrations of tracer in suspension, which is not unexpected as some degree of tidal advection, dispersion and dilution has occurred. Nonetheless, in both transects there is a noticeable temporal variability which we believe reflects the sensor travelling through very dilute, heterogeneous clouds of tracer in suspension.

Although no systematic deployment of the *in situ* fluorimeters was undertaken, and no concurrent water samples were collected to ground-truth the sensor voltages, these datasets provide unequivocal evidence that the these instruments can be used to detect tracer *in situ* across a range of concentrations.

Background Survey | **Tracer Deployment**



Survey transects – Day 1 (post tracer deployment) | **Survey transects – Day 2 (post collection of magnet samples)**

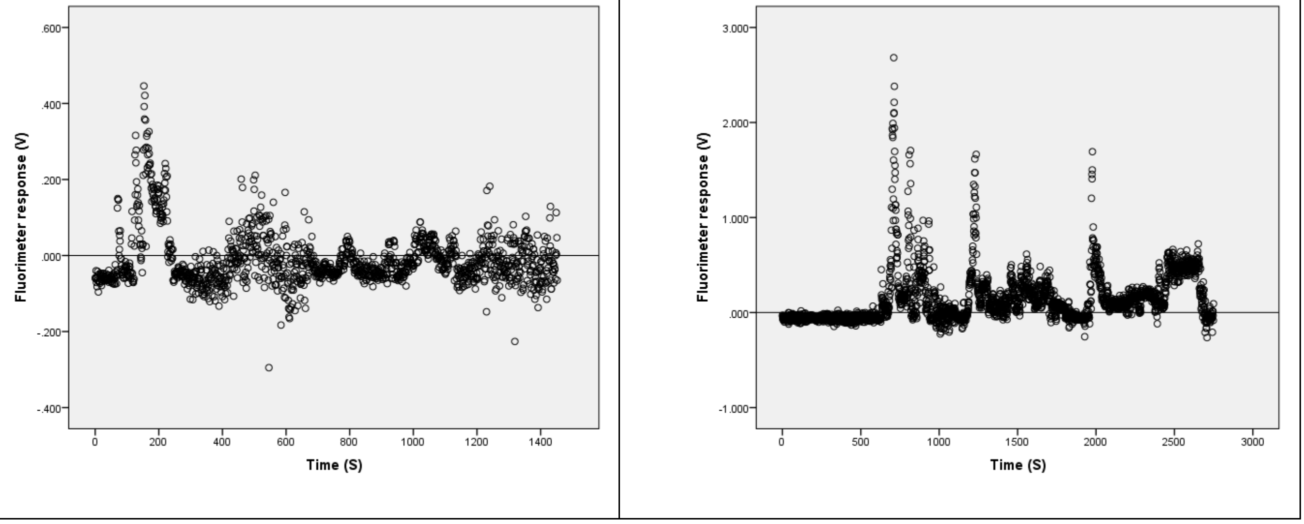


Figure 20. Data from the in situ fluorimeter collected throughout the study – the reference line on the axis indicates zero

7.4 ADCP Data

Figure 21 shows a time series of local tidal current magnitude and direction and as a frequency distribution (histogram) recorded by the ADCP sensor. This clearly shows that current magnitudes were very low (mean current ~0.033 m s^{-1}, maximum 0.09 m s^{-1}), which means that tidal advection distances will also be low and that sedimentation will be (on a relative level) promoted; this is an important hydrodynamic context for a more comprehensive understanding of the tracer plume dispersion.

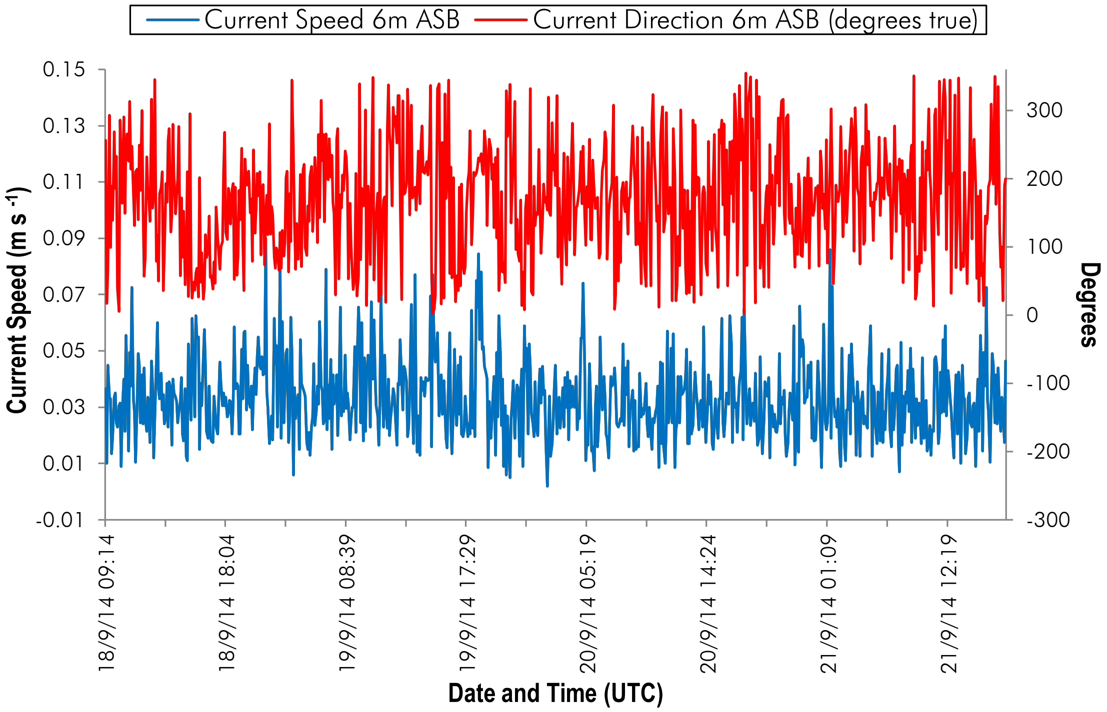


Figure 21. Time series of flow magnitude and flow direction at 6 m above seabed (ASB) from the ADCP record during the study period.

7.5 Data Interpretation

This study simulated a sediment – laden discharge from a storm water outfall at NBSD. Inspection of the data revealed that the sediment plume dispersed both vertically through the water column, and laterally in both a northerly and southerly direction due to advection and diffusion. Upon release, tracer was transported in the direction of the prevailing current flow (South). During high water slack, near field transport to the North was observed, driven by the jet flow. The depositional footprint is a function of the hydraulic properties of the tracer particles and the tidal forcing experienced during the release. The size distribution of the manufactured tracer has a Gaussian distribution; upon release, the coarser particles are thus anticipated to deposit sooner than the finer particles present within the tracer batch. The observed sedimentation patterns show a high deposition zone, elongated significantly in the mean flow direction. Extensive deposition of tracer within 100 m of the discharge zone is attributed to reduced current velocity at high water slack, and the general low ambient current velocities observed at the site.

Monitoring of the discharged sediment plume utilising an *in situ* fluorimeter and *in situ* magnetic sampling rigs provided estimation of the length and in-plume tracer concentrations. The plume, which developed during slack high water, was estimated to be 108 m in length, (assumed to be along the plume axis based on dominant current conditions). Estimated in-plume concentrations (peaking at 934 ug l-1) reduced exponentially along the assumed plume axis, attributed to continuous particle fallout at the bottom boundary layer, and the transition to a passive diffusion process.

The data revealed the critical role of tide and current, driving transport and deposition of fine sediment discharged from storm water outfalls.

8. CONCLUDING REMARKS

ESTCP demo project 1 was undertaken to assess the potential of particle tracking to investigate the transport of fine sediments discharged from a storm water outfall at NBSD. The chief findings of the study were as follows:

- Dual signature tracer proved to be an effective tracer able to be monitored effectively within, and recovered from, the environment following release.

- The designed tracer proved to be an effective analogue for fine sediment typically discharged from storm water outfalls.

- Generally low current velocities were observed at the site.

- Following release transport was observed in the direction of the prevailing current. As distance increased from source the plume dispersed laterally and vertically within the water column due to advection and diffusion processes. The depositional footprint was characterised by the following:

    1. A high concentration deposition zone within 100 m of the release zone.
    2. Greater deposition to the South of the release zone, in the direction of the prevailing current flow.

- The data captured by the high field magnets, revealed the transport pathway of the particles which remained in suspension through the tide.

- The findings of the study demonstrate the potential of the technique to provide site specific data useful in terms of both site characterisation and model validation.

This study provides baseline data useful for future field studies and validation of modelling approaches. The study has demonstrated a particle tracking methodology that can be used at the field-scale, within a complex, highly industrialised setting, to monitor the transport and deposition of fine sediments discharged from storm water outfalls at DoD sites.

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10. APPENDIX I_GENERAL TECHNICAL SPECIFICATION OF THE FLUOROSENS

Main Specifications

Device	**Specifications**
Excitation Sources	
Type	150W Xenon Arc Lamp
Spectral Range	200nm - > 1200nm
Adjustment	Factory aligned
Focus	Factory aligned
Intensity Stability	< 0.1%
Igniter	Auto-ignition of arc on instrument switch-on
Monochromators	
Type	Czerny-Turner
Focal Length	300mm
F/#	4 or faster
Wavelength Range	Zero-order to 1500nm(mechanical with 1200g/mm grating)
Wavelength Accuracy	0.2nm @ 1200g/mm
Wavelength Repeatability	0.1nm @ 1200g/mm
Stray Light Rejection	1:10^5
Slits	Continuously variable from 10µm to 3mm Motorized bi-lateral knife edge
Grating Mount	Kinematics single grating as standard, up to three gratings as options
Excitation Mono	Blaze @ 300nm, 1200g/mm, peak eff, >60%
Emission Mono	Blaze @ 500nm, 1200g/mm, peak eff, >60%

Sample Chamber	
Size	Large
Accessories	See below
Optics	Factory aligned
Lid	Slide, interlocked to PMT shutter
Front	Removable Panel
Detectors	

Photomultiplier	Hamamatsu R1527
Spectral Range	185 – 680 nm
Operating Mode	Photon counting
Dark Counts (at +25℃)	< 100cps
Reference Si Photodiode	
Type	UV100-L
Spectral Range	185 – 1100 nm
Operating Mode	Analogue
Area	1 cm^2
Data Acquisition	
Photon Counting Input	to 100M cps
Collection	Add/Subtract function by TTL control
Analogue Inputs	Ref. Photodiode
Abs. Photodiode (Option)	
NIR Photodiode (Option)	
Sample Temperature (Option)	

General Instrument	
Water Raman S/N	2500:1 or better
Optical Path Light Tightness	Single Photon guaranteed
Computer Interface	USB2.0
Power	**AC 220V/5A, 50Hz**
Compliance	CE
Low voltage Directive	
21CFR11	
Lead Free Electronics	
Footprint	0.83×0.6 m^2

ESTCP Project ER201214 Appendix 2

HPS FIELD REPORT (Study 2 Hunters Point San Francisco)

Demonstration of Fluorescent Magnetic Particles for Linking Sources to Sediments at DoD Sites

Study 2 Hunters Point San Francisco

January 2018

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EXECUTIVE SUMMARY

The particle tracking study conducted at Hunters Point former Naval station (HPNS), San Francisco formed the second field study of the wider ESTCP funded demonstration project designed to assess the overall utility of the dual signature particle tracking technology at DoD sites. For this study the method was applied to assist in the evaluation of hydrodynamic factors that might impact the performance of an activated carbon amendment cap installed at the site. Previous studies have highlighted concern regarding the efficacy of the amendment cap in situations where locally derived native material is redistributed and deposited upon the cap material and/or amendment material is 'lost' from the cap (e.g. via erosion and resuspension). To address these concerns Partrac employed their dual signature sediment tracers to evaluate the sediment transport pathways of both native sediment and the amendment cap material installed at the HPNS site.

'Tracers' are geological analogues which mimic the hydraulic properties of the target or native sediment. Once introduced to the environment tracer remains identifiable within the native sediment load due to the applied or inherent 'signatures'. These signatures enable the tracer particles to be tracked through time and across space. For the purposes of this study Partrac manufactured 200 kg of chartreuse (visually green) fluorescent and magnetic tracer (which closely mimicked the hydraulic properties of the native silt sized sediment) and 100 kg of pink fluorescent and magnetic tracer which closely mimicked the hydraulic properties of the amendment cap material (activated carbon) to inform the spatio-temporal distribution of both materials following introduction to the environment. The green tracer particles were introduced onto the seabed at an upland site to determine how much sediment from areas adjacent to the cap site potentially re-contaminates the capped area. The pink tracer was emplaced on the seabed in between two plots of amendment material already *in situ* at the site to track the loss of amendment material from the cap. Placement of both tracer materials was completed in September 2016.

An extensive multi-tool sampling campaign was employed to monitor the tracer particles on the seabed, both intertidally and sub-tidally. Active sampling of the surface sediments on the sea bed (using a hand-haulable grab) and determination of the dry tracer mass within these samples rigorously informed the assessment of the sediment transport pathways and the depositional footprints. To assess the near bed transport high field magnets were deployed *in situ*, fixed vertically on the bed to sample tracer travelling in suspension. In addition, a field grade fluorometer tuned to the peak emission-excitation spectra of the tracer particles was utilised to detect tracer presence in the water column. Throughout the study period 2 sampling campaigns (consisting of both sub-tidal and seabed sampling) were conducted resulting in the collection of 132 samples. In tandem with the particle tracking study *in situ* nearbed current measurements were recorded to provide context to the study findings.

From the data available the tidal currents at the site appeared to be broadly rectilinear with a principle tidal axis oriented approximately E – W. As expected within a protected shallow embayment, low current velocities ranging from ~ 0.01 m s^{-1} – 0.1 m s^{-1}were observed at the site. Interestingly, the data indicated that nearbed current velocities increase in the afternoon, postulated to be a function of the increasing wind speed which routinely occurs in this area of San Francisco Bay.

The tracer mass data revealed that throughout the study both the amendment cap material and local silts were distributed across the site during and immediately subsequent to the deployment. Broadly, however, the data show relatively high tracer concentrations remain within the area of the two drop zones indicating the site, during the observation period, was (relatively) minimally disturbed.

The pink and green tracer was recovered from both sea bed sediment grabs and magnet sampling rigs during both sampling campaigns. The data revealed that the pink tracer was distributed across the extent of the cap area and transported away from the cap both in broadly SSE and NW directions relative to the deployment

zone. The green tracer was found widely distributed across the site broadly along an approximate SE – NW axis relative to the deployment zone. Green tracer particles were found to the north and south of the amendment cap and at various locations across the cap.

The Partrac dual signature tracer has proved to be an effective tool to elucidate local sediment transport pathways. The study has confirmed the existence of a sediment transport pathway for native sediment (from the green tracer drop zone) derived from the north of the amendment cap through to the cap. Furthermore, due to the use of two uniquely identifiable tracers, transportation of amendment cap material across and away from the amendment cap has also been confirmed. Multidirectional transport is observed, which is a function of the various forcing mechanisms present at the site (wind, wave and current). The interaction of the amendment cap material with neighbouring sediments is postulated to reduce the efficacy of the cap for remediating contaminated sediments and the data reveals that significant interaction between contaminated 'upland' sediments and the amendment cap material effectively re-contaminating the cap site is highly likely.

These results, we consider, would benefit from further /continued field sampling campaigns to assess the interaction of native sediments and amendment cap material through time.

CONTENTS

FIGURES

TABLES

1. INTRODUCTION

Contaminated sediments are a continuing regulatory issue for DoD facilities. The determination and rapid characterisation of multiple complex contaminant sources and their linkage to nearby sediments represents a significant challenge that is essential to effective remediation. Particle tracking offers a practical means to map the transport pathways of contaminated sediments through time and across space. It is a relatively straightforward, practical methodology which involves the introduction of particulate tracers into a water body labelled with one or more signatures in order that they may be unequivocally identified following release (McComb and Black, 2005; Forsyth, 2000). Particle tracking has been used as a tool in sediment transport studies since the beginning of the last century (Crickmore, 1976; White, 1998; Black et al., 2007). The majority of historic studies have been directed towards understanding the transport pathways of sand size sediments (Black et al., 2007). However, many metal and organic contaminants are bound to surfaces of finer, silt (and clay) size particles (< 63 micron), and it is these particles that are of interest from regulatory and ecosystem health standpoints. Historically, silt tracking has received virtually no scientific attention excepting Sarma & Iya (1960) and a handful of Dutch studies (Draaijer et al. 1984; Louisse et al. 1986). However, since then Partrac have advanced the application of the methodology for this size fraction and have conducted studies using their proprietary dual signature tracers to examine Hg-contaminated silt transport in the Falkirk Canal (UK), and contaminated sediment transport in the Lower Duwamish Waterway, USA (Gries and Sloan, 2010), amongst others.

This study represents the second field demonstration stage of an ESTCP funded project designed to prove the utility of the dual signature particle tracking technology to improve understanding of contaminated sediment transport pathways at DoD sites. The second field demonstration site at HPNS (Figure 1) contains contaminated sediments associated with a former upland landfill at the site. To remediate this source of contamination a trial of an activated carbon amendment cap was emplaced in June 2015, primarily to assess the performance of two different types of amendment cap materials (AquaGate™ versus Sedimite – see Figure 2 for a schematic diagram of the layout of the amendment cap). Earlier work at this site suggested some sediment transport factors may affect the performance of an activated carbon amendment cap emplaced at this site (Luthy et al., 2009). Of particular concern was re-contamination of the cap by surrounding uncapped contaminated sediments and erosion or winnowing of sediment on the cap surface which may result in the loss of amendment cap material before it is worked into the sediments.

A particle tracking field study was designed to specifically address these concerns. In September 2016 a deployment of particulate tracer which mimicked the hydraulic properties of native sediment was undertaken on an upland site to determine whether (and if so how much) adjacent sediment re-contaminates the surface of the cap. A second deployment of tracer material which mimicked the hydraulic properties of amendment cap material (activated carbon) was emplaced on the seabed to track the loss of amendment material from the cap.

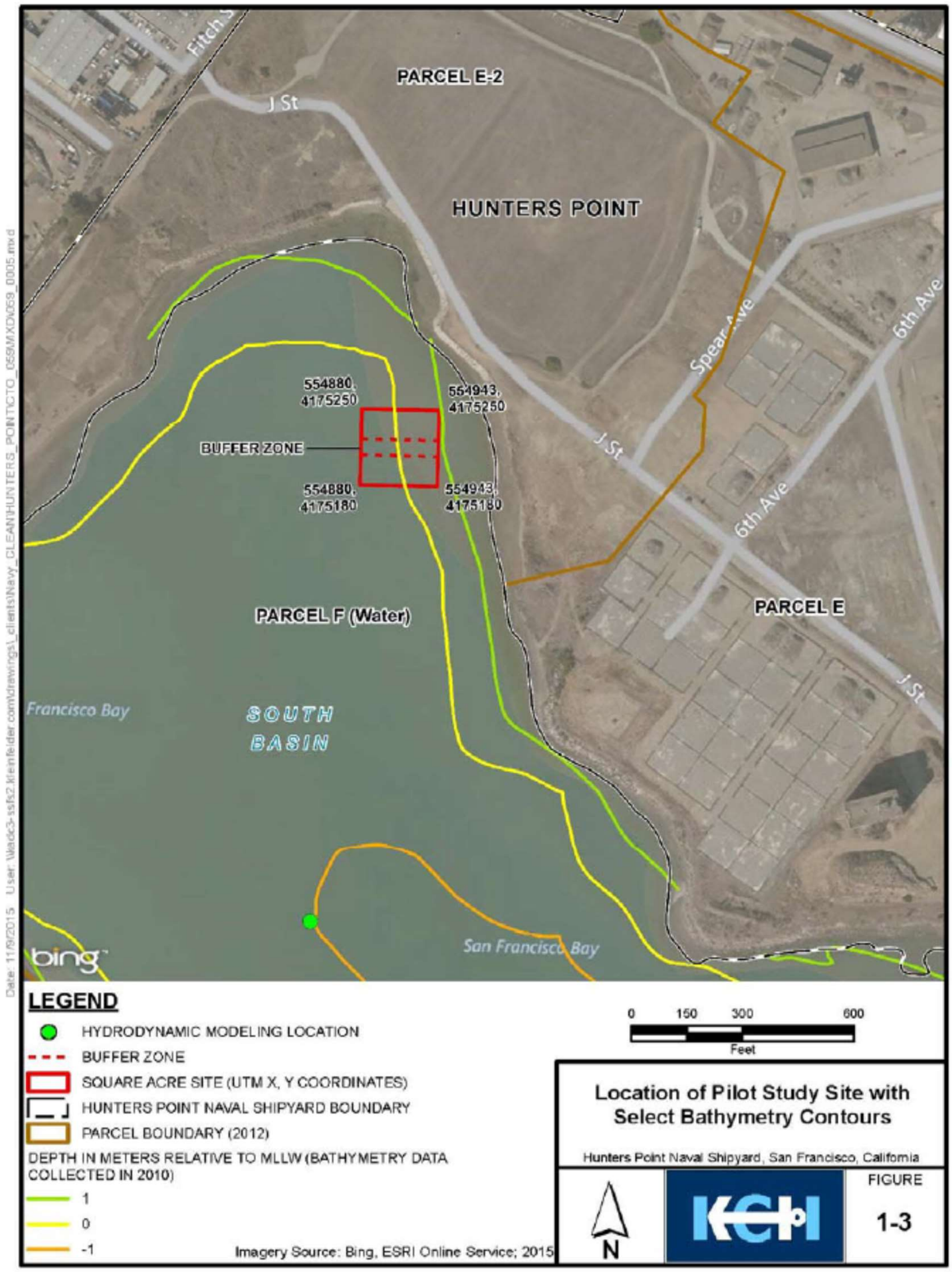

Figure 1. The Hunters Point study site. The red box depicts the spatial extent of the amendment cap. Source: SPAWAR

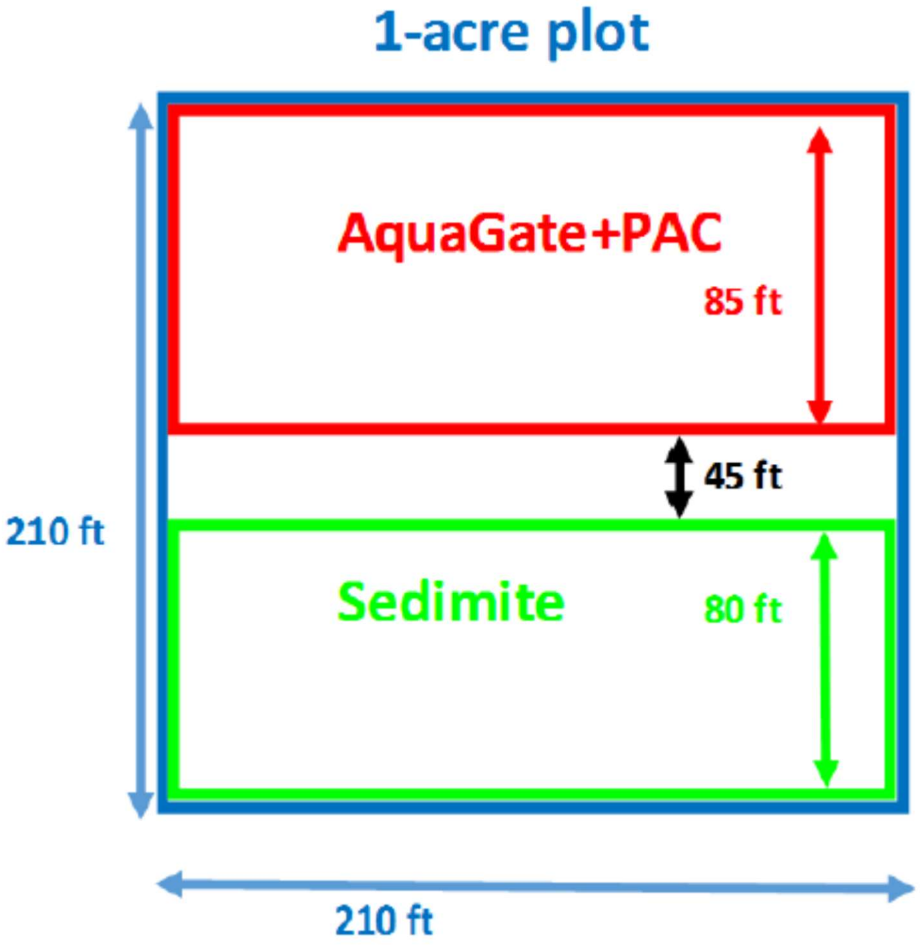

Figure 2 A schematic diagram showing the setup of the carbon amendment cap and how each material (AquaGate™ & Sedimite) was emplaced on the seabed. Source: SPAWAR.

1.1 Study Aims

The overarching aim of the study is to use the particle tracking methodology:

1) To test the postulated transport of locally derived (native) contaminated sediments onto the amendment cap thus re-contaminating the area; and,

2) Examine if the applied amendment cap material is eroded/ winnowed and transported away from the cap area during and following deployment.

To address the above aims Partrac have deployed their unique dual signature tracer material and methodology to investigate / track the movement of silt and activated carbon type materials in relation to the above described scenarios.

1.2 Dual Signature Tracers

Partrac employ proprietary 'dual signature' tracers. 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 ferrimagnetic character. Two types of dual signature tracer are available: coated (natural mineral kernel) particles, and entirely artificial particles. Coated particles possess a fixed grain density of ~ 2500 - 2600 kg m^{-3} whereas that for artificial particles can be adjusted through the range 1010 to 3750 kg m^{-3}. Coated particle grain sizes range from ~20 µm to 5 mm; artificial particles are commonly used to mimic particulates with lower settling velocity, 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. A coated particle is used within this study.

Four spectrally distinct fluorescent colours are available with which to label tracer. These are commercially available fluorescent pigments, which themselves comprise polymer nanospheres embedded within 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 reactive upon exposure to ultraviolet or blue light. 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 ferrimagnetic. Magnetism is controlled by the forces created by the spin and orbital angular states of the electrons within atoms (Dearing, 1994). The manner in which these motions are aligned, the number of electrons and the type of motions determine the magnetic moment of the atoms. Ferrimagnetic materials have populations of atoms which are strongly aligned, but exist as two sets of opposing forces. These materials display high susceptibility and are considered highly 'magnetic' materials. The tracer 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.*, 2010). 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 has profoundly limited tracer enumeration in many previous studies.

The degree of magnetisation 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 provides a comparative measure of the relative ease with which a material can acquire a magnetic field when exposed to a low frequency, low intensity alternating magnetic field; Fe or Fe bearing materials acquire a magnetic field far more easily than non-Fe bearing materials (Oldfield, 1999), hence they can be detected using this technique. Typically, manufactured tracer is ~400-500 times 'more magnetic' than quartz-rich beach sand. The ferrimagnetic attribute of tracer can also be exploited *in situ* through use of a field-portable, hand-held magnetic susceptibility sensor, which can be used in a semi-quantitative fashion to map tracer concentration on soil or sediment surfaces (van der Post, 1995; Black *et al.*, 2007).

2. TRACER DESIGN, MANUFACTURE AND TESTING

2.1 Introduction

A desk based study and discussions with Dr Jim Leather (SPAWAR) distilled the tracer specifications for use in the study. Two tracers were designed, one to mimic the hydraulic properties of the local sediments and the second (a lower density product), to mimic the hydraulic properties of the (activated carbon) cap material. In total 200 kg of fluorescent chartreuse (visually green) and 100 kg of fluorescent pink tracer were manufactured. Each tracer had enhanced ferrimagnetic character.

To ensure that the use of sediment analogues to track sediment movement in aquatic systems is valid the tracer material employed should, as best as possible, meet a series of underlying assumptions (see Foster, 2000). These are:

1. The tracer's hydraulic and bio-organic properties mimic those of the sediment of interest, and therefore the tracer is transported in the same way as the native sediment.
2. The tracer material does not change properties through time (at least over the timescales of interest) and can be monitored / detected.
3. The tracer does not manifestly change the transporting system in any way.

The following sections summarise characterisation tests performed on the tracer and are written in relation to [1] and [2]. As part of this testing sub samples collected from the bulk tracer batch were analysed to determine the following parameters:

- Particle size distribution;
- particle density (specific gravity);
- fall (settling) velocity (green tracer only);
- ferrimagnetic magnetic character; and,
- fluorescent properties.

2.1.1 Matching the hydraulic properties of activated carbon cap material

Determining the hydraulic properties of the activated carbon amendment material, on which tracer design could be based, was not a trivial matter. When matching the hydraulic properties of mineral sediments, the key properties to be matched are the dry particle size distribution (PSD) and dry particle density (specific gravity). However, when matching activated carbon amendment material, the hydraulic properties of the tracer was required to match the hydraulic properties of the wetted material to provide a suitable, traceable, analogue for the activated carbon amendment material once deployed to the sea bed (see section 3.4.2). In the absence of measured data, the target hydraulic properties (PSD and particle density), were determined through a review of the relevant literature.

Regarding the PSD, Nybom (2015) defined Powdered Activated Carbon (PAC) as 95 – 100% of particulates having a particle size < 200–300 microns, in size. Additional information regarding the PSD of PAC was garnered from Hillber & Bucheli (2010) who reviewed the physical properties, and applications, of activated carbon amendment materials. Table 1 presents data from this review. The particle size distribution of various amendment materials (including some defined as PAC materials) corroborates the definition provided by Nybom (2010), with the particle size distribution of materials being dominantly < 200 microns.

Table 1. The particle size of various activated carbon amendment materials. Table adapted from data presented by Hilber & Bucheli (2010).

Trade name	Type	Particle size (microns)	Reference
Norit SAE Super	PAC	15 - 150	Brandli *et al.* (2009)
n/a	PAC	mean particle size up to 109 microns	Saedi & Lotfollahi (2015)
TOG®	Unspecified	74 -177	Tomaszewski *et al.* (2007)
n/a	Unspecifed	37- 150	Cornelissen *et al.* (2006)
TOG® 50x200a	Unspecified	75 - 300	Zimmerman *et al.* (2004)

The particle density of activated carbon is highly dependent on the raw material, the production process, the activation process and the activity of the final product. The wetted particle density (i.e. the density of only the carbon particles, excluding the void volume between the particles but including all pores filled up with water) have a typical wetted particle density of 1,200 to 1,400 kg/m^3 (Desotec, 2017).

From these data the hydraulic properties required for the tracer designed to mimic the activated carbon material was defined as:

- PSD – 90% < 200 microns in size
- Particle density – 1200 – 1400 kg m^3

2.1.2 Matching the hydraulic properties of tracer to native (silt-sized) particles

The median grain size of the native sediment (target sediment of interest) at the HPS study site falls within the silt range. Thus, in this case the objective was to manufacture a dominantly silt sized tracer, to provide a suitable analogue for tracking silt sized mineral sediments. Therefore, the hydraulic properties required for the tracer designed to mimic silt sized sediments at HPS was defined as:

- PSD – mean grain size between 30 and 60 microns.
- Particle density – 2100 kg m^3 – 2600 kg m^3.

2.1.3 Particle Size Distribution

For the green tracer size spectrum measurements were made on a small sub-sample of the bulk tracer batch using a Malvern *Mastersizer 2000* Laser Diffraction instrument (Malvern Instruments Ltd). Figure 3 presents data from this analysis; d_{10}, d_{50} and d_{90} values for this distribution, respectively, are 13 μm, 30 μm and 79 μm.

For the pink tracer the particle size distribution was determined using a dry sieving technique. The grain size data was analysed using Gradistat, a grain size distribution and statistics package for the analysis of unconsolidated sediments (Blott and Pye, 2001). Figure 4 presents data from this analysis; d_{10}, d_{50} and d_{90} values for this distribution are, respectively, are 13 μm, 51 μm and 149 μm. See Appendix 3 for the full analysis.

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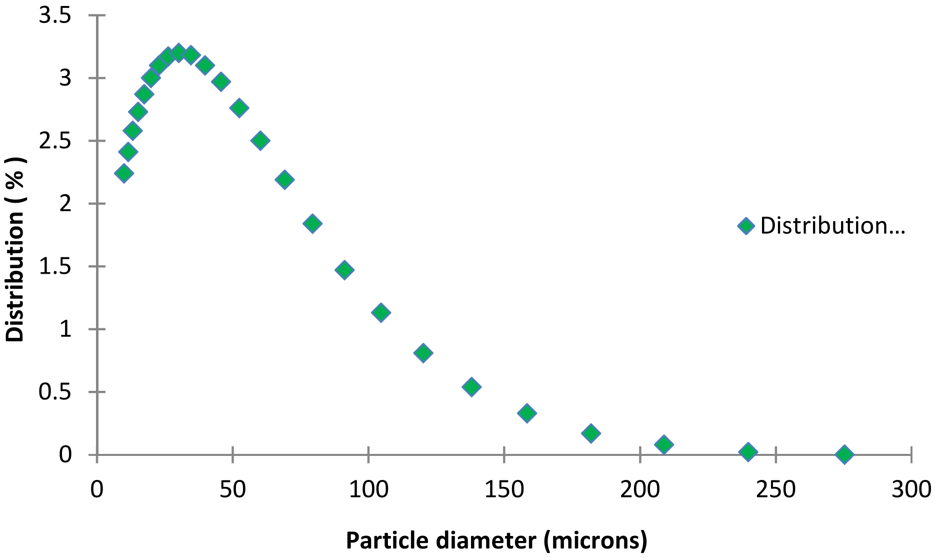

Figure 3. Particle size distribution of the green silt tracer material (3 replicate runs on a Mastersizer 2000 Particle Size Analyser).

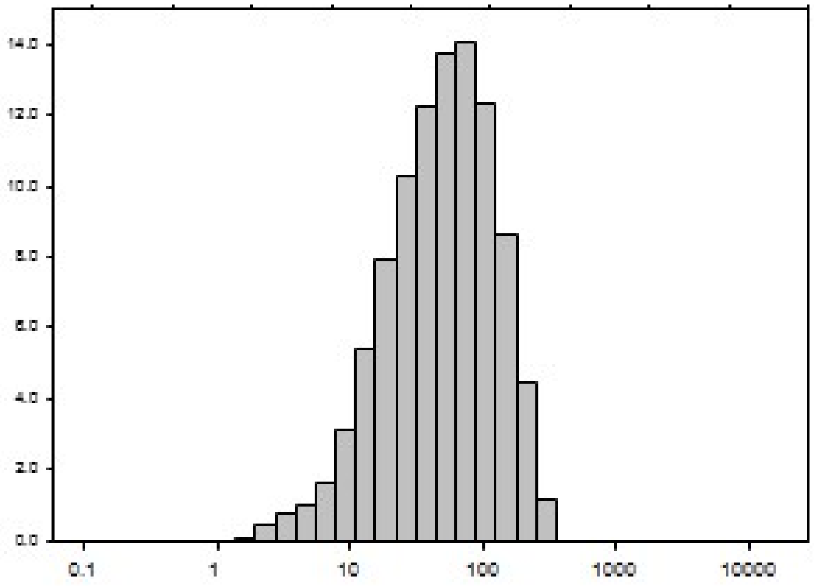

Figure 4. Particle size distribution data of the pink manufactured tracer derived from dry sieving techniques. The data was analysed using Gradistat, a grain size distribution and statistics package for the analysis of unconsolidated sediments developed from the algorithms presented by Blott and Pye (2001).

2.1.4 Particle Density (specific gravity)

Direct measures of tracer density were made on a sub-sample of the bulk green and pink tracer particles using a helium displacement density methodology (BS 1377-2:1990). This gave a density (specific gravity) of 2,182 kg m^{-3} and 1.293 kg m^{-3} for the green and pink coloured tracer, respectively (only one sample was analysed).

2.1.5 Settling (fall) Velocity

The settling (fall) velocity of green tracer particles[1] was measured using the low intrusive LabsFLOC (Laboratory Spectral Flocculation Characteristics) system of Manning and Dyer (2002). LabsFLOC utilises a video camera to observe flocs as they settle in a 190mm high by 100mm square perspex settling column. The video camera views all particles in the centre of the column that pass within a 1 mm depth of field, 45mm from the lens. The complete LabsFLOC configuration is illustrated in Figure 5. By measuring a floc population within a controlled volume, floc properties such as porosity, dry mass and mass settling flux can be calculated.

The results indicate tracer material particle ('floc') sizes of between 30 μm and ~200 μm, corresponding settling velocities range from ~0.1 to ~5 mm s^{-1} (Figure 6).

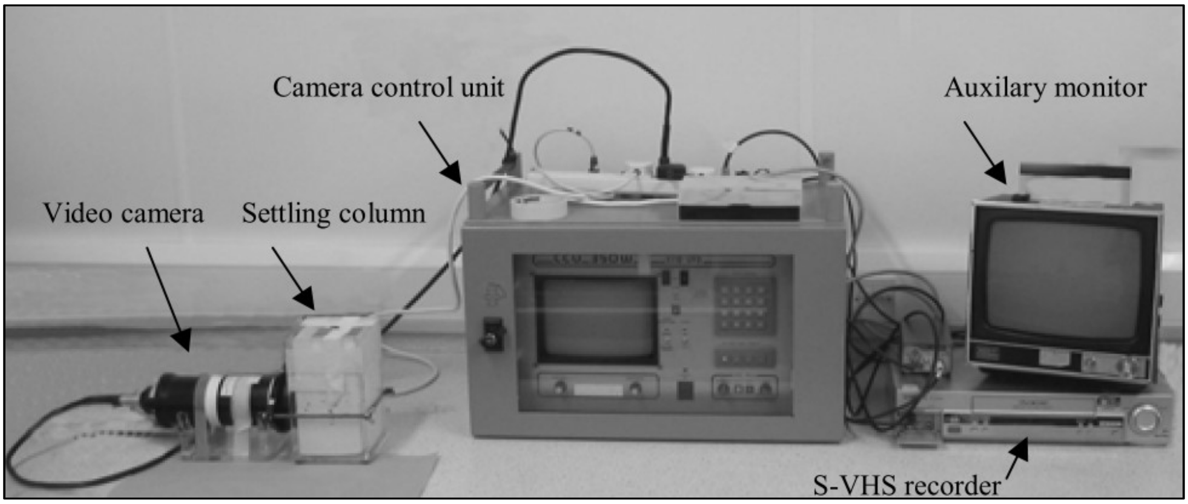

Figure 5: LabsFLoc setup.

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[1] The fall velocity of the pink tracer particles was not determined as these particles were delivered directly to the bed using AquaBlok^{TM}.

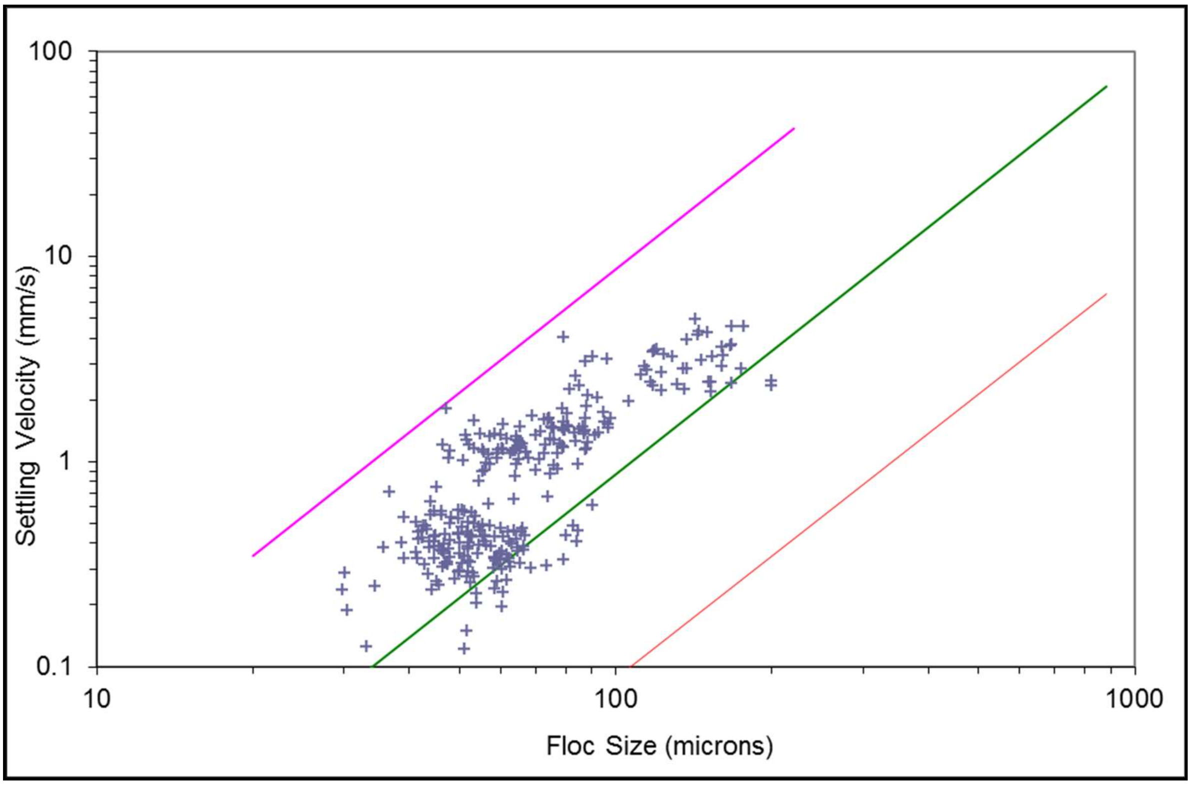

Figure 6: Settling velocity – tracer (floc) size relationship for a sample of the green tracer.

2.1.6 Ferrimagnetic Attribute

Particles with ferrimagnetic attributes were required, in order that magnets could be used to achieve magnetic separation (i.e. separation of magnetic particles [including tracer] from non-magnetic sediments). The degree of magnetisation of a sediment or soil can be quantitatively confirmed using a specific laboratory test which measures directly the geological mass-specific magnetic susceptibility (χ) of the material. This provides an index of the relative ease of which a soil or sediment sample can acquire magnetic attributes in the presence of an applied, low frequency (100 μT) alternating magnetic field. Fe or Fe bearing materials possess a greater propensity to acquire a magnetic attribute, and therefore display relatively high values of susceptibility, whereas largely non Fe bearing materials do not. The low frequency magnetic susceptibility was determined using a Bartington MS2B susceptibility sensor. In general, the coated tracer material is ~50 times ‘more susceptible to an applied magnetic field’ than quartzitic beach sand (Table 2).

A simple test was designed to establish the percentage (%) of tracer particles that are magnetic; a high field bar magnet (~11,000 gauss) was held in suspension 2- 3 mm above the sample and carefully passed over the sample three times. The magnetic material recovered was then weighed and compared to the known mass (g) of tracer particles present within the sample. This test was repeated 3 times. The results (Table 3) show that **<u>100% of tracer particles were magnetic</u>**.

Table 2. Low frequency mass specific magnetic susceptibility (χLF) of dual signature tracer particles and a quartzitic beach sand provided as a comparison.

Sample (material)	Mass (g)	Air 1	Sample 1	Sample 2	Air 2	*K* corrected	Mass specific χ_{LF} (x 10^{-8} kg m^3)
Tracer	1.866	0.3	165.2	165.2	0.3	165.3	308.4
Tracer	1.736	0.3	179.0	179.0	0.3	179.1	310.9
Tracer	2.012	0.3	159.3	159.3	0.2	159.45	320.8
Mean (χ_{LF})							**313.36**
Quartzitic sand	1.49	0.3	2.4	2.3	0.1	2.55	3.8
Quartzitic sand	1.911	0.1	1.9	1.9	0	2.25	4.3
Quartzitic sand	1.753	0.5	3.0	3.0	0.3	3.0	5.26
Mean (χ_{LF})							**4.45**

Table 3. The percentage of tracer particles that is magnetic.

Test	Tracer colour	Tracer mass (g)	Tracer mass recovered (g)	Percentage of tracer particles recovered (%)
1	green	1.453	1.453	100
2	green	2.322	2.322	100
3	green	1.992	1.992	100
4	pink	0.987	0.987	100
5	pink	1.234	1.234	100
6	pink	2.212	2.212	100

2.1.7 Fluorescent Colour

To determine the integrity of the fluorescent-magnetic coating both pink and green tracer particles were assessed under UV-A (400 nm) illumination using an LSM 510 Meta laser scanning confocal fluorescence microscope (Zeiss Ltd) and an image was captured with an Axio imager 2 (Zeiss Ltd) (Figure 7). At non - microscopic scale, an image was captured using a 750D Digital SLR camera (Canon Ltd), fitted with a 50 mm lens (Figure 8). To capture an image under blue light a yellow dichroic filter was fitted to the lens. In addition, the tracer batch was qualitatively assessed using a blue light torch (of wavelength 395 nm). These tests indicated **100% of tracer particles were fluorescent.**

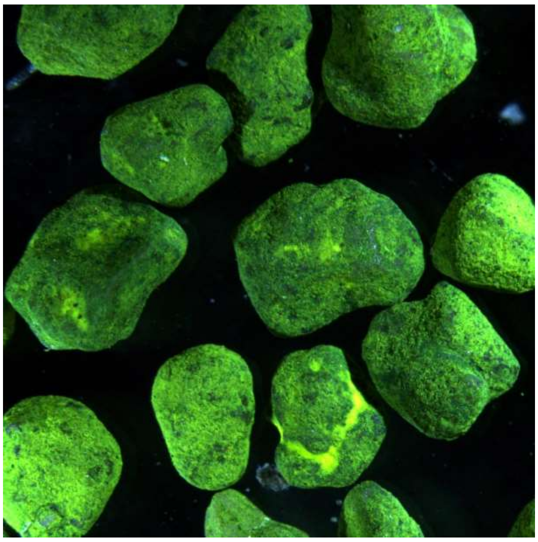

Figure 7. Tracer particles photographed under a fluorescence microscope. The image is captured under ultraviolet light (UV-A 400 nm) on an LSM 510 Meta laser scanning confocal fluorescence microscope used with Axio imager 2, imaging facilities (Zeiss Ltd).

Figure 8. The green and pink tracers photographed under blue light illumination (395 nm). The green tracer appears to generate a 'stronger' fluorescent emission as the peak emission spectra is closer to the wavelength of the blue light in comparison to the pink tracer peak emission spectra.

The two colours were selected, as although their respective absorption (excitation) spectra overlap, importantly, there is no spectral overlap between the peaks of the respective emission spectra, within the electromagnetic radiation frequency spectrum (Figure 9). To measure the fluorescent emission of the sample, two fluorometers, were used (Chelsea Technologies Group, UK). The fluorescein probe, employed to detect *Chartreuse* tracer particles was configured to excite fluorescence at 470 nm and collect emission at 530 nm. The rhodamine probe employed to detect the *Pink* tracer particles is configured to excite fluorescence at 530 nm and collect emission at 625 nm (Figure 9).

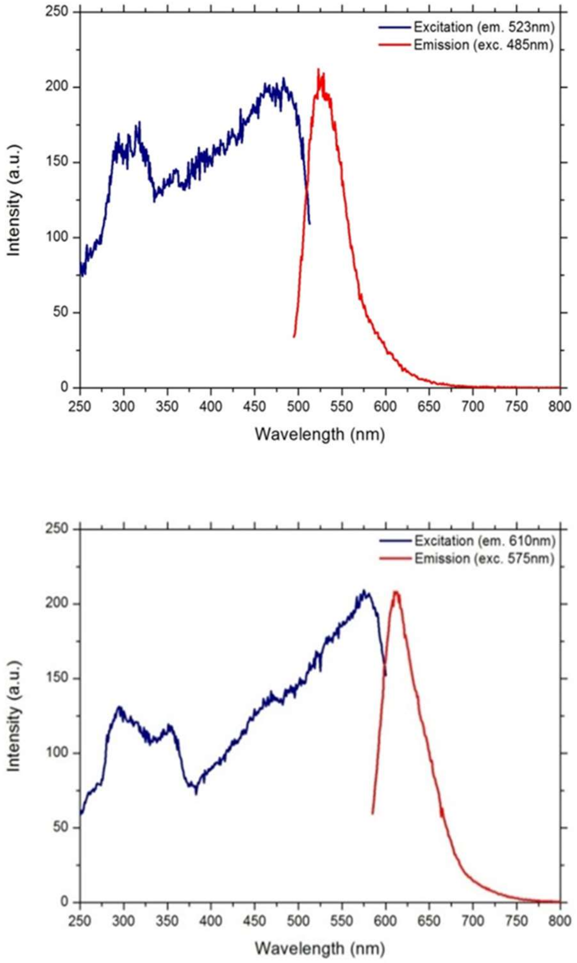

Figure 9. The emission-excitation spectra for the chartreuse tracer pigment (top) and the pink tracer pigment (bottom). The peak excitation and emission wavelengths are noted.

2.1.8 Summary Characteristics

Table 3 provides a summary for each of the hydraulic properties of the two tracers released at the Hunters Point site.

Table 4. Summary of the characteristics of the two tracers.

Colour	Quantity (kg)	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)	Particle Density kg m^{-3} (± 115)	Particle fall velocity mm s^{-1}	Magnetic mass fraction %	Fluorescent fraction %
Green	200	13	30	79	2,182	~0.1 to ~5	100	100
Pink	100	13	51	149	1,293	N/A	100	100

3. METHODOLOGY

3.1 Introduction

The particle tracking study was conducted in four stages: -

1) Background survey and study preparation.
2) Tracer preparation and introduction.
3) Sampling.
4) Tracer enumeration.

3.2 Navigation and positioning

For all survey operations an R/V IVY CAT, 33 ft. twin 225 4 stroke powered catamaran landing craft was used (Figure 10). The vessel was ideally suited to these operations as the front of the landing craft could be lowered to the water surface. Positioning during tracer deployment and subsequent grab sampling was undertaken using the vessels on board DGPS positioning system.

Figure 10. The vessel used during all operations. Source: Leviathan Environmental Services LLC.

3.3 Background Survey and Study Preparation

A ‘background’ site survey is undertaken as part of the particle tracking methodology. The purpose of the background survey is to establish several issues:

- The nature, and typical mass, of naturally magnetic (but non-fluorescent) particulates in the water column; this information is of generic use in regard to the use of suspended magnets to collect magnetic tracer material.
- The nature, and typical mass, of naturally magnetic (but non-fluorescent) particulates in the bed sediments; this information is of generic use in regard to the analytical methodology used to determine tracer dry mass in sediment samples.
- The abundance, if any, of naturally occurring magnetic *and/or* fluorescent particulates at the site.
- The need to collect sediment material for use in preparation of standard curves within the analytical methodology.

3.3.1 Background Data Collection

A ‘background’ sample of the sea bed sediment was collected using a hand haulable grab sampler (a petite ponar grab sampler) from the site upland from the amendment cap on the 15th September 2016 (see Figure 15). The grab sampler provided a sampling area of 152 mm x 152 mm of the seabed surface. The background sample was sub-sampled to approximately 2 cm depth to capture the immediate sediment surface. The samples were appropriately sealed and stored and then shipped back to the laboratory where they were tested for their fluorescent and magnetic attributes, and utilised in the tracer enumeration methodology.

Alongside the collection of the grab sample three of the magnets deployed prior to tracer deployment (see Section 3.3.2) were routinely checked after 24 hours to assess the volume of Fe-bearing material in the water column[2] across the site.

As part of the demonstration of the tools and techniques associated with the particle tracking approach a submersible field fluorometer[3] was used to verify the presence of pink tracer in suspension during the deployment. This is akin to the use of fluorometers for dissolved dye dispersion studies, but modified in context for particulates. Using the foregoing rationale for magnet and grab sampling, a background moving vessel fluorometer survey across the tracer material deployment zone was completed on the 15th September.

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[2] At this time if it was found that the magnets were ‘saturated’ with Fe bearing material the sheaths would have been cleaned and replaced and the sampling frequency of the study program increased.

[3] Partrac utilise two UniLux fluorometers manufactured by Chelsea Technologies Ltd. One fluorometer is specifically designed to target the peak excitation-emission spectra of the pink tracer and the other is specifically designed to target the peak excitation-emission spectra of the green tracer.

The response of each fluorometer to increasing tracer concentrations within a fluid medium was determined in the laboratory (Figure 11). Least-squares regression analysis (Fowler *et al*., 1998) was performed on the data to generate calibration functions which were subsequently used to determine tracer concentration from the probe response in volts. The results of the background fluorometer survey are presented in Figure 12, indicating a residual and fairly constant background signal (likely due to suspended phytoplankton and benthic microalgae) centred upon ~12.5 μg l^{-1}.

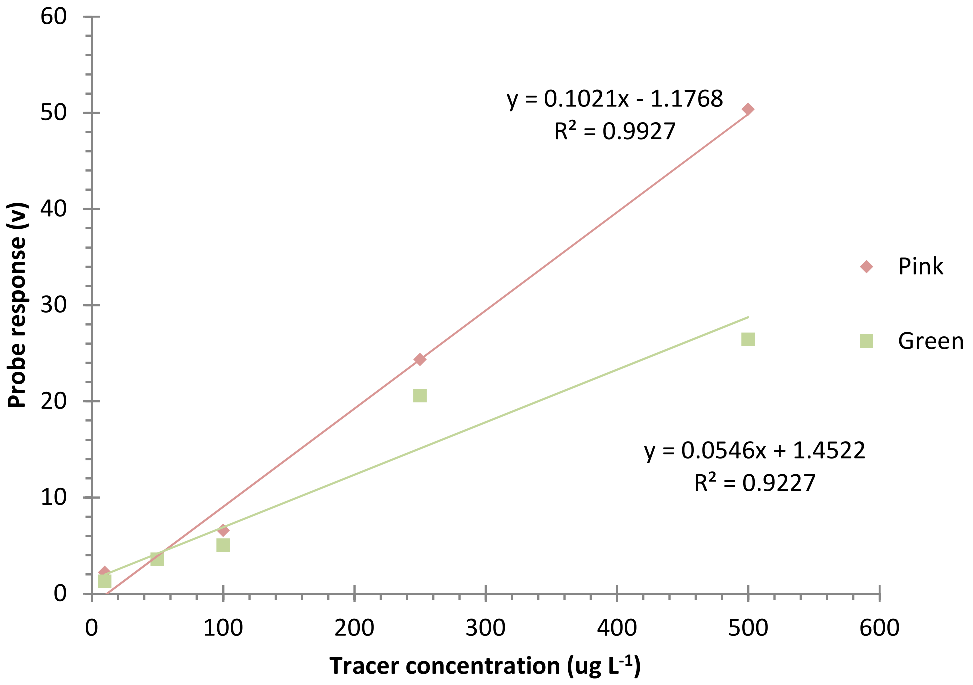

Figure 11. The fluorometer probe response when exposed to increasing tracer concentrations of the target tracer (i.e. the probe targeted at the peak excitation-emission spectra of the green tracer exposed to the green tracer) within a fluid medium.

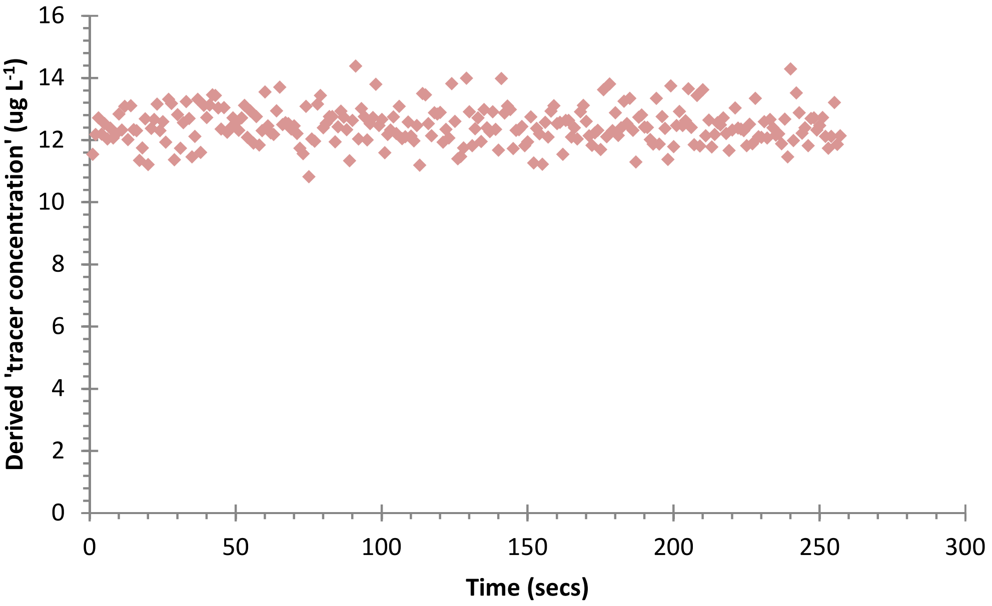

Figure 12. The response of the fluorometer (targeted at the peak excitation-emission spectra of the pink tracer) during the 'background' fluorometer survey of the deployment zone. The x axis is labelled 'tracer concentration' where in fact there is no tracer present within the system and this fluorescent signal arises from native particles present at the site.

3.3.2 Study preparation prior to tracer deployment

In total 31 magnet bed frames were deployed to the seabed prior to tracer deployment. Each 'rig' consisted of a high field (powerful) cylindrical rare earth element (REE) magnet (0.3 m in length). When deployed each magnet was encapsulated in a plastic sheath with end caps (Figure 13). These magnets were deployed to the seabed on a bed frame so that the magnet was positioned vertically above the bed virtually flush with the seabed surface (Figure 14).

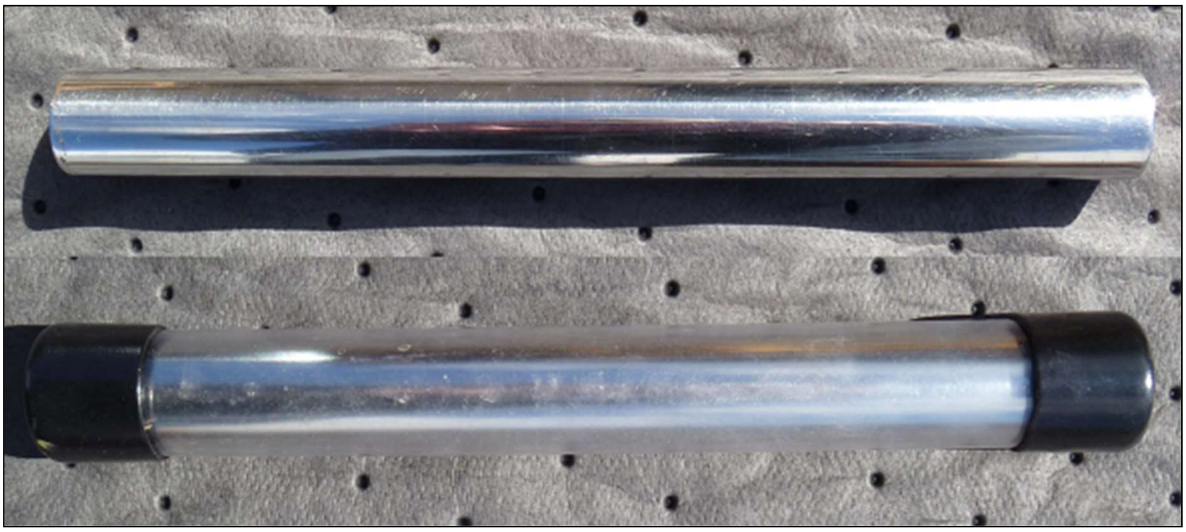

Figure 13. One of the high field (powerful) permanent REE magnets used in this study (top) and housed in the sheath with endcaps (bottom).

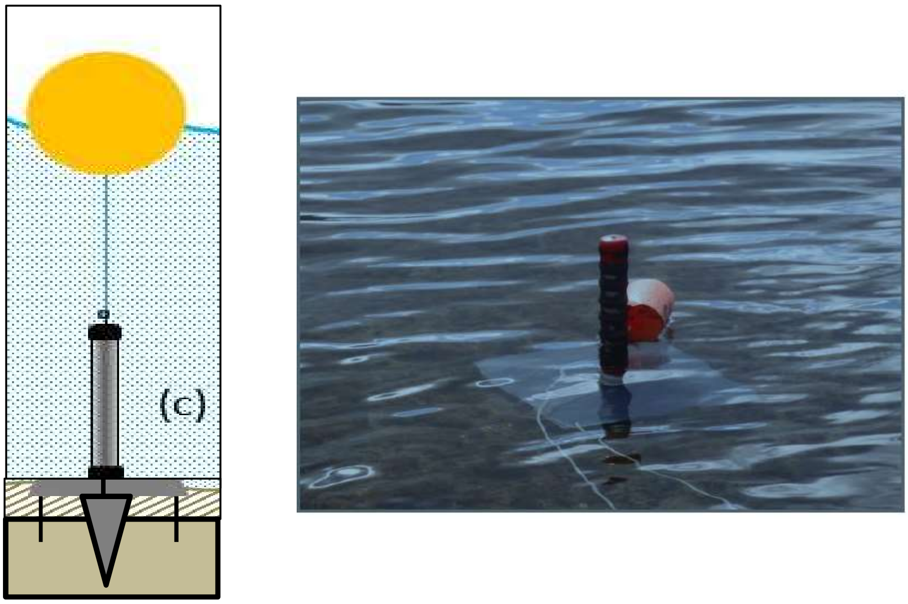

Figure 14. A schematic diagram (left) showing the design of the magnetic rig (NB; this schematic is not to scale) and a photograph (right) showing the vertical bed-frame mounted magnet to capture tracer moving in the bottom boundary layer deployed.

3.3.3 Supporting Oceanographic Data

To support the interpretation of the present study in the context of local hydrodynamic conditions (tidal currents) SPAWAR deployed a Nortek Aquadopp Profiler sensor in ~ 3 meters of water to the west of the study area (Figure 15). The Aquadopp was routinely recovered throughout the study period for servicing and maintenance.

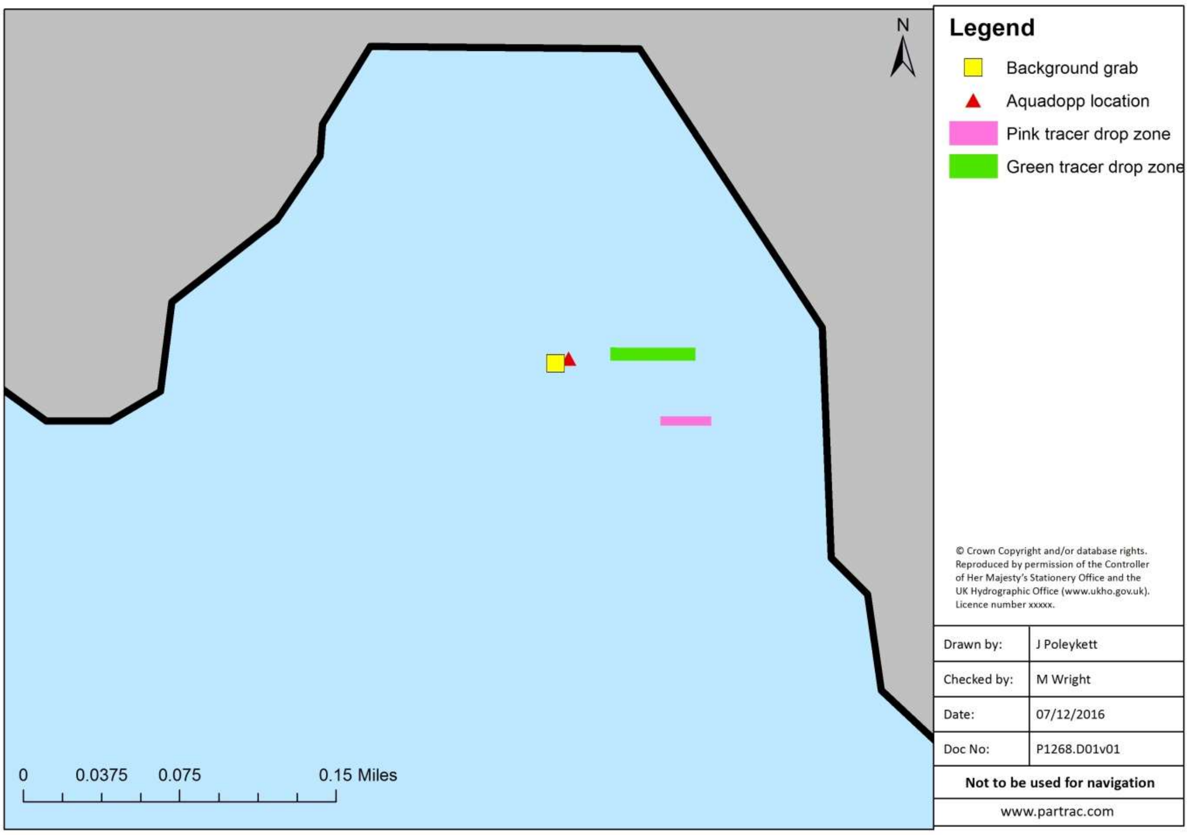

Figure 15. The location of the Aquadopp profiler in relation to the two drop zones at the site. The tracer drop zones, location where the background seabed grab was taken and the location of the Aquadopp profiler is marked.

In addition, the meteorological conditions, specifically the wind direction and speed, experienced during the study from the meteorological station situated at San Francisco International Airport (located ~ 10 miles away from the Hunters Point site), were monitored and recorded.

3.4 Tracer Preparation and Introduction

3.4.1 Archive Sample

A sub-sample of both tracers and the tracer AquaBlok™ composite was collected during manufacture which acts as a material archive sample for the project.

3.4.2 Tracer Preparation

AquaBlok Ltd design and manufacture the AquaGate™ product which is a composite aggregate sealant resembling small stones that is comprised of a limestone aggregate core wrapped with powdered sodium bentonite clay. In this application the AquaGate™ is combined with activated carbon to create the amendment cap material that is deployed from the side of a vessel to the seabed. Once submerged in water the bentonite clay expands creating a cap layer that 'lays' across the surface of the contaminated sediments significantly reducing the likelihood of transport of contaminated sediment. The pink tracer (designed to mimic the hydraulic properties of activated carbon) was delivered to AquaBlok Ltd, dry. The tracer was then incorporated (the specific methodology is unknown) into a AquaGate™ - tracer- particles using a 5 % tracer addition formulation (i.e. 5 % of each particle mass manufactured by AquaBlok consisted of tracer particles). In total, 100 kg of tracer was delivered to AquaBlok resulting in ~ 2000 kg of AquaGate™-tracer particles being delivered to the Hunters Point study in 25 kg batches. Figure 16 shows a photograph of the tracer-

AquaGate^{TM} particles manufactured for the study and Figure 17 shows the particles being unpackaged ready for deployment.

Figure 16. The pink tracer particles incorporated to AquaGate^{TM} to create a tracer-AquaGate^{TM} particle . Source: AquaBlok Ltd.

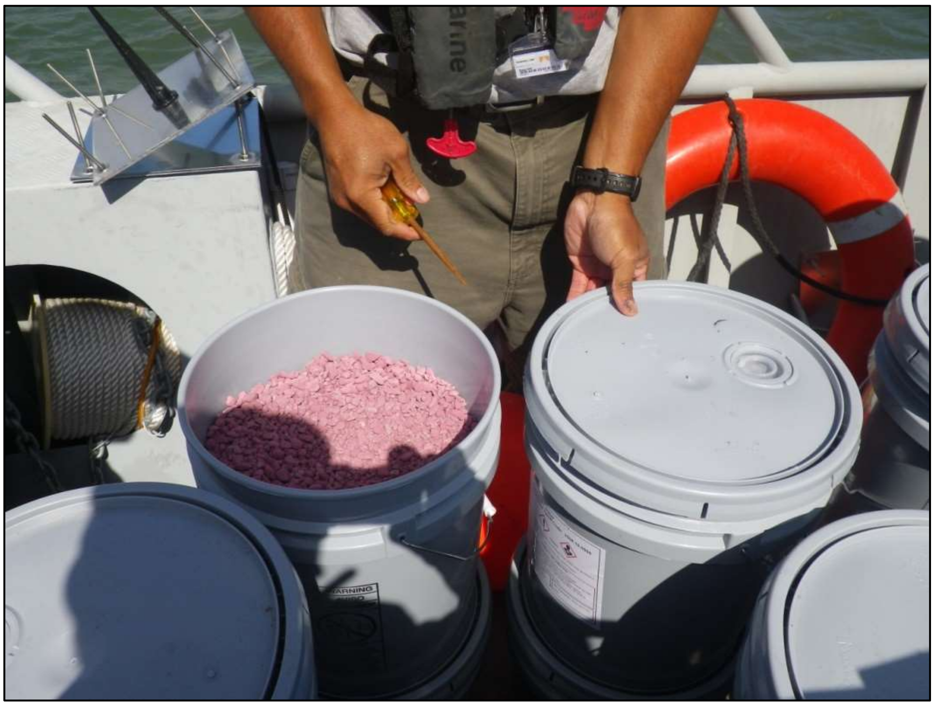

Figure 17. The AquaGate^{TM}-tracer particles on deck ready for deployment.

The green tracer was delivered to Hunters Point shipyard in 25 kg batches. During manufacture of the green tracer ~10 -15 % by mass seawater was added to each batch and this had been repeated by SPAWAR staff prior to commencement of the study; this is principally to reduce in advance surface-active effects associated with the tracer, and this substantially simplifies tracer deployment. However, the presence of water promotes consolidation of the tracer mass, and therefore upon opening each drum a blade was used to agitate and disaggregate the tracer.

3.4.3 Tracer Introduction

Tracer material deployment was completed on 15th September 2016 during calm conditions. Material was deposited across two “drop zone” areas. The pink tracer was deposited in a shore - normal strip between the two plots of different amendment cap material (AquaGate™ and Sedimite). The green tracer was deposited in a shore normal strip in the ‘upland’ area to the NW of the site of the amendment cap material. The AquaGate™-tracer particles (pink tracer) were deposited manually from the vessel at HW simulating the original deployment method. In a similar fashion, the green tracer was deposited manually at LW[4]. The area of the drop zone was carefully delineated by GPS fixes and the tracer material was deployed as best, and as uniformly as possible, along transects so as to be well distributed over the drop zone. This enabled controlled deployment of tracer as a swath throughout the deployment zone. This methodology was repeated until all of the tracer had been deployed to the seabed. Figure 18 shows the approximate repeat vessel tracks that were followed during tracer deployment.

Figure 18. The approximate vessel tracks during deployment of the pink and green tracer. Note; the vessel tracks during the green tracer deployment do not cross the pink deployment zone so as to ensure no resuspension occurred due to propeller wash. Note; this diagram is not to scale. Source: Google Earth.

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[4] Site access issues restricted deployment of tracer to the surface of the intertidal sediments. Deployment of high concentrations of silt tracer through the water column in shallow water would result in the majority of the tracer reaching the bed, yet the creation of a surface plume during tracer deployment was, unfortunately, inevitable.

Figure 19. Partrac and SPAWAR staff deploying the tracer.

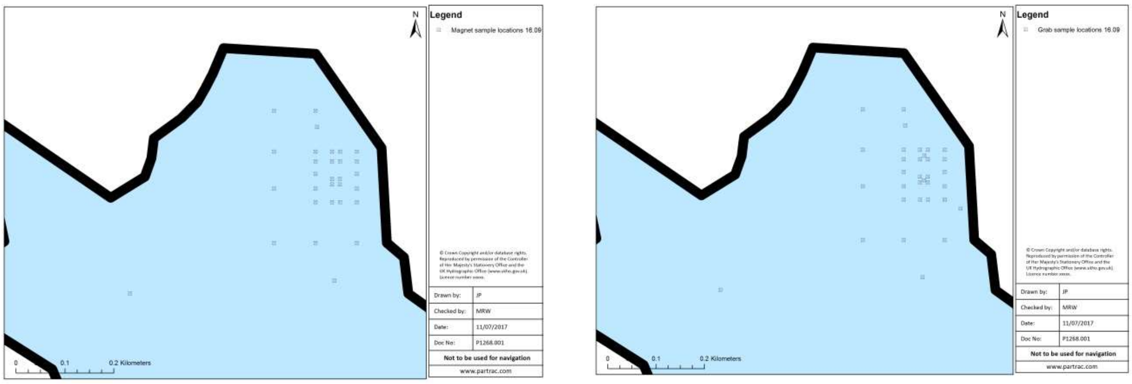
Figure 20. Partrac and SPAWAR staff deploying the tracer.

3.5 Sampling

To monitor the presence/absence of tracer particles within the water column during the deployment of the AquaGate™-tracer particles a fluorometer survey was conducted.

At each sampling location, during each of the sampling campaigns the magnet bedframe and the seabed were sampled. In addition, as a quality assurance measure, 5 duplicate samples were collected from various locations. In total, 2 sampling campaigns were conducted being 24 and 144 hours following tracer material deployment. Surveys were timed so that they were conducted at HW to enable the survey vessel to sample the inshore sampling sites. The 2 sampling campaigns resulted in the collection of 132 samples. Table 4 shows the dates and number of samples collected during the sampling surveys conducted. Figure 21shows the locations of the sample locations and Appendix I detail the locations of the samples collected during the 2 sampling campaigns.

Magnet sample locations 16.09.2016 *Grab sample locations 16.09.2016*



Magnet sample locations 21.09.2016 *Grab sample locations 21.09.2016*

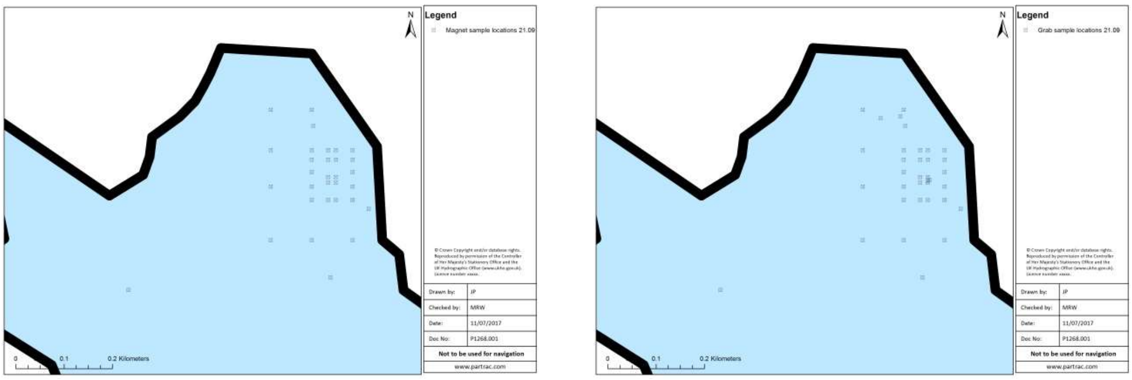


Figure 21. The spatial sampling grid during the study period (magnets and grabs).

Table 5. Post deployment sampling surveys and the number of samples collected.

Sampling survey (hours post deployment)	Date of sampling	No. of samples collected
24	16th September 2016	30 magnet samples
		34 seabed samples
144	21st September 2016	32 magnet samples
		36 seabed samples

3.5.1 *In situ* Fluorometer Survey

During deployment of the pink tracer a continuous fluorometer survey was conducted at a 1 Hz sampling rate. The fluorometer, targeted to excite fluorescence and capture the emission intensity in volts at the peak excitation-emission spectra of the pink tracer, was mounted on a pole and deployed ~ 0.5 m below the water surface from the bow of the vessel. The fluorometer, controlled from a graphical user interface on a field laptop stored in the cabin of the vessel, was routinely activated during transects over the site during deployment and the data saved following each transect.

3.5.2 Post Deployment Grab Sampling

During each sampling campaign sea bed grab samples were collected using a using a hand haulable bottom sediment grab sampler (petite ponar type). The grab was deployed manually from the bow of the survey vessel. The top sediment layer (~2-3 cm) was then sampled using an adapted sediment sampling tool and appropriately stored for analysis. Samples were discarded and resampled where any draining/loss of the sample was observed. The 2 sampling campaigns to date resulted in the collection of 70 sea bed sediment grab samples.

3.5.3 Post Deployment Magnet Sampling

During each sampling campaign the magnet bedframes were sampled. To do this, the frame was recovered from the seabed and brought onto the deck of the vessel. The magnet was unscrewed from the bedframe and the plastic sheath carefully removed and transferred to a sampling pot. The material on the sheath was then washed into the pot. The sheath was then placed back on the magnet and the magnet was secured to the bedframe and redeployed to the bed. The 2 sampling campaigns to date resulted in the collection of 70 magnet samples.

4. TRACER ENUMERATION

4.1 Introduction

Spectrofluorimetry was employed to determine the dry mass of tracer (in grammes) within a sample. A fluorimeter is a device used to measure parameters of fluorescence: its intensity and wavelength distribution of emission spectrum after excitation by a certain spectrum of light. These parameters can be used to identify the presence and the amount of specific dye molecules in a fluid medium. Modern fluorimeter's are capable of detecting fluorescent molecule concentrations as low as 1 part per trillion. This approach offers a means with which to obviate the additional mass due to the presence of magnetic but non-fluorescent particulates[5] simply and directly. It also provides a very high analytic resolution which facilitates detection of very low (mg quantities) tracer mass. The fluorometer signal output can be empirically related to tracer mass (g) through a series of tracer (colour) specific, reference standards. The tracer mass were normalised to a unit area (g m^2, g m^3), which is the formal unit quoted in many tracer studies (Black et al., 2007).

Prior to use of the spectrofluorometric method environmental samples (grabs, magnet samples) are pre-processed. The chief aim of pre-processing is to remove all native non-fluorescent, non-magnetic particles.

4.2 Sample Preparation

4.2.1 Grab Samples

Each sample is washed into a shallow container. The sample is then stirred thoroughly to ensure all particles are (and remain) in suspension. At this time a permanent, high field Ne-Bn 11,000 Gauss magnet is stirred through the sample, facilitating separation of magnetic particles. This procedure is repeated, with intermittent cleaning and recovery of the particles from the surface of the magnet, until no further magnetic particles are extracted.

4.2.2 Magnet Samples (and grab samples following magnetic separation, section 5.2.1)

Each sample is dried in an oven at 40^0C until no further change in mass is observed. Following drying each sample is disaggregated in a pestle and mortar and inspected under blue light illumination (395 nm). The sample is then weighed and transferred to a 50 ml Eppendorf tube.

The magnetic fraction is then ready for spectrofluorometric analysis.

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[5] Magnetic (but non-fluorescent) particles would be expected in relatively high abundance in an industrialised port / inshore environment.

4.3 Spectrofluorometric Methodology

The analyses were carried out using a Gilden Photonics Fluorosens fluorometer. The Fluorosens fluorometer incorporates single photon counting sensitivity into a fully computer controlled spectrometer (Figure 22). As the peak excitation and emission wavelengths of the dye coating is known (e.g. chartreuse green = peak excitation 470 nm, peak emission 530 nm) an emission scan across the emission wavelengths (500 – 600 nm) provides fluorescent intensity (V) readings at the chosen emission wavelength (530 nm). Each sample was run in triplicate and the mean value determined.

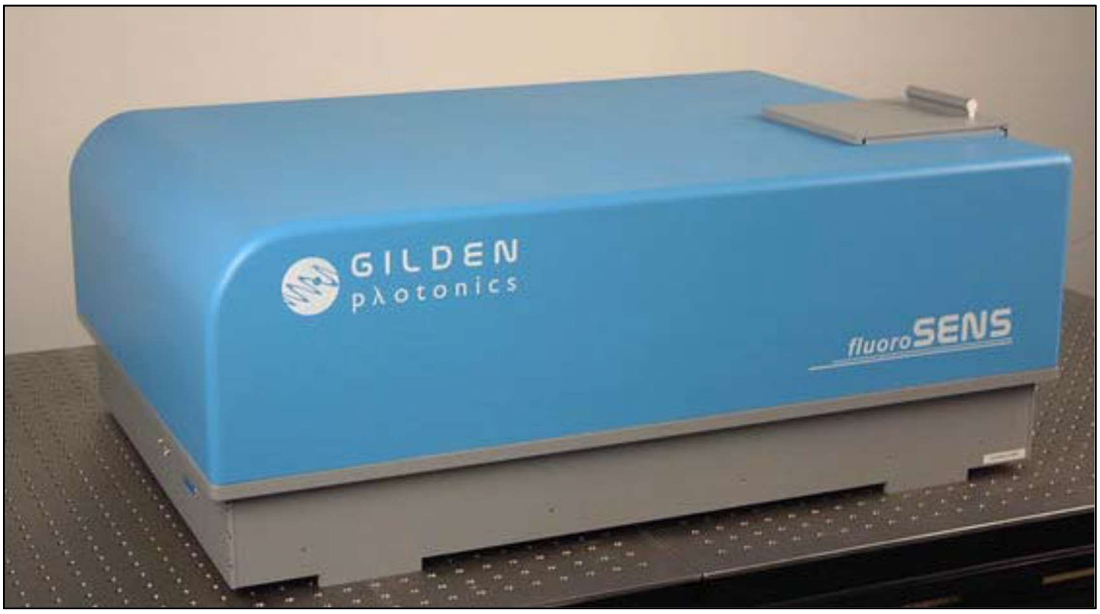

Figure 22. The Fluorosens laboratory spectrofluorometer.

The Fluorosens fluorometer is especially suited to the present task as measurement is recorded in a highly stable controlled environment. The general technical specification of the Fluorosens instrument is provided in Appendix 2.

A detailed **Standard Operating Procedure** for the analysis is commercially sensitive. The method in general terms involves a series of common steps:

1. dissolution of the fluorescent pigment into an analytical grade solvent for a period of 168 hours (7 days);
2. centrifugation if necessary (to remove all particulates);
3. dilution to a known level using analytical grade solvent;
4. analysis of the fluorescence intensity of the dye solution using a Fluorosens spectrofluorometer; and,
5. derivation of tracer particle dry mass (M_g) using calibration functions (dose response curves).

4.3.1 Standard (Dose Response) Curves

Eluted dye solutions for the tracer are prepared by adding a known dry mass of tracer particles to a known volume of analytical grade solvent. The solution is then left to equilibrate for 168 hours (7 days). This time period has been established as optimal for maximal extraction of the pigment into the solvent. Dose response curves were obtained by filling the calibration cell with 2 ml of analytical grade solvent, recording a baseline reading and then adding sequential 200 μl aliquots of the stock solution, mixing and recording further readings. Due to the (significant) non-fluorescent magnetic background material present at the project site, dose response curves were prepared with both tracer and native material to account for the quenching effects of the native material. Consequently 2 individually tailored dose response curves were prepared to enumerate the tracer mass from the samples collected, 1 dose response curve showing the response of green and pink tracer to the peak emission spectra of the green tracer (530 nm) and one showing the response to the peak emission spectra of the green tracer (580 nm[6]). Table 6 details how the samples used to develop the dose response curves were prepared.

Table 6. The preparation of samples used to develop the dose response curves (colour specific reference standards).

Tracer colour	Dosed tracer mass (g)	Dosed (background) native material (g)	Solvent volume added (ml)	Time sample eluted for (hours)	Dosed to equivalent tracer dry mass (g)	r^2 Value
Green	0.1	3.461 (avg. background magnetic non-fluorescent material recovered)	30	168	0.7	0.92
Pink	0.1	3.461 (avg. background magnetic non-fluorescent material recovered)	30	168	0.7	0.95

Least-squares regression analysis (Fowler *et al*., 1998) was performed on the data to generate calibration functions. Standard (dose response) curves were developed to relate spectrofluorimetric measurements (probe reading in volts) to tracer dye concentration over the range of dry masses (0 – 0.7 g) (Figure 23 and Figure 24). Consistently high coefficients of determination (r^2) are found (Table 6).

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[6] The peak emission spectra of the pink dye was previously determined at 610 nm but it was observed that when using the fluorosens spectrofluorometer the peak emission spectra was found at 580 nm. This value was subsequently used for analysis of all samples.

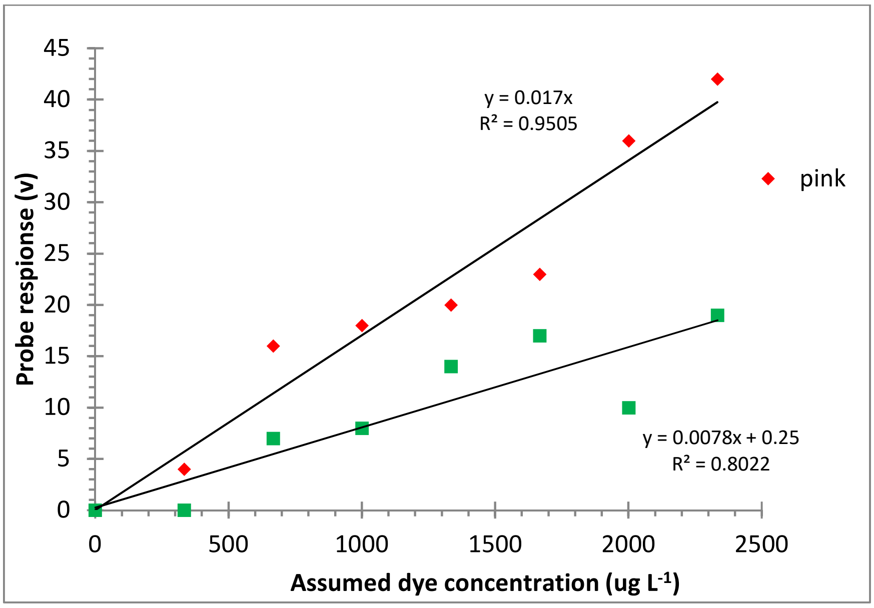

Figure 23. Dose response curves for both the green and pink tracer exposed to the peak emission excitation spectra for the pink tracer (excitation 570 nm and emission 580 nm). In practise the point concentration values on the x-axis are interchangeable with the corresponding tracer dry mass of each curve.

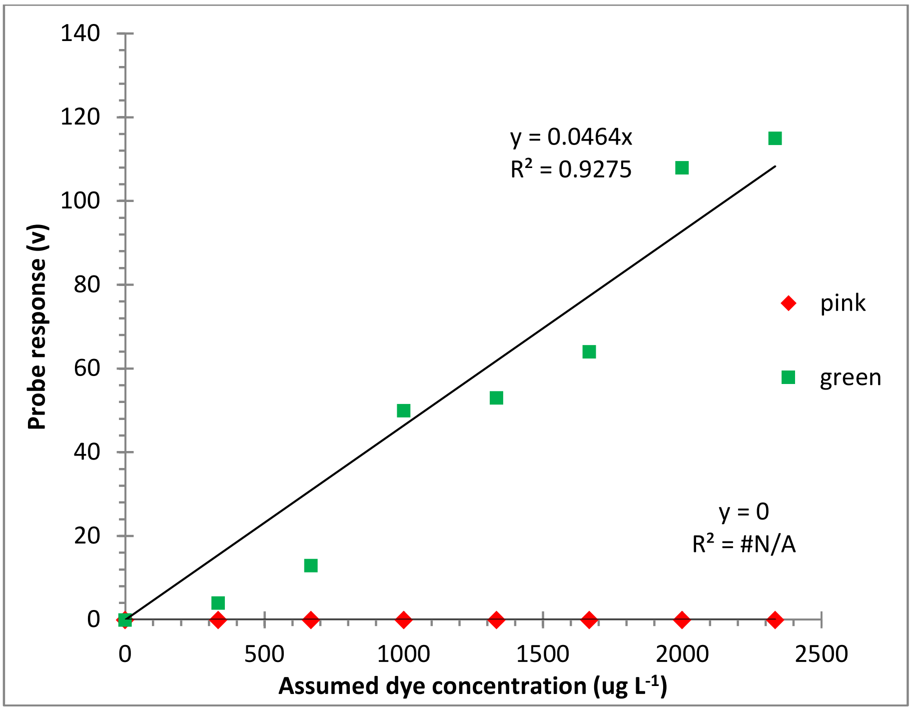

Figure 24. Dose response curves for pink tracer (top) and green tracer (bottom). Each sample was analysed at the peak emission spectra of the green tracer (excitation 470 nm, emission 530 nm). In practise the point concentration values on the x-axis are interchangeable with the corresponding tracer dry mass of each curve.

By using the data obtained from the dose response curves developed for the peak emission spectra, exposed to both coloured dyes (Figure 23 and Figure 24), it is possible to determine the dye concentration for the two-different tracer colours within one sample. Within this approach there are two simultaneous equations with two unknowns (Equation 1). These two simultaneous equations, solved algebraically generate the two unknown concentrations for both dyes:

$$S_G = SL_{FG} \times (G_r) + SL_{FP} \times (P_r) + O_F$$

and

$$S_P = SL_{RG} \times (G_r) + SL_{FP} \times (P_r) + O_R \qquad (1)$$

Where, SL_{FG} is the slope of the green dye response at the peak emission spectra for the green dye. SL_{RG} is the slope of the green dye response at the peak emission spectra for the pink dye. SL_{FP} is the slope of the pink dye response at the peak emission spectra for the green dye. SL_{RP} is the pink dye response at the peak emission spectra for the pink dye. O_F is the offset (the solvent blank signal) for the peak emission spectra for the green dye and O_R is the offset for the peak emission spectra for the pink dye. G_r and P_r is the response of the spectrofluorometer at the peak emission spectra for the green and pink dye respectively, to the sample.

Tracer dry mass (TDM) for each tracer colour is then calculated using the following equation;

$$TDM = \left(\frac{DC}{DC_{max}}\right) TDM_{max} \qquad (2)$$

Where, DC_{max} is the maximum assumed dye concentration (ug L^{-1}) and TDM_{max} is the equivalent tracer dry mass value.

4.3.1 Minimum Resolvable Mass (MRM)

The MRM is derived from the lowest possible fluorimeter response (which is 1 volt). This value is then propagated through Equation 1 and 2 to determine the MRM, which is given by the intercept of the regression line on the y-axis. MRM values are summarised inTable 7.

Table 7 Summary of MRM values for each dose response curve.

Tracer Colour	MRM (g)
Green	0.007
Pink	0.018

Figure 25 shows photographic examples of the sample analysis process for sample OB01 – W. Further examples can be found in Appendix 2.

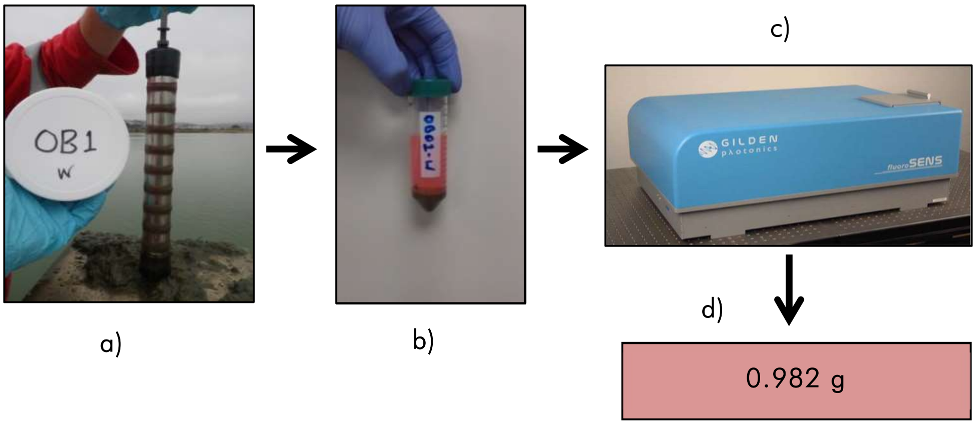

Figure 25. A series of photos depicting the different stages of sample analysis. The schematic shows a) collection of the sample (OB01 –W) in the field; b) the sample following elution; c) the spectrofluorometer where the sample (stock solution shown in b) is analysed; and, d) shows the derived dry tracer mass value following analysis.

4.4 Quality Assurance

An analytical quality control / assurance methodology was developed in tandem with the development of the spectrofluorometric method. This involved inclusion of the following within the laboratory testing strategy:

1. Visual observations
2. Periodic testing of blanks
    a. 18 samples tested in total;

In addition, a description of the methodological bias is provided for the readers consideration based on previous testing conducted.

4.4.1 Visual Observations

Prior to spectrofluorimetric analysis all samples were routinely visually inspected under blue light illumination to assess tracer presence. Qualitative descriptions were developed as follows:

1) Trace -~< 10^{-3} g
2) Low -~10^{-3}g
3) Intermediate -~10^{-2} g
4) High -~10^{-1} g
5) Very high –~10^{0} g

Note: - Due to quenching effects of the background non-fluorescent magnetic material, burial and aggregation during the drying process and the low wavelength of a standard blue light inspection lamp (395 nm), the probability exists of a negative visual inspection and a positive spectrofluorometric result. Cross-comparison of qualitative descriptions with the spectrofluorometric data should accordingly be undertaken with caution.

4.4.2 QC Data – Periodic Testing of Blanks

A check on the performance of the spectrofluorometric analytical procedure is made through periodic testing of blanks. In total 18 blank samples were analysed (Table 8). Blanks are solutions made up in entirely the same manner as samples but without inclusion of a sediment / tracer sample. Note the testing of blanks provides the offset values in Equation 1.

Table 8 Periodic testing of laboratory blanks for green and pink tracer dye.

	Probe response (V) at peak emission wavelength (nm)	
Sample #	Green (530 nm)	Pink (580 nm)
1	0	0
2	0	0
3	0	2
4	0	0
5	0	0
6	0	0
7	0	0
8	0	0
9	0	2
10	0	0
11	0	4
12	0	0
13	0	0
14	0	0
15	0	0
16	0	0
17	0	0
18	0	0

4.4.3 Methodological Bias

In order to establish the methodological bias associated with the spectrofluorometric analytical procedure blind samples were submitted for testing to the laboratory. Blind samples are prefabricated dual - colour sediment samples within which the tracer dry mass is unknown to the analyst. Figure 26 shows a plot of calculated tracer mass vs. measured tracer mass.

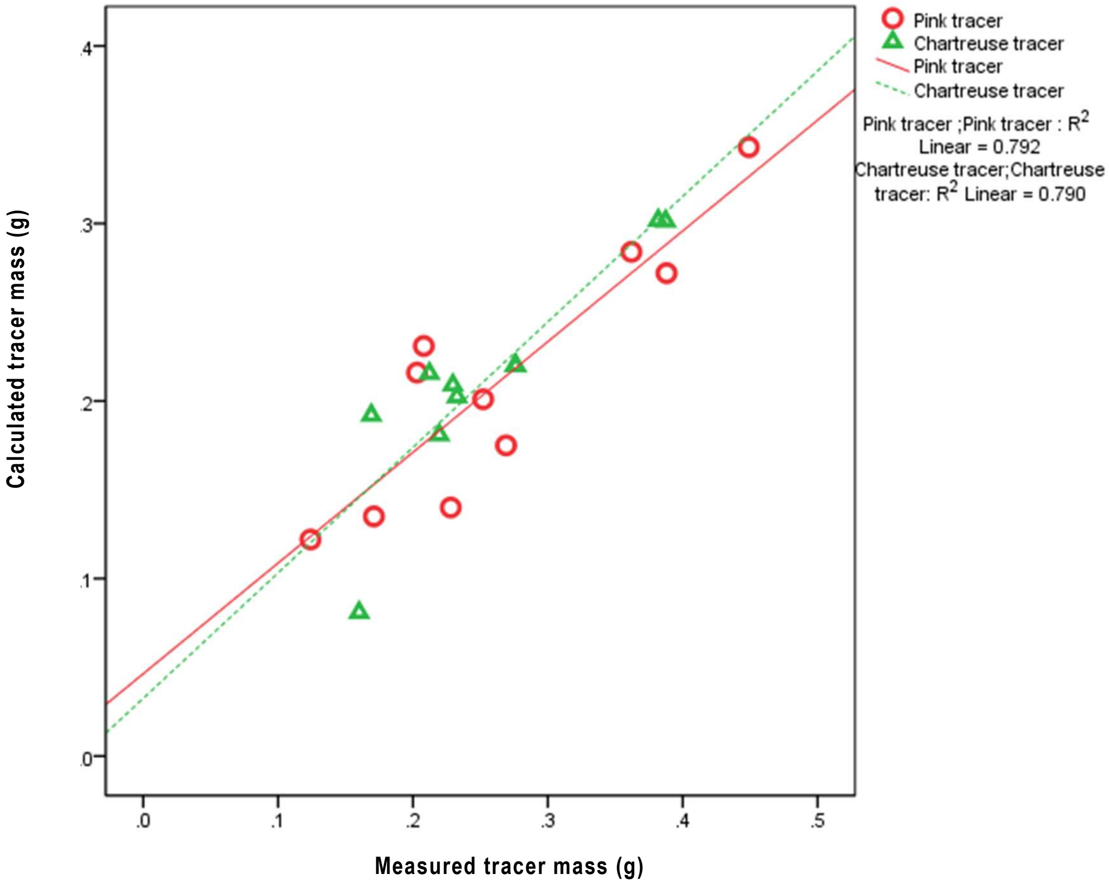

Figure 26. An example of tracer mass vs. calculated tracer mass for samples with two tracer colours and various native sediment material(s) derived from the peak emission wavelengths of the pink and green tracer respectively.

Table 9 provides an example of the results of blind testing where two tracer colours (green and pink) are mixed with various quantities of background (non-fluorescent) sediment. Based on this testing a conservative methodological bias on calculated dry tracer mass of **± 30 %** was quantified.

Table 9. An example of the results of blind testing of spiked samples containing various quantities of green and pink tracer mixed with low (< 0.5 g), moderate (0.5 - 2 g) and high (> 2 g) of non-fluorescent sediment.

Actual tracer mass (g)		Added sediment volume (background non-fluorescent material)	Calculated tracer mass (g)		Difference (%)	
Green Tracer	Pink Tracer		Green tracer	Pink tracer	Green tracer	Pink tracer
0.346	0.269	Low	0.433	0.175	25	35
0.212	0.267	Low	0.216	0.150	2	44
0.230	0.438	Low	0.209	0.207	9	53
0.169	0.228	Low	0.192	0.140	14	38
0.382	0.203	Moderate	0.302	0.216	21	6
0.387	0.449	Moderate	0.301	0.343	22	24
0.220	0.362	Moderate	0.181	0.284	18	21
0.233	0.124	Moderate	0.202	0.122	13	2
0.276	0.388	High	0.220	0.272	20	30
0.276	0.171	High	0.220	0.135	20	21
0.585	0.252	High	0.475	0.201	19	20
0.160	0.208	High	0.081	0.231	49	11

4.5 The spectrofluorometric enumeration methodology – a brief discussion

The spectrofluorometric analytical procedure was adapted and developed to exploit the fluorescent attribute of the tracer particles, to provide directly, the dry tracer mass (*M,* g). The dye concentration was proportioned to dry mass of fluorescent tracer particles through the use of colour specific reference standards. The spectrofluorometric method was validated and applied to the determination of representative environmental samples spiked with various quantities of one or two tracer colours. The representative environmental samples indicated that background material (native environmental particulates of the sample) reduced the fluorescent emission of derived dye solution due to static quenching effects by up to 67%, dependant on the quantity of background material within the sample. This was accounted for empirically by determining colour specific reference standards with known masses of representative native material. This methodology provided a relatively simple, fast and non-resource intensive approach to tracer enumeration within fluorescent tracing studies, which contributed to the improvement of the general utility of the technique.

Within the spectrofluorometric technique a range of factors affect the specific coefficient of fluorescence intensity vs. tracer dry mass. Potential sources of error include: 1) human error, which can be obviated by using an experienced technician with a practical and theoretical understanding of spectrofluorimetry (Gunn, 1963); and, 2) the empirical relationship between the assumed concentrations of a sample to tracer dry mass; the homogenous mixing of the particles and the native sediment; particle size distribution and surface area of the particles; the dye loading on the surface of the individual tracer particles; and the properties of the solvent and dye pigment. These potential sources of error can be significantly reduced if the coefficient is determined empirically for each combination of conditions (Carey, 1989, Gunn, 1963).

The methodological bias is considered tolerable within the sediment tracing methodology, due to the error associated with other enumeration techniques e.g. an error of 5 - 10 % was attributed by Carrasco et al. (2013) to counting fluorescent tracer grains (sand sized) by eye. Further, the error related to models of sediment transport are judged to be of the order of a factor of 10 (Eidsvik, 2004), reduced to a factor of 5 or better once validated (Soulsby, 1997).

5. RESULTS AND DISCUSSION

5.1 Hydraulic Similarity

One of the central tenets of the tracking methodology is that the tracer forms an accurate analogue (mimic) of the material under consideration (Foster, 2000). In this study, for the results to be informative this means that the tracer hydraulic properties must bear close similarity to those of the target sediment and those of the amendment material (i.e. closely match the target properties proposed in section 2.1.1 and 2.1.2). The result of testing indicates that this condition is satisfied and the tracer very closely matches the target hydraulic properties of the two materials (activated carbon [see section 2.1.1 and Table 4] and local silts [see section 2.1.2 and Table 4). These results indicate both tracers deployed will be cycled (eroded, mobilised, transported and deposited) in the same fashion (and at the same rate) as the target material, and thus the movement of tracer is judged to represent the movement of the target material.

5.2 Hydrodynamic (tidal currents) and Meteorological (wind) Conditions

The field testing at HPS occurred over 2 weeks starting the week of September 12, 2016. Typical dry season weather conditions occurred during this entire period, with calm to light winds (<10 knots) in the morning and evening, with stronger winds (10 – 20 knots) during the afternoon hours. During the study the currents were monitored using a Nortek AquaDopp current profiler. The data from the AquaDopp were processed and quality controlled to remove any unreliable data bins. The AquaDopp cannot accurately measure the bottom 20 cm (referred to as the blanking layer) from the seabed due to conflict between the reflected signal from particulates and directly from the seabed. As such, it was necessary to use the data from the lowest 3 'good' 10 cm bins to represent the datum 50 cm above the bed. Due to concerns related to security the instrument was deployed and recovered during field operations thus a discontinuous view of the current regime at the site has been captured, though current velocity data has been recorded on both an ebb and flood tide.

Data on the wind strength and direction was captured from the meteorological station located at San Francisco International Airport. The modal wind direction is from the west (280°) with an average speed of 13 kts (Figure 27). Daily average data was recorded throughout the study period and is presented in Table 10.

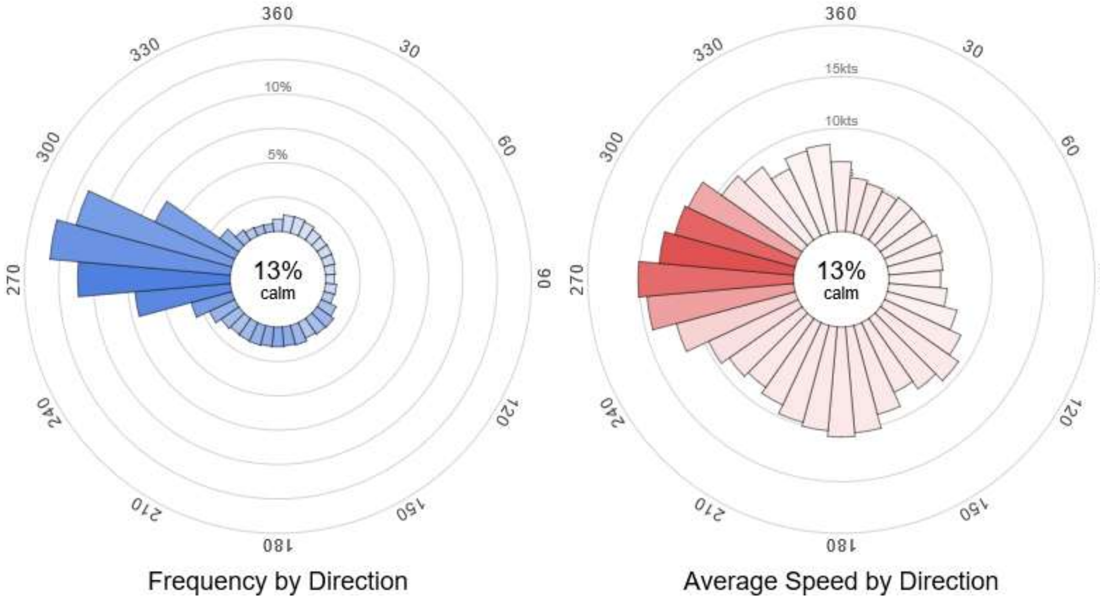

Figure 27. A wind rose showing historic wind data captured at San Francisco International Airport. The length of each bar is proportional to the frequency the wind comes from each direction and the colour is proportional to the average speed (source: http://windhistory.com).

Table 10. Meteorological data captured at San Francisco International Airport (~ 10 miles from site) throughout the study period.

Date	Average wind direction	Average speed (km hr^{-1})	Average speed (knots)	Description
09/15/2016	W	25.9	14	Gusts increasing in afternoon
09/16/2016	WNW	18.5	10	Gusts increasing in afternoon
09/17/2016	WSW	12.1	2.8	Gusts increasing in afternoon
09/18/2016	W	15.2	8.2	Gusts increasing in afternoon
09/19/2016	W	15.7	8.5	Gusts increasing in afternoon
09/20/2016	WSW	12.1	6.5	Gusts increasing in afternoon
09/21/2016	W	15.2	8.2	Gusts increasing in afternoon
09/22/2016	WNW	13.9	7.5	Gusts increasing in afternoon
09/23/2016	W	11.4	6.2	Gusts increasing in afternoon
09/24/2016	W	13.3	7.2	Gusts increasing in afternoon

From the limited data available (presented in Figure 28, Figure 29 and Figure 30) the tidal currents at the site appear to be broadly rectilinear in form with a principle tidal axis oriented approximately E – W. As expected within a protected shallow embayment, low current velocities are observed at the site ranging from ~ 0.01 m s^{-1} – 0.1 m s^{-1}. Interestingly, the data indicates that nearbed current velocities increase in the afternoon, and this is postulated to be a function of the increasing wind speed which routinely occurs in the afternoon (Table 10). The impact on near bed currents of strong winds in the afternoon is further evident from the data (Figure 28 and Figure 30) where the prevailing current direction of the nearbed currents on two flood tides (data captured early morning and early afternoon respectively) are reversed. These data demonstrate the likely significant contribution of wind in driving sediment transport at the Hunters Point site.

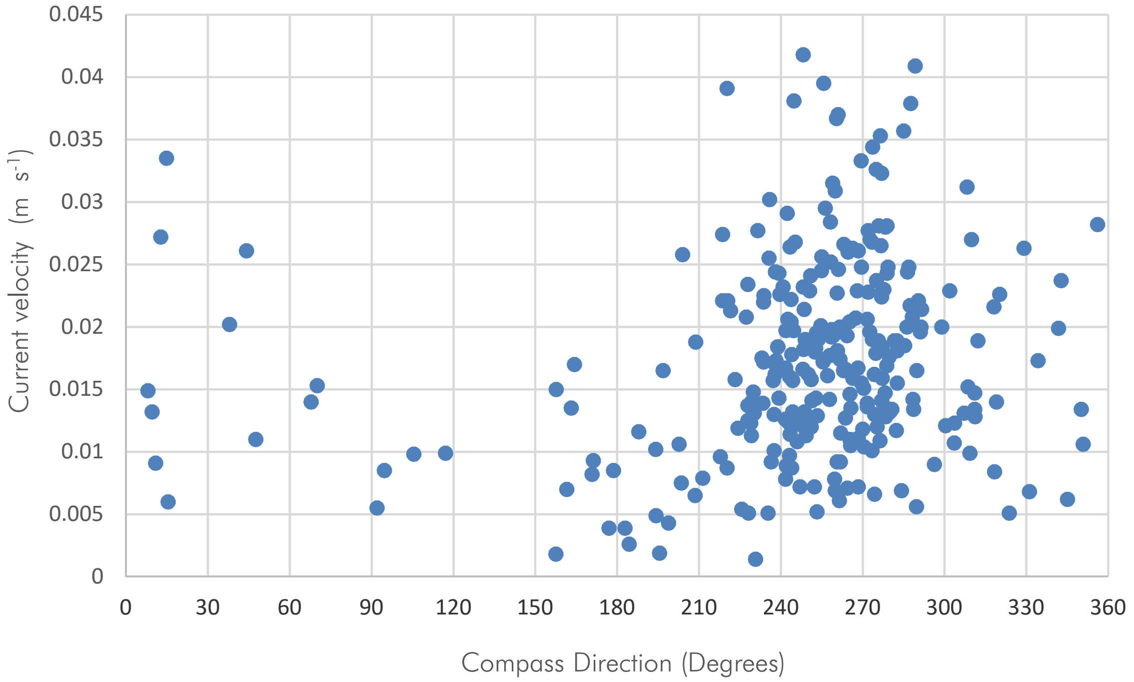

Figure 28. A plot of the current velocity vs direction captured using the AquaDopp profiler on the 15/09/2016 during flood tide between 10:00 and 12:00.

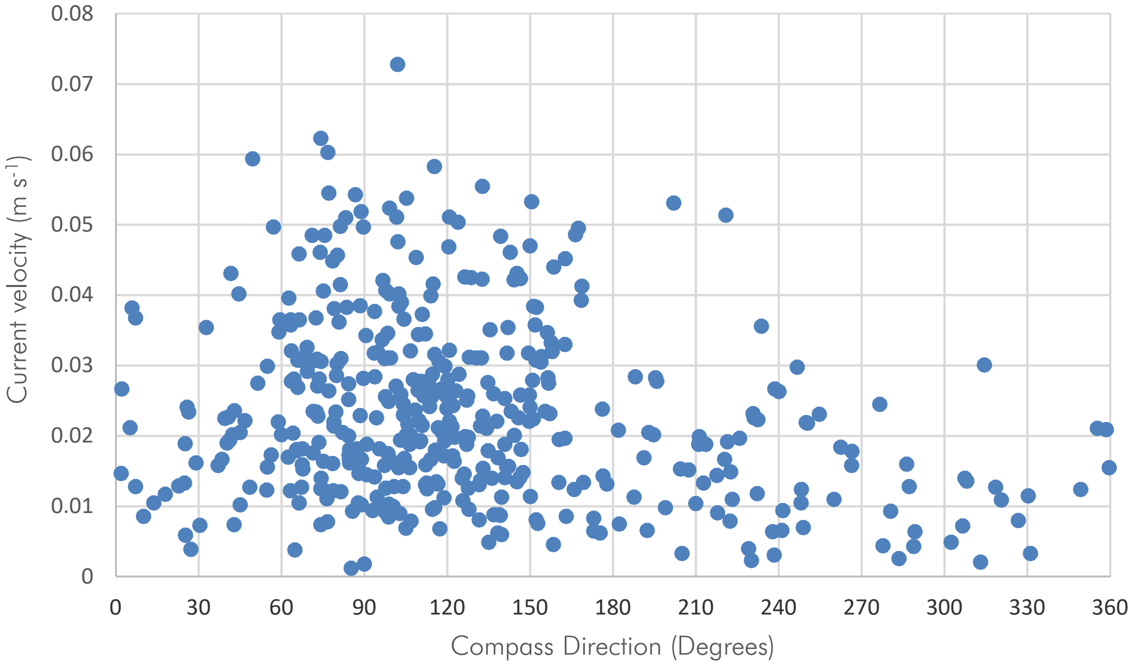

Figure 29. A plot of the current velocity vs direction captured using the AquaDopp profiler on the 15/09/2016 during ebb tide between 12:30 – 14:45.

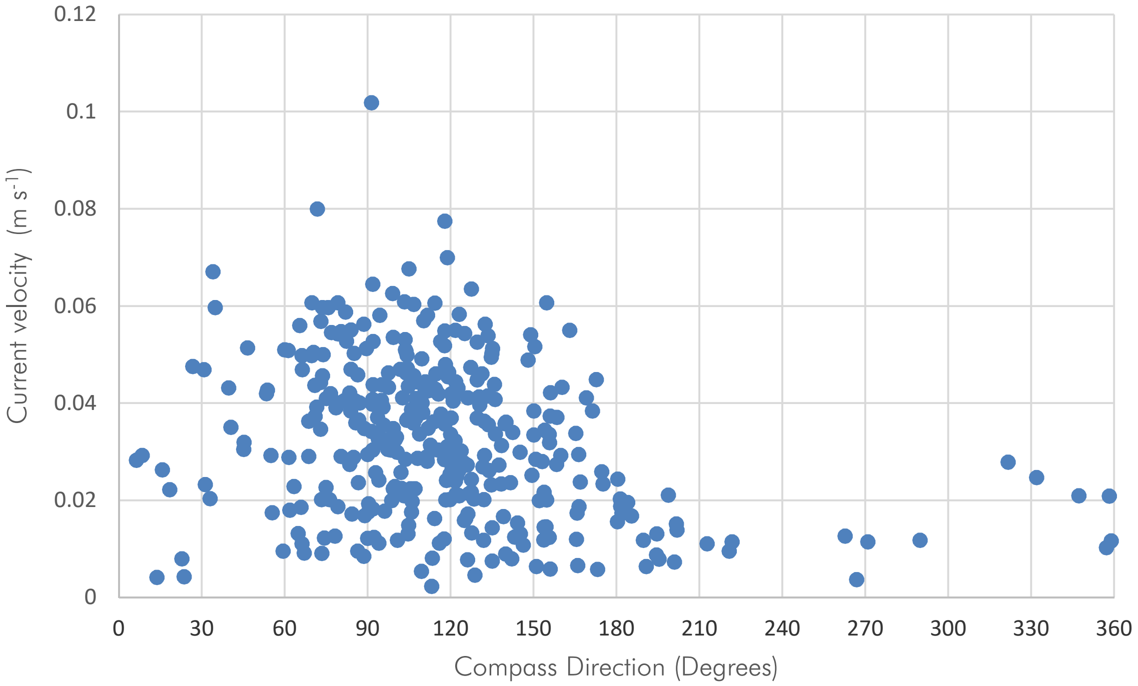

Figure 30. A plot of the current velocity vs direction captured using the AquaDopp profiler on the 21/09/2016 during flood tide between 12:00 – 14:00.

Figure 31 shows the response of the fluorometer during deployment of the tracer providing a time series of tracer concentration within the water column below the vessel. Note the gaps in the data are primarily due to the fluorometer being turned off during vessel transit in-between periods of tracer deployment. Tracer concentrations of up to 236 μg L^{-1} are observed indicating significant tracer presence within the water column during deployment, which is significantly over the background concentration (~12 μg L^{-1}).

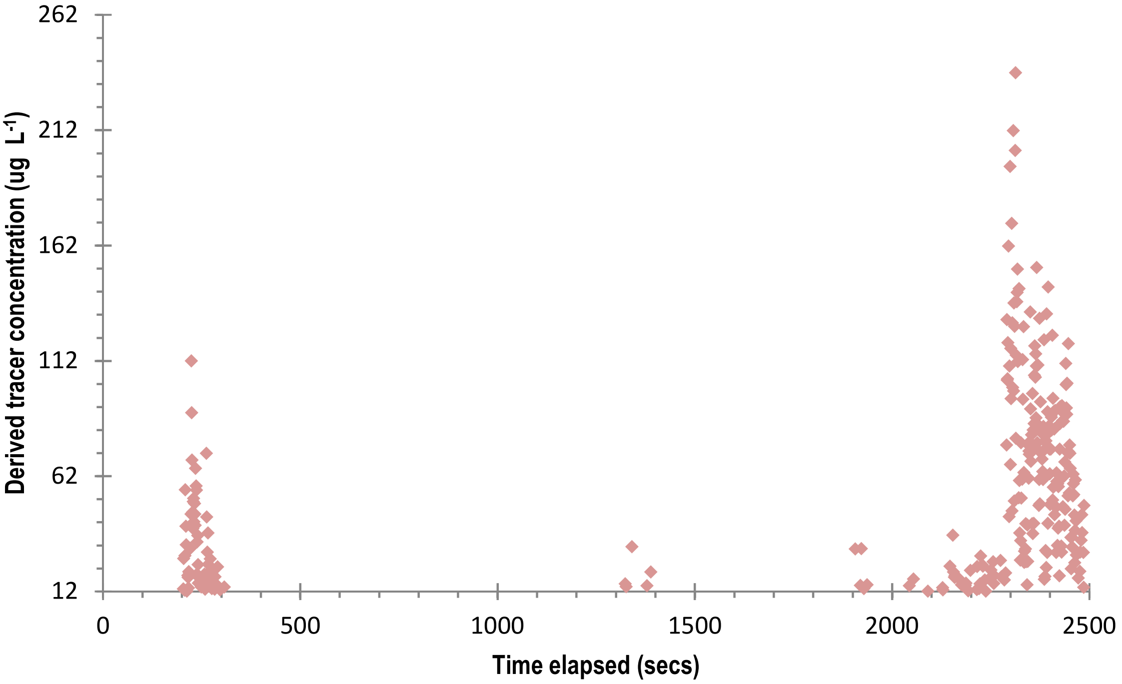

Figure 31. The response of the fluorometer during deployment of the pink tracer (designed to replicate the properties of the carbon amendment material). As determined during the background survey the threshold value (12 ug l^{-1}) represents the baseline response of the native sediments at the site. Where values exceed this threshold this indicates the presence of tracer within the water column.

5.3 Tracer Dry Mass Data

Table 11 presents results for all samples analysed for tracer dry mass. The sediment grab data is expressed as an area density metric (g m^{-2}).

Table 11. Tracer dry mass data

Sample ref.	Type	Date collected	Normalised Tracer mass (g m^{-2})		Tracer mass (g)	
			Green	Pink	Green	Pink
OB01 – w	Magnet	09/16/2016			0.091	0.982
OB02 – w	Magnet	09/16/2016			0.013	0.047
OB03 – w	Magnet	09/16/2016			0.000	0.035
OB04 – w	Magnet	09/16/2016			0.000	0.047
OBO5 – w	Magnet	09/16/2016			0.000	0.000
OB06 – w	Magnet	09/16/2016			0.000	0.000

Sample ref.	Type	Date collected	Normalised Tracer mass (g m^{-2})		Tracer mass (g)	
			Green	Pink	Green	Pink
OB07 – w	Magnet	09/16/2016			2.321	0.000
OB08 – w	Magnet	09/16/2016			0.123	0.000
OB09 – w	Magnet	09/16/2016			0.000	0.000
OB10 – w	Magnet	09/16/2016			0.000	0.000
UP01 – w	Magnet	09/16/2016			2.140	0.000
UP02 – w					Sample lost	
UP03 – w	Magnet	09/16/2016			0.485	0.000
UP04 – w	Magnet	09/16/2016			0.000	0.041
BZ01 – w	Magnet	09/16/2016			0.116	0.458
BZ02 – w	Magnet	09/16/2016			0.000	0.000
BZ03 – w	Magnet	09/16/2016			0.039	1.658
BZ04 – w	Magnet	09/16/2016			0.058	4.349
AQ01 – w	Magnet	09/16/2016			1.752	0.000
AQ02 – w	Magnet	09/16/2016			1.564	0.000
AQ03 – w	Magnet	09/16/2016			0.588	0.000
AQ04 – w	Magnet	09/16/2016			0.000	0.000
AQ05 – w	Magnet	09/16/2016			0.013	0.000
AQ06 – w	Magnet	09/16/2016			0.000	0.000
SD01 – w	Magnet	09/16/2016			0.970	0.000
SD02 – w	Magnet	09/16/2016			0.097	0.097
SD03 – w	Magnet	09/16/2016			0.026	1.347
SD04 – w	Magnet	09/16/2016			0.000	0.109
SD05 – w	Magnet	09/16/2016			0.000	0.000
SD06 – w	Magnet	09/16/2016			0.000	0.000
OB01 – T7 - w	Magnet	09/21/2016			0.026	0.817
OB02 – T7 - w	Magnet	09/21/2016			0.000	0.000
OB03 – T7 - w	Magnet	09/21/2016			0.000	0.000

Sample ref.	Type	Date collected	Normalised Tracer mass (g m^{-2})		Tracer mass (g)	
			Green	Pink	Green	Pink
OB04 – T7 - w	Magnet	09/21/2016			0.000	0.000
OBO5 – T7 - w	Magnet	09/21/2016			0.000	0.000
OB06 – T7 - w	Magnet	09/21/2016			0.013	0.000
OB07 – T7 - w	Magnet	09/21/2016			0.485	0.000
OB08 – T7 - w	Magnet	09/21/2016			0.187	0.000
OB09 – T7 - w	Magnet	09/21/2016			0.000	0.076
OB10 – T7 - w	Magnet	09/21/2016			0.013	0.000
OB11 – T7 - w	Magnet	09/21/2016			0.045	0.000
UP01 – T7 - w	Magnet	09/21/2016			0.181	0.000
UP02 – T7 - w	Magnet	09/21/2016			0.116	0.000
UP03 – T7 - w	Magnet	09/21/2016			0.000	0.047
UP04 – T7 - w	Magnet	09/21/2016			0.000	0.035
BZ01 – T7 - w	Magnet	09/21/2016			0.071	0.497
BZ02 – T7 - w	Magnet	09/21/2016			0.026	0.235
BZ03 – T7- w	Magnet	09/21/2016			0.052	3.540
BZ04 – T7 - w	Magnet	09/21/2016			0.052	3.981
AQ01 – T7- w	Magnet	09/21/2016			0.226	0.000
AQ02 – T7 - w	Magnet	09/21/2016			0.304	0.000
AQ03 – T7 - w	Magnet	09/21/2016			0.013	0.100
AQ04 – T7 - w	Magnet	09/21/2016			0.019	0.000
AQ05 – T7 - w	Magnet	09/21/2016			0.000	0.000
AQ06 – T7 - w	Magnet	09/21/2016			0.000	0.000
SD01 – T7 - w	Magnet	09/21/2016			0.116	0.141
SD02 – T7 - w	Magnet	09/21/2016			0.032	0.320
SD02 (DUP) T7 - w	Magnet	09/21/2016			0.013	0.435
SD03 – T7 - w	Magnet	09/21/2016			0.026	1.735
SD04 – T7 - w	Magnet	09/21/2016			0.013	0.329

Sample ref.	Type	Date collected	Normalised Tracer mass (g m^{-2})		Tracer mass (g)	
			Green	Pink	Green	Pink
SD05 – T7 - w	Magnet	09/21/2016			0.000	0.000
SD06 – T7 - w	Magnet	09/21/2016			0.013	0.100
OB01 – Sed	Grab	09/16/2016	0.000	0.000		
OB02 – Sed	Grab	09/16/2016	0.000	0.000		
OB03 – Sed	Grab	09/16/2016	0.000	0.000		
OB04 – Sed	Grab	09/16/2016	0.000	0.000		
OBO5 – Sed	Grab	09/16/2016	0.000	0.000		
OB06 – Sed	Grab	09/16/2016	0.000	0.000		
OB07 – Sed	Grab	09/16/2016	0.000	0.000		
OB08 – Sed	Grab	09/16/2016	0.000	0.000		
OB09 – Sed	Grab	09/16/2016	0.000	0.000		
OB10 – Sed	Grab	09/16/2016	0.000	0.000		
OB11 - Sed	Grab	09/16/2016	27.418	0.000		
UP01 – Sed	Grab	09/16/2016	1.960	0.000		
UP02 – Sed	Grab	09/16/2016	0.000	0.000		
UP03 – Sed	Grab	09/16/2016	0.000	0.000		
UP04 – Sed	Grab	09/16/2016	0.000	2.038		
BZ01 – Sed	Grab	09/16/2016	0.000	0.000		
BZ02 – Sed	Grab	09/16/2016	0.000	0.000		
BZ03 – Sed	Grab	09/16/2016	0.000	0.000		
BZ04 – Sed	Grab	09/16/2016	0.000	0.000		
AQ01 – Sed	Grab	09/16/2016	3.713	0.000		
AQ02 – Sed	Grab	09/16/2016	0.000	0.000		
AQ03 – Sed	Grab	09/16/2016	0.000	0.000		
AQ04 – Sed	Grab	09/16/2016	0.000	0.000		
AQ05 – Sed	Grab	09/16/2016	0.000	0.000		
AQ06 – Sed	Grab	09/16/2016	0.000	0.000		

Sample ref.	Type	Date collected	Normalised Tracer mass (g m^{-2})		Tracer mass (g)	
			Green	Pink	Green	Pink
SD01 – Sed	Grab	09/16/2016	0.000	0.000		
SD02 – Sed	Grab	09/16/2016	0.000	1.532		
SD02 – Dup Sed	Grab	09/16/2016	1.116	0.000		
SD03 – Sed	Grab	09/16/2016	0.000	0.000		
SD04 – Sed	Grab	09/16/2016	0.000	0.000		
SD05 – Sed	Grab	09/16/2016	0.000	0.000		
SD06 – Sed	Grab	09/16/2016	0.000	0.000		
DZ01 – Pink drop zone sed	Grab	09/16/2016	0.000	0.000		
DZ02 – Green - Sed	Grab	09/16/2016	1.402	0.000		
OB01 – T7 - Sed	Grab	09/21/2016	0.844	0.000		
OB02 – T7 - Sed	Grab	09/21/2016	1.675	0.000		
OB03 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
OB04 – T7 - Sed	Grab	09/21/2016	0.844	0.000		
OBO5 – T7 - Sed	Grab	09/21/2016	2.804	0.000		
OB06 – T7 - Sed	Grab	09/21/2016	0.000	1.779		
OB07 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
OB08 – T7 - Sed	Grab	09/21/2016	0.558	0.000		
OB09 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
OB10 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
OB11 – T7 - Sed	Grab	09/21/2016	10.074	0.000		
UP01 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
UP02 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
UP03 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
UP04 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
BZ01 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
BZ02 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
BZ03 – T7 - Sed	Grab	09/21/2016	0.000	0.000		

Sample ref.	Type	Date collected	Normalised Tracer mass (g m^{-2})		Tracer mass (g)	
			Green	Pink	Green	Pink
BZ04 – T7- Sed	Grab	09/21/2016	0.000	0.000		
AQ01 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
AQ02 – T7 - Sed	Grab	09/21/2016	0.286	0.000		
AQ03 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
AQ04 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
AQ05 – T7 - Sed	Grab	09/21/2016	0.000	2.038		
AQ06 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
SD01 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
SD02 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
SD02 – T7 - Dup Sed	Grab	09/21/2016	0.000	0.000		
SD03 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
SD04 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
SD05 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
SD06 – T7 - Sed	Grab	09/21/2016	0.000	0.000		
DZ01 – T7 - Pink drop zone sed	Grab	09/21/2016	0.000	77.374		
DZ01 – T7 - pink dup sed	Grab	09/21/2016	0.000	57.018		
DZ02 – T7 - Green - Sed	Grab	09/21/2016	27.418	0.000		
DZ02 – T7 - dup green sed	Grab	09/21/2016	6.712	0.000		

5.3.1 Geospatial Presentation of Tracer Dry Mass

Figure 32 through Figure 39 present the results of the sample analysis and the datasets reveal aspects of the redistribution of tracer by wave and current action through time.

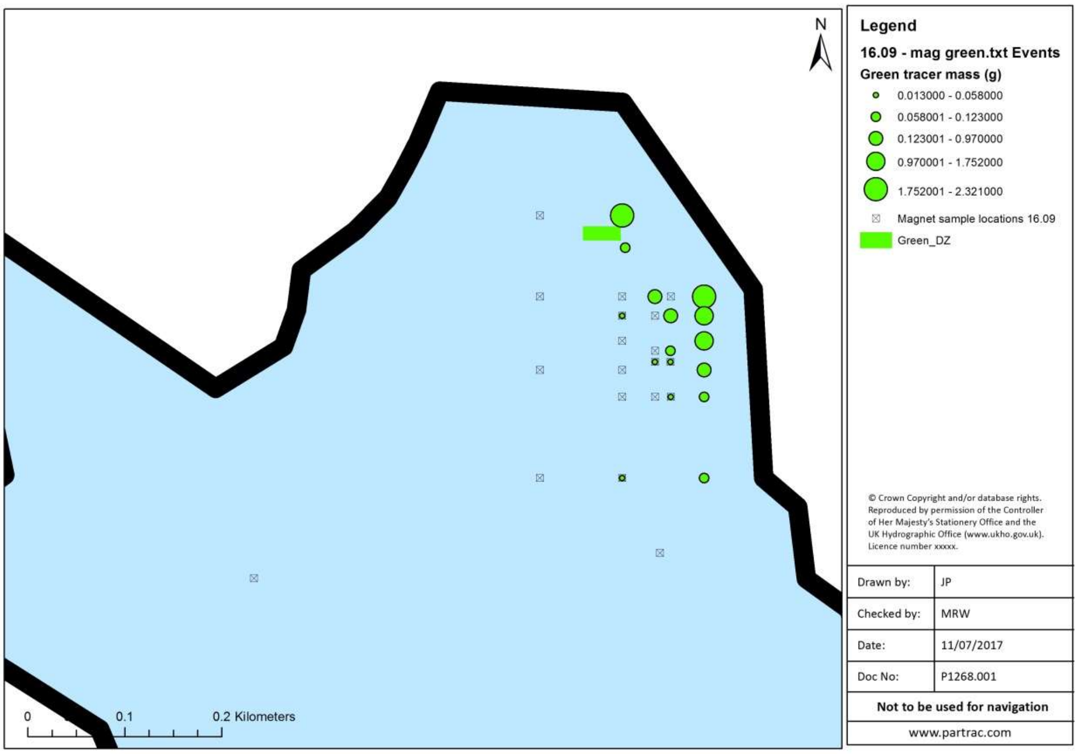

Figure 32. Geospatial distribution of green tracer dry mass (g) on magnets ~ 24 hours following tracer release.

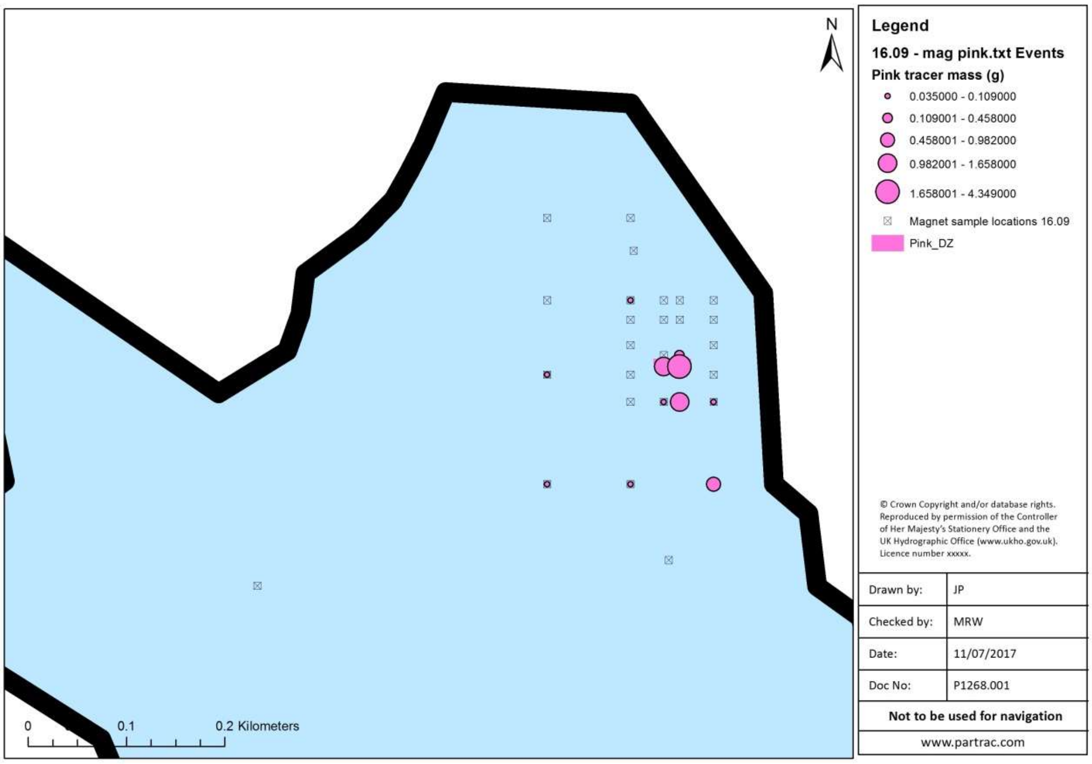

Figure 33. Geospatial distribution of pink tracer dry mass (g) on magnets ~ 24 hours following tracer release.

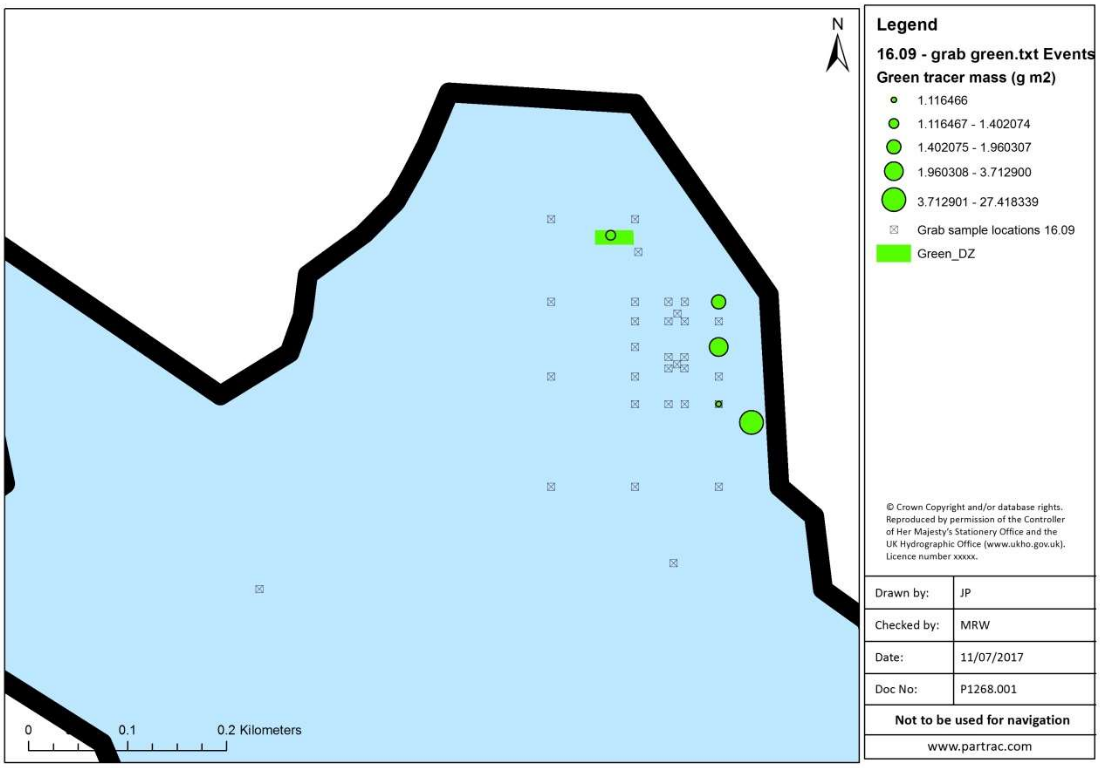

Figure 34. Geospatial distribution of green tracer dry mass (g m^{-2}) on the seabed (grab) ~ 24 hours following tracer release.

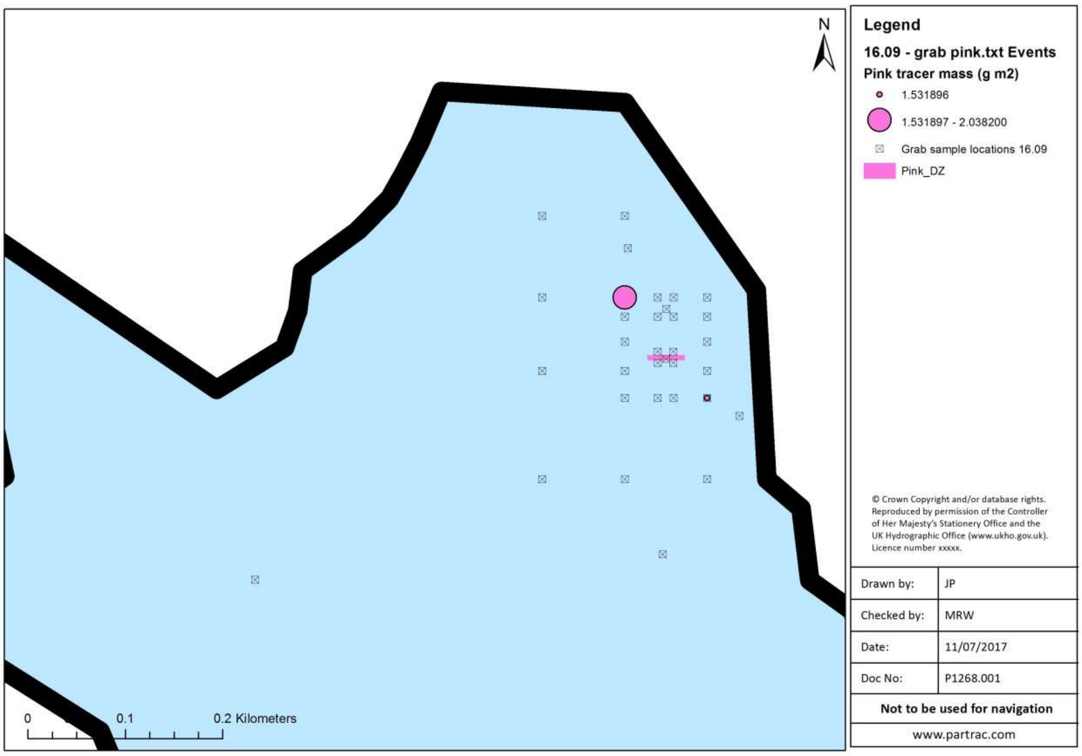

Figure 35. Geospatial distribution of pink tracer dry mass (g m^{-2}) on the seabed (grab) ~ 24 hours following tracer release.

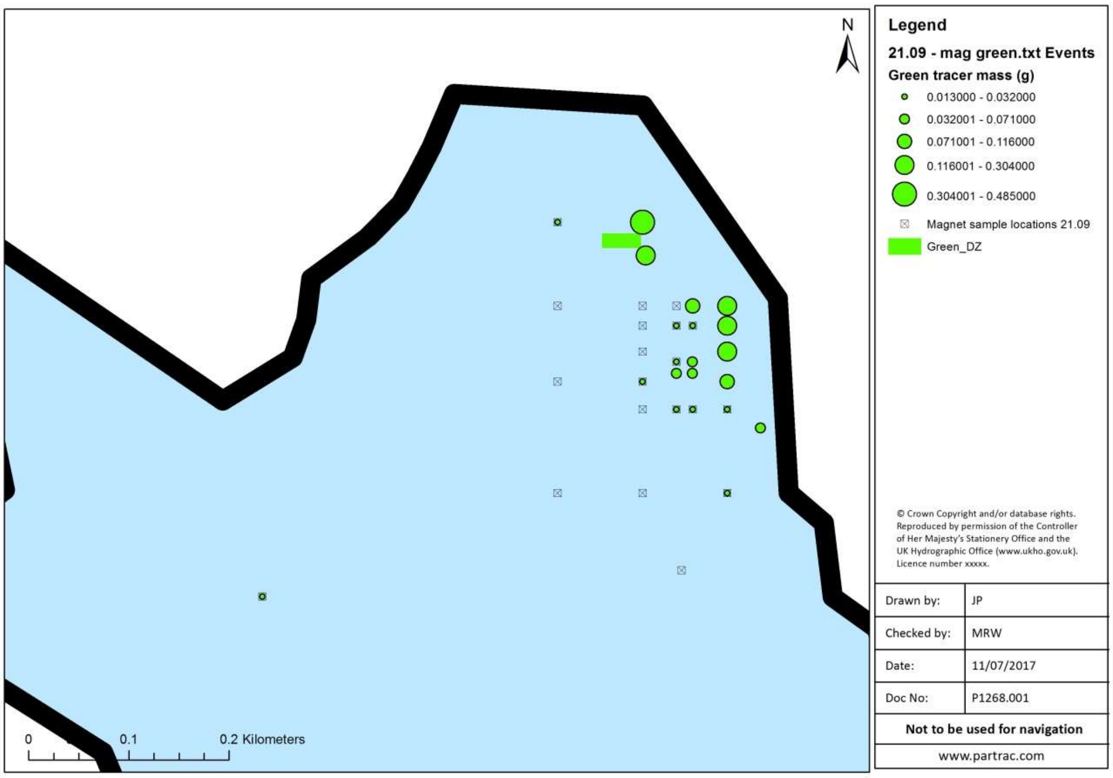

Figure 36. Geospatial distribution of green tracer dry mass (g) on magnets ~ 6 days following tracer release.

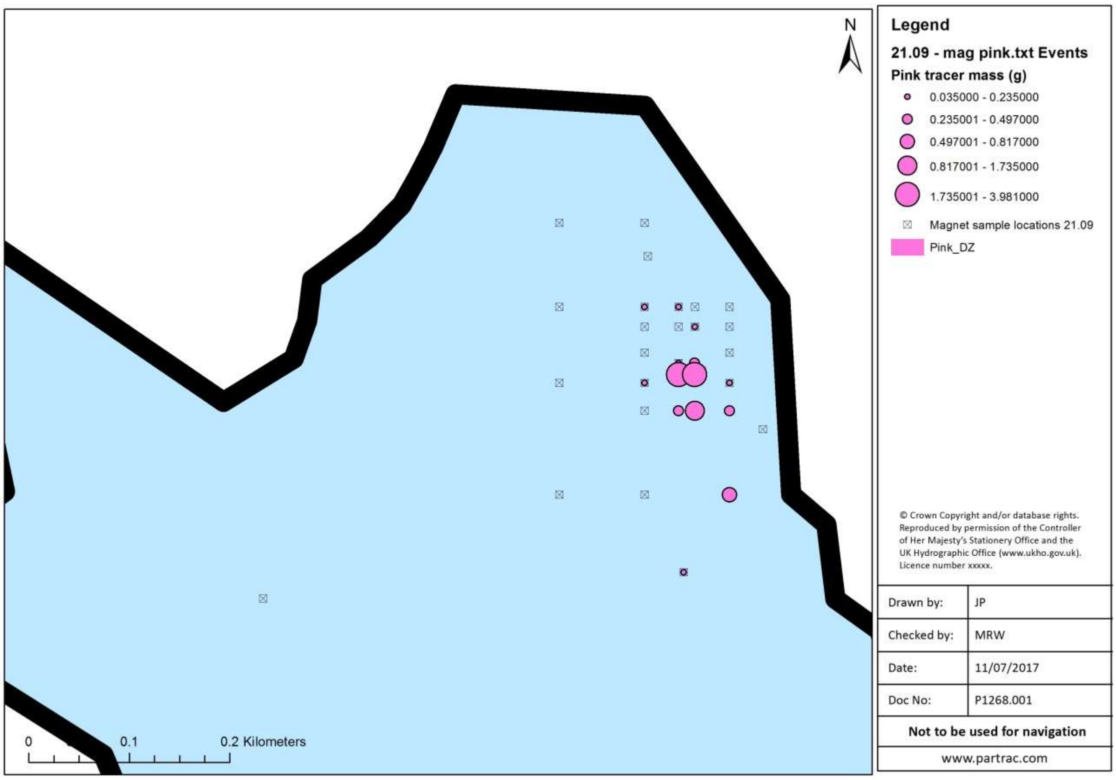

Figure 37. Geospatial distribution of pink tracer dry mass (g) on magnets ~ 6 days following tracer release.

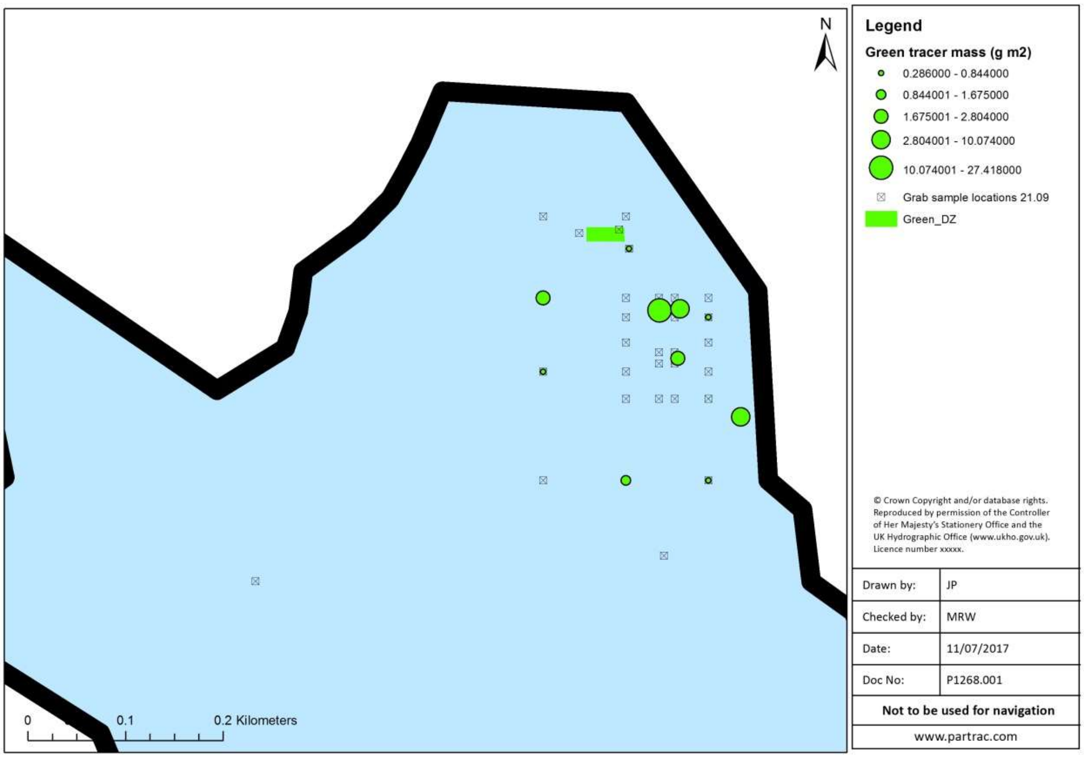

Figure 38. Geospatial distribution of green tracer dry mass (g m^{-2}) on the seabed (grabs) ~ 6 days following tracer release.

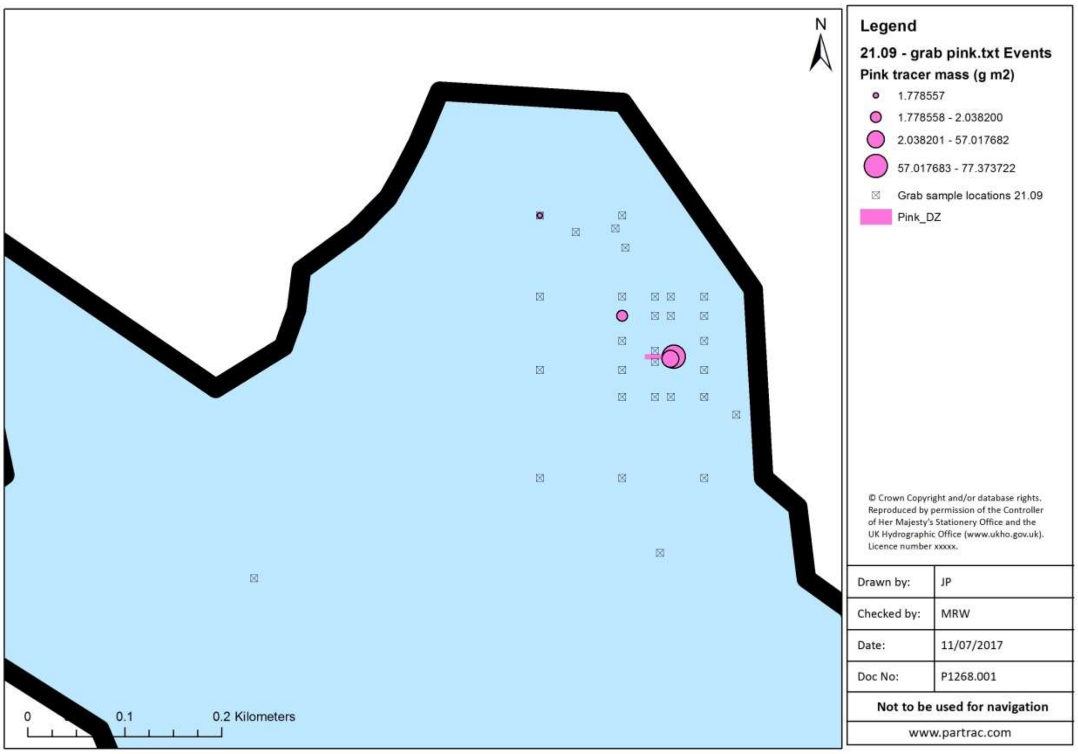

Figure 39. Geospatial distribution of pink tracer dry mass (g m^{-2}) on the seabed (grabs) ~ 6 days following tracer release.

5.3.2 The spatial distribution of tracer through time

From inspection of the tracer mass data captured from the sea bed grabs and the *in situ* magnets (designed to sample material travelling in suspension just above the bed) it is clear that both the amendment cap material and local silts have been distributed across the site following deployment (Figure 36- Figure 39).

Throughout the study period the tracer mass data shows relatively high tracer concentrations remain within the area of the two drop zones indicating the site, during the observation period, was (relatively) minimally disturbed (Figure 38 and Figure 39), however it is clear that some transport of material has occurred at and around both tracer drop zones.

The (green) tracer mass data demonstrates that native sediments, once mobilised, will be transported across and deposit upon the amendment cap. Further (through the use of two tracer colours), the study has unequivocally demonstrated that during deployment, and during the time following deployment, amendment cap material is distributed across the extent of the cap area and transported away from the cap area (i.e. the amendment material is 'lost' to the wider environment). The direction of transport of both native sediments (green tracer) and amendment cap material (pink tracer) generally appears to be multidirectional, though, despite the limited temporal data available, initial transport of both tracers is observed broadly along a SE – NW axis. Through time the direction of transport appears to become broadly westerly.

The pink tracer was recovered from both sea bed grabs and magnet samples during both sampling campaigns (conducted 1 day and 6 days following tracer release) (Figure 33, Figure 35, Figure 37 and Figure 39). The data reveals that the amendment cap material is distributed across the extent of the cap area and transported away from the cap both in SSE and NW directions relative to the deployment zone. Following 6 days, no tracer is found to the south of the deployment zone indicating transport in a NW direction relative to the deployment zone. Following 24 hours and 6 days after tracer release high concentrations of tracer were recovered from the magnets in the vicinity of the deployment zone indicating the amendment cap material is mobile and travelling in suspension across the site, though concentrations reduce as the distance from source (deployment zone) increases. Pink tracer is also found on the seabed, initially only at locations on the amendment cap but after 6 days at one location away from the cap.

The green tracer was found widely distributed across the site (Figure 32, Figure 34, Figure 36 and Figure 38). Post deployment, multidirectional transport was observed along an approximate SE – NW axis. Green tracer particles were found to the north and south of the amendment cap and at various locations across the cap. 6 days after release the tracer is still found to both the north and south away from the cap and within the extent of the capped area. As the study progressed the direction of transport broadly moves to a west south west direction. The *in situ* magnet data reveals significant distribution with high concentrations of tracer captured in the vicinity of the deployment zone steadily decreasing as the distance from source increases. Green tracer was also found on the seabed at a number of locations across the site. These data generally agree strongly with the *in situ* magnet data providing corroborating evidence for the direction of transport being along the SE – NW axis moving increasingly towards an E – W axis through time.

Due to site restrictions no onshore or intertidal sampling was completed, consequently no information regarding the onshore (transport in a broadly easterly direction relative to the two drop zones) is available.

5.3.3 Discussion

Two tracers were designed to match the hydraulic characteristics of the two materials (amendment cap material and native sediment) of interest within this study. To mimic real world processes the tracer designed to mimic the properties of amendment cap material (activated carbon) was processed in the same fashion as the AquaGate™[7] cap amendment material deployed as part of the original study. AquaGate™ uses an aluminum sulfate based controlled-release formulation to deliver the activated carbon in a controlled manner to the seabed. The amendment material (in this case, the pink tracer) is bound to a stone shaped limestone particle ranging in size from 0.6 – 0.9 cm in diameter. The high settling velocities of the limestone core aids in targeted placement as it enables material to be 'dumped' at a location relatively accurately, and with minimal advection. Following deployment, upon contact with water, the coating swells releasing the activated carbon material to the seabed. The results of this study clearly demonstrate that during deployment activated carbon amendment cap material is 'lost' to the wider environment. This is best, and elegantly, evidenced by the data captured from the *in situ* fluorometer and the *in situ* magnet data. The fluorometer data (Figure 31) shows that during deployment sediment tracer concentrations within the water column ranged from 13 – 236 μg L^{-1}. These high concentrations of tracer are attributed to material that was delivered to site loose (i.e. not properly bound to limestone particles and/or material which had become unbound during product transit). This evidence is corroborated by the data garnered during the first sampling campaign where distribution of tracer across the cap location and away from the cap is observed. No mass balance-type calculations have been undertaken within this report at this stage to assess the general magnitude of the quantity of lost material, but this could be done. It is considered that loss of amendment material during deployment would likely impact the efficacy of the cap and it would be judicious to investigate this process further during future deployments.

Sediment transport at the seabed generally occurs in response to the action of tidally generated currents and oscillatory wave action, which often occur in combination. Sediments are mobilised when the frictional drag (the 'bed stress'; τ_0) exerted by nearbed currents exceeds the submerged weight of particles, which act to retain particles on the bed; the stress at which sediment motion is first produced is called the 'critical bed stress', denoted $\tau_{0crit.}$ When $\tau_0 > \tau_{0crit.}$ sediments are mobilised. In addition to astronomically driven tidal currents, meteorological forcing (wind) may also generate additional currents which depending on the site potentially may be greater in magnitude relative to the astronomical currents. Wind blowing across a water body induces an approximately uniform shear stress across the water surface generating a wind-induced current ('wind drift') with a depth averaged velocity which is dependent upon the velocity profile and is a function of wind speed, water depth and surface conditions. In addition, set up and propagation of waves occurs when wind shear is persistent, and waves exert an oscillatory shear on the seabed sediments which can give rise to resuspension. Thus, wind on the water surface in shallow systems such as this can both promote resuspension (via the orbital velocities) as well as induce horizontal transport of sediments via the wind drift.

The study has illustrated well the two principal aspects of postulated sediment transport at the site: it has confirmed the existence of a sediment transport pathway for native sediment from the drop zone to the north

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[7] As part of the original study two different types of amendment material were deployed AquaGate™ and Sedimite. The amendment cap material AquaGate™ was simulated during this study.

of the amendment cap, to the cap. Further, due to the use of two uniquely identifiable tracers, a transport pathway for amendment cap material across and away from the amendment cap has also been confirmed. Multidirectional transport is observed, but some trends are apparent within the data and identifying the chief forcing's present at the site (i.e. wind, wave and current) responsible for the observed tracer distribution is useful.

The Hunters Point site is a shallow embayment comprising both intertidal and sub-tidal components, with a weak tidal signature (Figure 28 - Figure 30). The potential influence of wind in such environments, directly via wind drift and / or indirectly via orbital velocities, is proportionately greater. High westerly winds impact the bay during the afternoon periods (Table 10) and the data captured by the Aquadopp current profiler (Figure 28 - Figure 30), whilst limited in time, revealed clearly a flow reversal event during which a westward flowing (flood) tide on the morning (no wind) of 09/15 is almost wholly reversed by wind action on the afternoon of 09/21. Under such circumstances one might expect tracer concentrations to be multi-directional but in terms of gradients and trends to indicate higher concentrations centrally and to the east and southeast of the drop zones. This is quite clearly the case for the green tracer (and wind may thus be the principal driver of native sediment transfer onto the cap site), and evident also in the pink tracer dataset but less pronounced. The presence of tracer on the submerged magnets at and across both sites provides *direct evidence* of transport as suspension, and the data collected provide useful *process level information* on the mode of transport, the relative intensity for a given location and the direction of transport, all key elements of utility in assessing sediment transport at contaminated sediment sites. The deposition of upland sediments on the cap surface and the 'loss' of amendment material to the wider environment is postulated to reduce the efficacy of the cap for remediating contaminated sediments and the data reveals that both these processes are occurring. However, once again, no mass balance-type calculation has been undertaken within this report at this stage, but it is clear from tracer concentration measurements at each of the drop zones after 6 days that only a relatively small fraction of the bottom sediments is mobilised and transported, indicative of a generally stable or only weakly dispersive seabed system.

The objectives at this site were twofold: i) to assess the stability against wave and tidal erosion of AC cap amendment material and ii) to investigate natural deposition and recontamination from the surrounding sediments onto the cap surface. From these results it should not be concluded that the emplaced activated carbon amendment material is not re-suspended and transported offsite at any time, rather that offsite transport during the study period was not pronounced. Further, these results highlighted that the potential exists for offsite – onsite transport of native sediments to occur, however quantifying the quantity/mass of material flux is not achievable from this dataset, and was beyond the scope of the study. Caution should be used in offering any conclusions concerning the longer-term movements of the tracer due to the short duration of the actual demonstration, and the relatively quiescent conditions observed during the demonstration study, which was designed to show the utility of using sediment tracer studies to address site specific sediment transport questions. To address longer term transport questions, additional longer-term field studies would be recommended to assess the interaction of native sediments and amendment cap material through time, particularly under a greater range of forcing conditions (e.g. stormier periods, given the influence of wind). A study specifically designed for these purposes could provide information on the following scenarios postulated to reduce cap efficacy:

- The loss of amendment cap material through time to the wider environment.
- The deposition of native sediments on top of amendment cap material.
- The long-term transport trends (pathway(s)) of native sediments.
- The long-term transport trends (pathway(s)) of amendment cap material.

6. CONCLUDING REMARKS

This study was developed and undertaken to demonstrate the use of, and applied methodology, of dual signature particulate tracers to map the spatio-temporal distribution of fine sediments owing to concerns related to the remediation of contaminated sediment at Hunters Point, San Francisco. There is some support to the idea that the efficacy of an amendment cap may be impacted by factors such as type of cap material used, deployment methodology and the general interaction of these materials with the wider environment. A study using geological analogues (tracers) was designed to address these issues. The following concluding remarks aim to capture the chief findings of the study.

- Dual signature tracer, and associated sampling tools including the use of submerged permanent magnets and underway in situ fluorimetry, proved to be an effective tool to elucidate local sediment transport pathways.
- The use of two tracer colours enabled investigation of two hydraulically different material types, and two differing source zones.
- Local sediment transport was observed to be multi-directional which is a function of wind and current direction; however, the following transport pathways were elucidated:
    - transport of deployed amendment cap material across and away from the cap; and,
    - transport of native sediments onto the cap.
- Meteorological effects on the current direction/velocity are pronounced and are likely a key driver of sediment transport at the site.
- Both tracers were found dispersed across the site highlighting potential processes which may limit the efficacy of the amendment cap.
- Native sediments, once mobilised, are observed depositing on the cap surface, constituting a form of re-contamination, and this may have mitigation / management implications.
- Dispersion (loss) of cap material during deployment and following deployment is observed.
- The findings indicate that further study would be useful to better understand the transport of amendment cap material and the interaction of the cap with the surrounding sediments over longer timeframes.

We have provided some remarks detailing potential future sampling which we hope will be beneficial for NAVFAC’s ongoing and future remediation of contaminated sediments at HPNS.

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APPENDIX 1 SAMPLE LOCATIONS.

Sample ref.	GPS Location (WGS 84)	
	Latitude	Longitude
OB01	37.721647	-122.376509
OB02	37.721647	-122.37727
OB03	37.721647	-122.378031
OB04	37.722441	-122.378031
OB05	37.72298	-122.378031
OB06	37.723576	-122.378031
OB07	37.723576	-122.37727
OB08	37.723339	-122.377241
OB09	37.721095	-122.37692
OB10	37.720909	-122.380678
OB11	37.721228	-122.376211
UP01	37.72298	-122.376509
UP02	37.72298	-122.376819
UP03	37.72298	-122.376964
UP04	37.72298	-122.37727
BZ01	37.722583	-122.376821
BZ02	37.722583	-122.376964
BZ03	37.722501	-122.376964
BZ04	37.722501	-122.376821
AQ01	37.722654	-122.376509
AQ02	37.722839	-122.376509
AQ03	37.722839	-122.376819
AQ04	37.722839	-122.376964
AQ05	37.722839	-122.37727
AQ06	37.722654	-122.37727
SD01	37.722441	-122.376509
SD02	37.722243	-122.376509
SD03	37.722243	-122.376819

SD04	37.722243	-122.376964
SD05	37.722243	-122.37727
SD06	37.722441	-122.37727

APPENDIX 2 GENERAL TECHNICAL SPECIFICATION OF THE FLUOROSENS SPECTROFLUORIMETER

Main Specifications

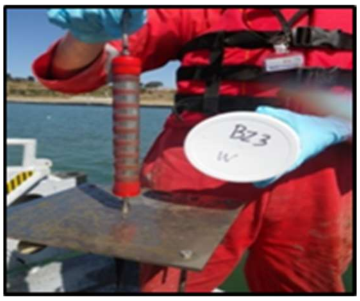
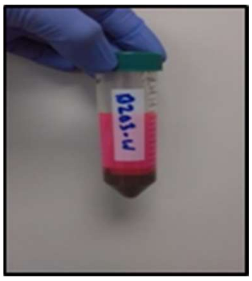
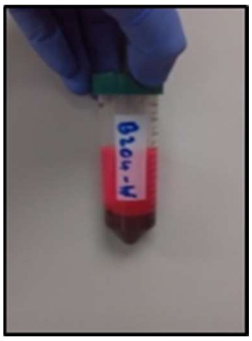
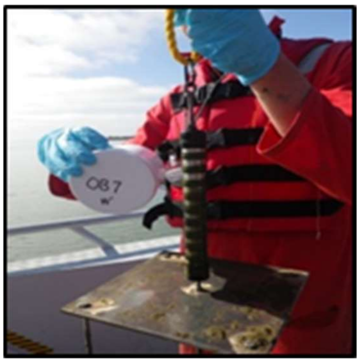
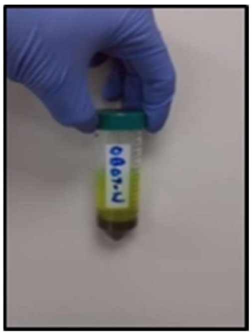
Device	**Specifications**
Excitation Sources	
Type	150W Xenon Arc Lamp
Spectral Range	200nm - > 1200nm
Adjustment	Factory aligned
Focus	Factory aligned
Intensity Stability	< 0.1%
Igniter	Auto-ignition of arc on instrument switch-on
Monochromators	
Type	Czerny-Turner
Focal Length	300mm
F/#	4 or faster
Wavelength Range	Zero-order to 1500nm(mechanical with 1200g/mm grating)
Wavelength Accuracy	0.2nm @ 1200g/mm
Wavelength Repeatability	0.1nm @ 1200g/mm
Stray Light Rejection	1:10^5
Slits	Continuously variable from 10μm to 3mm Motorized bi-lateral knife edge
Grating Mount	Kinematics single grating as standard, up to three gratings as options
Excitation Mono	Blaze @ 300nm, 1200g/mm, peak eff, >60%
Emission Mono	Blaze @ 500nm, 1200g/mm, peak eff, >60%

Sample Chamber	
Size	Large
Accessories	See below
Optics	Factory aligned

Lid	Slide, interlocked to PMT shutter
Front	Removable Panel
Detectors	
Photomultiplier	Hamamatsu R1527
Spectral Range	185 – 680 nm
Operating Mode	Photon counting
Dark Counts (at +25℃)	< 100cps
Reference Si Photodiode	
Type	UV100-L
Spectral Range	185 – 1100 nm
Operating Mode	Analogue
Area	1 cm^2
Data Acquisition	
Photon Counting Input	to 100M cps
Collection	Add/Subtract function by TTL control
Analogue Inputs	Ref. Photodiode
Abs. Photodiode (Option)	
NIR Photodiode (Option)	
Sample Temperature (Option)	

General Instrument	
Water Raman S/N	2500:1 or better
Optical Path Light Tightness	Single Photon guaranteed
Computer Interface	USB2.0
Power	AC 220V/5A, 50Hz
Compliance	CE
Low voltage Directive	
21CFR11	
Lead Free Electronics	
Footprint	0.83×0.6 m^2

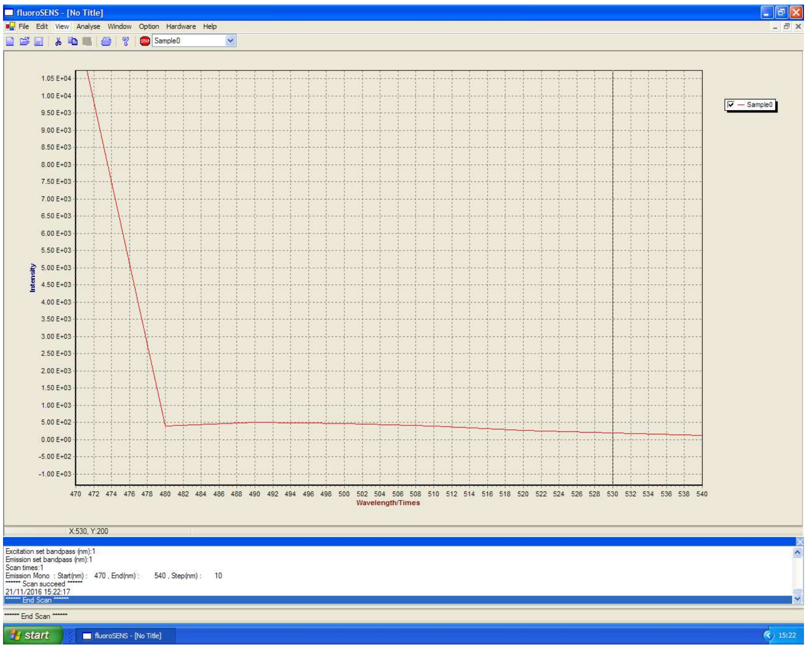
APPENDIX 3 FURTHER PHOTOGRAPHIC EXAMPLES OF THE TRACER ENUMERATION PROCESS 'FROM FIELD TO LABORATORY'.

Sample	Field photo	Laboratory photo	Derived tracer mass (g)
DZO1 – Pink Sed Dup			**1.317** **(Please note in Table 10 this data is presented as an area density metric (g m^{-2}))**
BZ03 - W			**1.658**
BZ04 - W			**4.349**
OB07 - W			**2.321**

APPENDIX 4 AN EXAMPLE OF THE FLUOROSENS SPECTROFLUORIMETER USER INTERFACE

Sample AQ01 – W

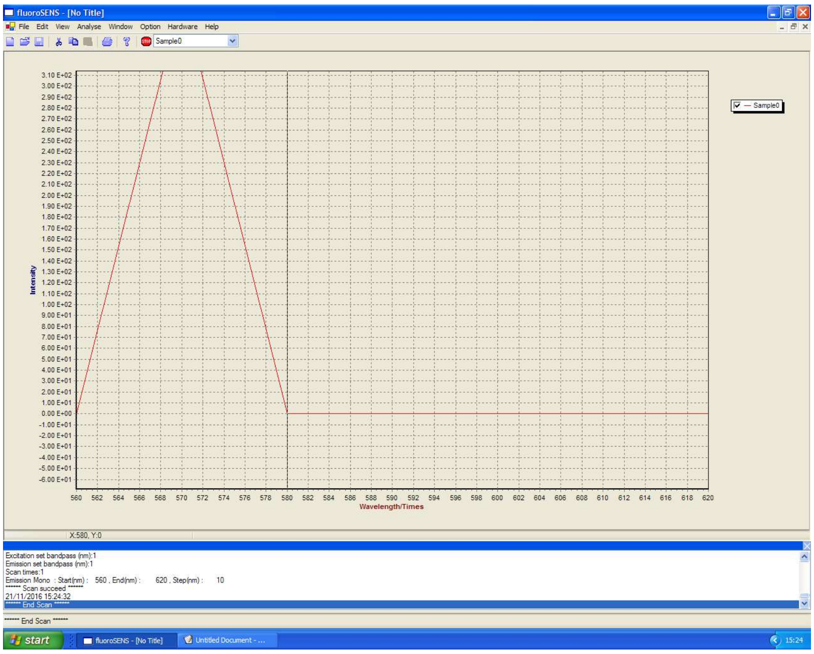
Emission spectra captured for green tracer.



```
Excitation set bandpass (nm):1
Emission set bandpass (nm):1
Scan times:1
Emission Mono  : Start(nm) :   470 , End(nm) :      540 , Step(nm) :      10
****** Scan succeed ******
21/11/2016 15:22:17
****** End Scan ******

****** End Scan ******
```

Emission spectra captured for pink tracer.

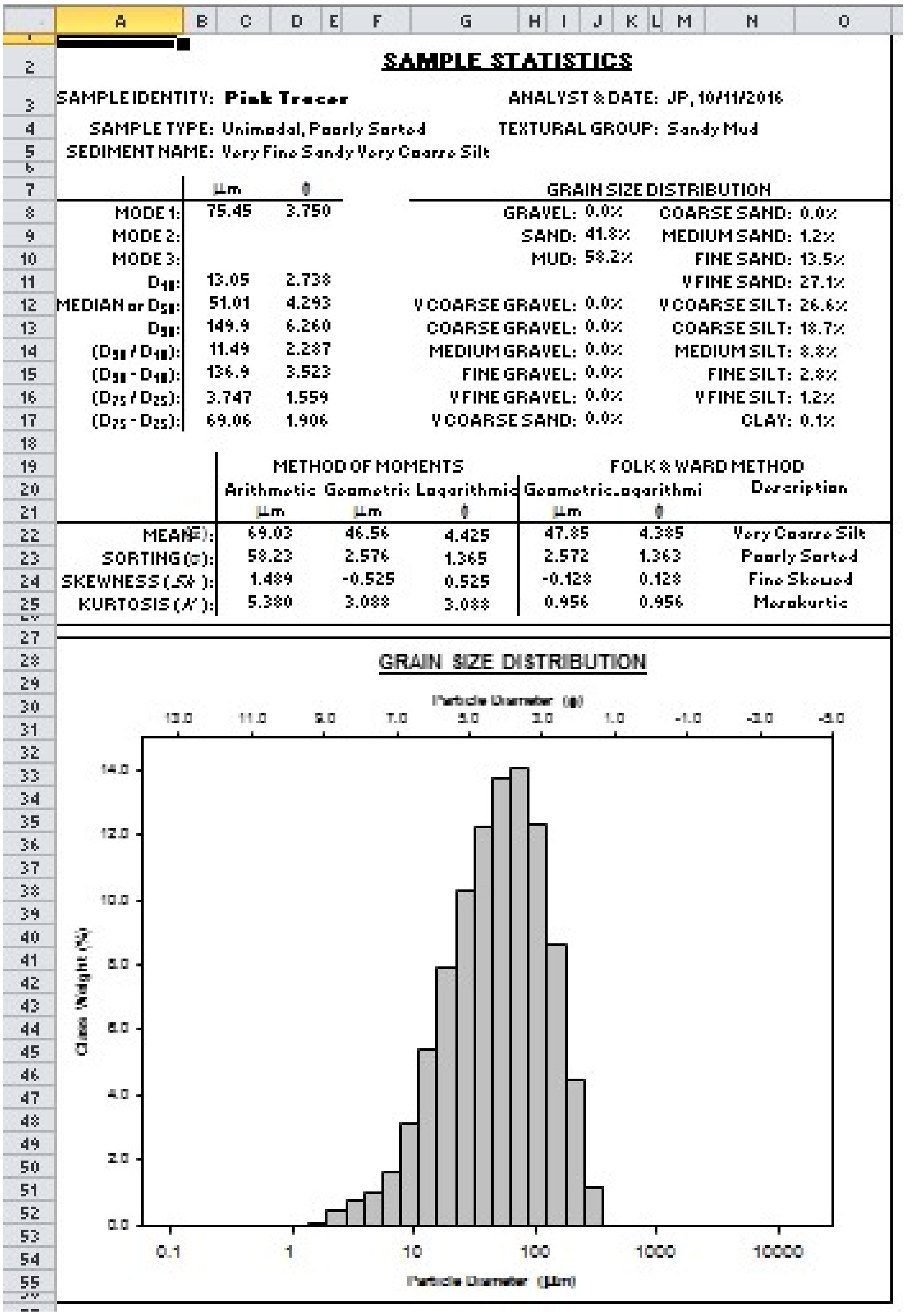


```
Excitation set bandpass (nm):1
Emission set bandpass (nm):1
Scan times:1
Emission Mono  : Start(nm) :   560 , End(nm) :      620 , Step(nm) :      10
****** Scan succeed ******
21/11/2016 15:24:32
****** End Scan ******

****** End Scan ******
```

APPENDIX 5 GRADISTAT STATISTICS

The particle size distribution of the tracer manufactured to mimic the properties of activated carbon analysed using Gradistat.



SAMPLE STATISTICS

SAMPLE IDENTITY: **Pink Tracer**
ANALYST & DATE: JP, 10/11/2016
SAMPLE TYPE: Unimodal, Poorly Sorted
TEXTURAL GROUP: Sandy Mud
SEDIMENT NAME: Very Fine Sandy Very Coarse Silt

	μm	φ
MODE 1:	75.45	3.750
MODE 2:		
MODE 3:		
D_{10}:	13.05	2.738
MEDIAN or D_{50}:	51.01	4.293
D_{90}:	149.9	6.260
(D_{90} / D_{10}):	11.49	2.287
(D_{90} - D_{10}):	136.9	3.523
(D_{75} / D_{25}):	3.747	1.559
(D_{75} - D_{25}):	69.06	1.906

GRAIN SIZE DISTRIBUTION

GRAVEL:	0.0%	COARSE SAND:	0.0%
SAND:	41.8%	MEDIUM SAND:	1.2%
MUD:	58.2%	FINE SAND:	13.5%
		V FINE SAND:	27.1%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	26.6%
COARSE GRAVEL:	0.0%	COARSE SILT:	18.7%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	8.8%
FINE GRAVEL:	0.0%	FINE SILT:	2.8%
V FINE GRAVEL:	0.0%	V FINE SILT:	1.2%
V COARSE SAND:	0.0%	CLAY:	0.1%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic	Geometric	Logarithmic	Geometric	Logarithmic	Description
	μm	μm	φ	μm	φ	
MEAN ($\bar{x}$):	69.03	46.56	4.425	47.85	4.385	Very Coarse Silt
SORTING (σ):	58.23	2.576	1.365	2.572	1.363	Poorly Sorted
SKEWNESS (Sk):	1.489	-0.525	0.525	-0.128	0.128	Fine Skewed
KURTOSIS (K):	5.380	3.088	3.088	0.956	0.956	Mesokurtic

GRAIN SIZE DISTRIBUTION

ESTCP Project ER201214 Appendix 3

Partrac Tracer Study Standard Operating Procedure (SOP)

PARTRAC

ESTCP

Particle Tracking Field Study

Standard Operating Procedure

Appendix 3

Sept 2017

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DOCUMENT CONTROL

Version History					
Version	Date	Prepared by	Reviewed by	Approved by	Approved as
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APPENDIX 3 PARTICLE TRACKING FIELD STUDY

Standard Operating Procedure (SOP)

Particle tracking is a useful tool capable of providing information which aids in the protection of ecological habitats, supports the development of sediment management plans, and provide baseline data to inform sediment transport models, important for long term planning and development at the coastal scale. This report identifies 6 key steps, formed into a methodological framework, critical to successful implementation of a practical sediment tracing study, using introduced sediment tracers. This framework provides a standard operating procedure (SOP) for robust tracking of actively transported sediments and should be considered regardless of study aims and objectives, environment or study context. The methodological framework aids decision making, project and budget planning, and assists the practitioner, manager or interested party at the planning stage.

Sediment, including both water - and wind transported material, are a ubiquitous component of coastal ecosystems and is considered crucial to their management (Kay and Alder 1999; Walker et al. 2001; Hamilton and Gehrke 2005). Transport of sediment and associated nutrients, contaminants and microbes, can create a range of environmental issues at both the sediment source and sink (Droppo 2001; Gillan et al. 2005; Cordova-Kreylos et al. 2006). Increasingly, it is recognized that it is important to understand the pathways, processes and fate of actively transported material, in order to enable appropriate environmental management and mitigation strategies to be developed (Apitz et al. 2005; Heathwaite et al. 2005; Magar and Wenning 2006). To garner information on the origin of sediment, its associated transport pathway, and eventual fate, a particle tracking technique may be utilized.

Particle tracking involves the use of natural and artificial tracer materials with an identifiable label (sometimes referred to as a tag or signature(s)) through which they can be unequivocally identified when introduced to the environment (Drapeau et al. 1991). Sediment tracing can be used to identify point sources of sediment (Cromey et al. 2002; Magal et al. 2008; Guymer et al. 2010), elucidate transport pathways (Polyakov and Nearing 2004; Kimoto et al. 2006a; Carrasco et al. 2013), and assess zones or areas of accumulation / deposition (Kimoto et al. 2006b; Collins et al. 2013). Furthermore, the methodology, if applied correctly, provides quantitative data regarding the volume of sediment in transit (Ciavola et al. 1998), and the transport rate (Ingle 1966; Ciavola et al. 1998; Vila-Concejo et al. 2004a). In addition, the data obtained from sediment tracing studies are useful for the development, calibration and validation of numerical models (Cromey et al. 2002; Merritt et al. 2003; Papanicolaou et al. 2008).

Recent developments in tracer design and methodological approach have revolutionized the technique (Black et al. 2007), leading to novel application and commercial enterprise within the sector. A unified methodological approach (SOP) is required to provide consistency, given increasing application of the tracing technique to real-world sediment management problems. A robust methodological framework should provide an effective sequence of steps that should be considered, regardless of choice of tracer material, environment or study context. Herein, the most appropriate steps and sequence of the particle tracking approach are proposed. The crucial elements of each step are reported.

Any tracing study should begin with an assessment of the problem or issue that is to be investigated. Once study aims and objectives have been determined, six methodological steps can ensure that a robust, practical tracing study is conducted (see Figure 1).

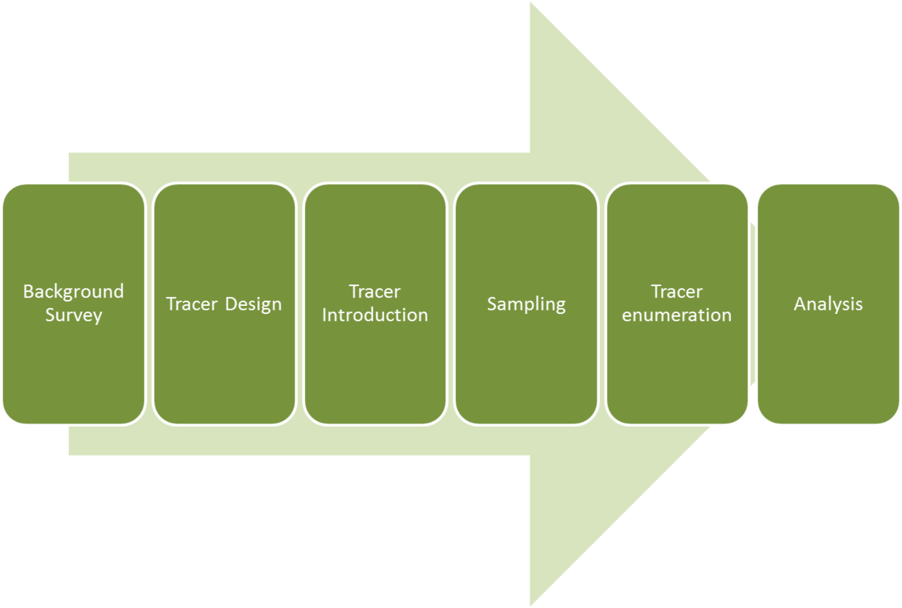

Figure 1. The six key methodological steps to ensure a robust tracing / tracking study is conducted.

The six key steps identified are: 1) perform a background survey; 2) design a tracer by matching the tracer properties to those of the native sediment; 3) introduce the tracer to the environment; 4) post introduction sampling and monitoring; 5) enumerate the mass of tracer in environmental samples; and 6) analysis of results. The detailed requirements of each step are outlined below.

Step 1: Perform a background survey

The purpose of a background survey is threefold: 1) provide a comprehensive assessment of the properties of the native sediment on which tracer design can be based; 2) determine the presence / absence of sediment or anthropogenic particles within the study region with the same or similar characteristics as the proposed tracer; and 3) evaluate environmental baseline readings by testing any sampling techniques proposed. This can only be assessed through sampling, and testing, of the environmental sediment. Sediment samples (e.g., cores, grabs) should be collected throughout the study area, focusing on potential source areas, transport pathways and deposition zones. It is recommended that > 3 core samples are collected from each (potential) distinct sediment zone per km^2 within the study area (e.g., upper and lower foreshore, areas of accumulation). Additional samples may be required if statistically significant variation in sediment hydraulic properties is found. Alternatively, if heterogeneous sediment characteristics are found (or known) throughout the area of interest, it is possible to reduce the volume of samples collected whilst still maintaining statistical significance using a random sampling technique (Wang et al. 2012). The sediment within each sample should be analyzed for the physical characteristics considered critical to sediment transport, such as particle size distribution, specific gravity (particle density) and settling velocity (Dyer 1986). This information enables tracer design or tracer selection to be based upon the physical characteristics of the native or target sediment. The bulk density of the native sediment should also be measured, to help determine the appropriate quantity of tracer required.

At this stage, in order to inform deployment methodologies and sampling strategy, where possible a qualitative geomorphological site assessment should be made (e.g., to consider evidence of erosion, beach profiles, anthropogenic influence and management), as this may provide additional information regarding possible sediment transport rates and pathway(s) within the study area. In addition, where possible, relevant data regarding the forcing mechanisms should be collected at the site (e.g., measurement of current velocity data, beach profiles, historic oceanographic data). The data and qualitative information generated from an assessment of this kind are eminently useful when considering study design i.e. tracer deployment locations and sampling grid layout.

Step 2: Tracer design and matching the tracer to the native sediment

A tracer that matches the native sediment in terms of its hydraulic attributes must be designed. Two hydraulically-matched, or hydraulically equivalent, sediments will be cycled (eroded, mobilized, transported, deposited) in the same way by a fluid flow (Dyer 1986). Matching the tracer hydraulic properties to the native sediment is straightforward; samples collected within the background survey and the manufactured tracer are tested for characteristics that influence transport, namely size distribution, density and settling velocity, and the results statistically compared. Commonly the results of this similarity matching are compared and the percentage difference reported (e.g., d_{50} tracer / d_{50} native). Permissible differences between the hydraulic characteristics of the native sediment and tracer have been outlined in the literature (Black et al. 2007). The median grain size (or modal grain diameter) of the tracer should be within ± 10 % of the native sediment (White and Inman 1989), and the specific gravity (particle density) should be within ± 6 % (Black et al. 2007), in order to limit the effects on field observations.

Matching is particularly critical when tracing the finer sediment fractions (< 63 μm) (Louisse et al. 1986) but it is also more challenging given their cohesive nature (Brown et al. 1999), and the hydraulic matching process may be based upon different precepts to those of coarse sediment. Unlike sand and gravel particles, within aquatic environments, cohesive sediment is transported primarily as flocs (Droppo 2001). Thus it is critical that any tracer mimicking cohesive sediment must be able to flocculate (on its own), and thereby resemble a natural floc aggregate (Spencer et al. 2011b), an approach called direct floc mimicking. Unfortunately, tracers able to mimic a floc are not widely available, not least because it is difficult to establish that the tracer flocs behave through time in the same way as native flocs, in terms of aggregation and disaggregation processes (Louisse et al. 1986; Spencer et al. 2010; Spencer et al. 2011b). A practical approach termed floc tagging which requires the tracer particles to have similar hydraulic characteristics (i.e. size, density and settling rate) to one or more of those constituent sediment size fractions found within naturally flocculated material (Spencer et al. 2010) facilitates floc tracing by directly labelling them (Fig. 2). For this approach, the key information is the particle size distribution (following acid digestion e.g., Laubel et al. (2003)) of the native floc. As silts are by definition < 63 μm in size, a tracer of size e.g., 25-55 μm would be suitable for the majority of projects where flocking is a consideration. Figure 2 illustrates the principle of floc tagging.

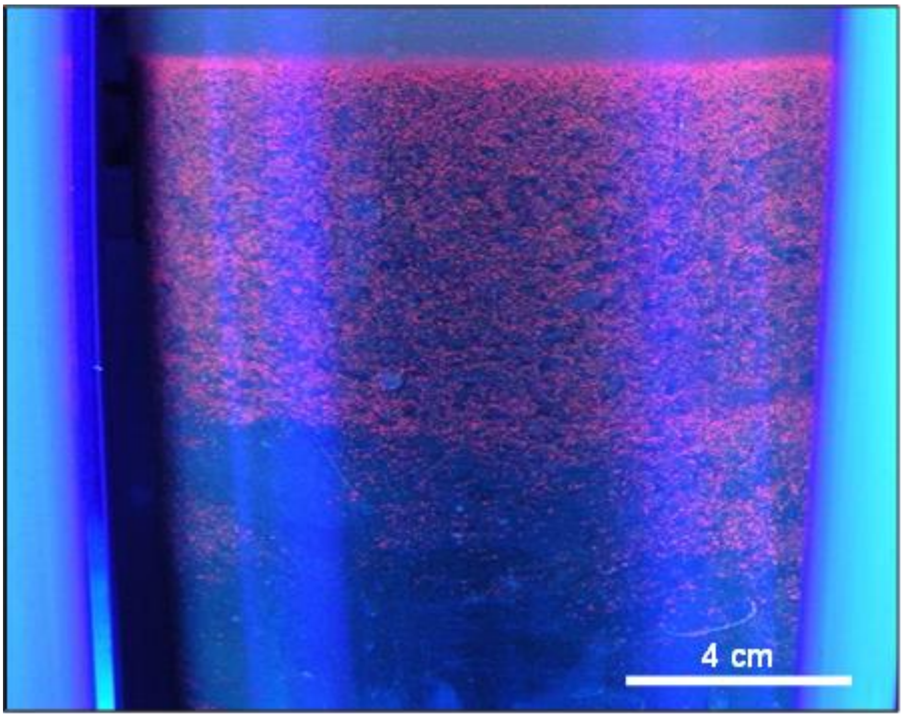

Figure 2. The image captured under ultraviolet illumination shows a core of cohesive peat sediment mixed with a fluorescent pink silt tracer. The hydraulically matched tracer has been thoroughly mixed with the peat and left to settle. The image demonstrates that the hydraulically matched tracer and peat, due to the similar hydraulic characteristics of one or more of the constituent sediment particles have a similar settling rate, resulting in the tracer flocculating with, and becoming entangled with, peat material. Thus the peat flocs have been 'tagged' with an identifiable 'signature' enabling cohesive sediment transport to be assessed. The tags will ensure that ensuing transport processes may be tracked and transport pathways delineated. Image provided by Partrac Ltd.

Step 3: Tracer introduction

Tracer introduction methodologies are project-specific, but for all applications it is important that the tracer particles are introduced into, or onto, the area of interest with minimal loss and redistribution. To ensure representative data are obtained, it is critical that the tracer is introduced throughout the active transport layer, if this is known or can be estimated. There are two primary methods of tracer introduction: 1) the foregoing introduction method (FIM) where tracer is introduced to the environment at one point in time; and the continuous introduction method (CIM) which involves continuously introducing tracer to a point at a steady rate.

For studies which require that the tracer is deployed to the surface sediment layer, where there is access to the surface sediment layer tracer should be introduced in a shallow trench (< 10 cm deep). Ideally, tracer should be introduced to the environment combined with native sediment in a 50:50 ratio, to aid incorporation and ensure that no redistribution of the tracer particles by aeolian transport occurs. This is particularly important for cohesive sediment projects. In addition, the tracer should be mixed with a small amount of (locally derived) water prior to introduction on the surface, or to a trench. Adding a small amount of detergent (< 5 %) to the tracer / water admixture reduces the surface tension properties of the particles, a factor which is generally helpful to stop tracer being transported on the water surface due to surface tension.

When introducing coarse tracer to a sub-aqueous bed it is generally recommended, tracers should be deployed through a subsurface pipe within shallow water studies (< 10 m), and using dissolvable bags within deep water studies (> 10 m). In certain cases (e.g., to study entrainment, mobilization or erosion of deposited silts), it is necessary to introduce the tracer onto a sub-aqueous bed without loss of material to the water column. To do this, tracer should be encapsulated in ballasted ice, as this provides a secure, robust vehicle able to deliver tracer to the bed. The colder the blocks can be made generally the better they perform as this increases the timeframes for encapsulation, enabling tracer introduction to greater depths.

Where studies are solely investigating suspended sediment transport (using fine sediment tracers), there is often no requirement for the tracer to be deployed to the bed. The tracer can be deployed to simulate a floc or plume of suspended sediment directly by sub-surface flushing of tracer down a tube in suspension. It is recommended that the tracer is pre-mixed with salt or fresh water, to create a high- concentration tracer slurry which can be manoeuvred easily with trowels or shovels. It is recommended that high flow water pumps, able to create a turbulent field, are used to ensure complete disaggregation of the tracer particles within the slurry, as the slurry is deployed to the receiving water.

Step 4: Sampling

Recovering tracer for enumeration or subsequent measurement, or determining the presence of tracer *in situ*, requires spatial and temporal sampling. Due to the dynamic nature of sediment transport within all environments, dilution and dispersal of the tracer to beyond / below the detection limit can occur. Therefore an adaptive sampling regime which considers sampling in the entire near field, mid-field and far field- relative to the tracer introduction locality, and incorporates a strategy for recurrent sampling (through time), is desirable. Poor sampling strategies can lead to flawed conclusions, the most common being the conclusion that tracer is not present, whereas it might simply be that it has not been detected. The sampling step is an inherently critical part of the sediment tracing methodology.

By far the most popular sampling tool within tracing studies is the collection of sediment cores. When collecting a core sample, it is critical to sample through to the base of the active sediment layer, to maximize the chance of tracer recovery (following mixing), and to determine the mass (volume) of sediment in transport, investigate burial trends and calculate sediment transport rates through the environment. If the thickness of the active layer is unknown, dual signature tracers can be used as a horizon marker to ensure the sample has been collected through the active layer. Other tools commonly used to sample sediment in coastal environments include sediment grab samplers, sediment traps, water samplers, and *in situ* magnetic sampling. The use of sensor based systems (e.g., field deployable fluorometers) has found practical application in the *in situ* measurement of tracer. As a result of the surface disturbance created during active sampling, samples should only be taken following a transport event.

Sampling is either spatially or temporally driven. Spatial sampling (also referred to as Lagrangian sampling), is where identified sample locations are sampled only once, whereas temporal sampling is where identified sample locations are sampled repeatedly over time. Predominantly spatial sampling is employed when sampling coarse sediment that have been transported as bed load (often associated with beach face, longshore transport type studies), whereas temporal sampling is most commonly used to sample sediment transported in suspension. It is recommended, where possible, to incorporate a combination of the two utilizing passive sampling techniques to inform appropriate sampling strategy (e.g., magnetic susceptibility surveys or ultra violet (UV) light inspection surveys). These techniques enable sampling strategies to be adaptive rather than reactive.

A combination of random and systematic sampling techniques is recommended within tracing studies. Where no information is available regarding the direction of transport, practice dictates that a systematic sampling grid is used usually arranged to cover all potential transport directions from the point where tracer was introduced. The samples are collected in a given order relative to the first collection point, requiring the use of systematic sampling zones. However, where transport direction is known *a priori*, the use of systematic grids have the potential to introduce bias, and a more complex approach which uses both random and stratified sampling may be more appropriate. Further, temporal sampling does not account for episodic or event driven sediment transport and therefore a combination of spatial and temporal sampling is preferable. In practical terms sampling grid layout and size are often dictated by landscape features, man-made structures, morphology, and budgetary and time constraints. As a result, and given that within the majority of studies the dispersion rates of tracer are unknown prior to deployment, the collection of measurements at intermediate locations along the transport pathway, in addition to the target receptor, is also desirable. To improve upon any tracing study, simply increasing the sample scope in terms of both the spatial and temporal variability provides greater information regarding the distribution of tracer particles throughout the study area.

Remote Sensing/Passive Sampling

Semi quantitative qualitative sampling techniques (such as submersible fluorescence imaging, and night time UV lamp surveys are driving innovation within tracing studies. These techniques should be used to monitor the spatial distribution of tracer particles in a non-intrusive manner, prior to using intrusive sampling techniques to quantify tracer content within the sampling grid. The application of new technologies (e.g., Unmanned Aerial Vehicles (UAVs), Remote operated Vehicles (ROVs) and drone technology) has the potential to increase the spatial coverage of passive sampling techniques, thus reducing the requirement for intrusive sampling. Techniques such as these could potentially increase the spatial and temporal resolution of studies without significantly increasing the associated time and cost of laboratory analysis of sediment and water samples and would be considered a significant step forward within the field of sediment tracing utilising introduced tracers.

Step 5: Tracer measurement and enumeration

The ultimate aim of any tracing study is to determine the tracer concentration (mass per unit volume), or dry mass of tracer from within each sampling location or time step. The preferred measurement method should be able to accurately analyze a large number of samples within a short period of time. This allows for many more samples to be collected from the field and analyzed within a given resource budget, a fact which substantially improves many tracing studies.

Step 6: Analysis

Tracer measurement or enumeration provides point-specific tracer mass/concentration data at a single instant in time. These data can be used to determine tracer presence/absence, map sediment transport pathways and deposition patterns and determine sediment transport rates and the volume of sediment in transit. As sediment tracing is fundamentally an empirical, evidence-based approach, it is important to consider all lines of evidence gathered during sampling (e.g., both qualitative and quantitative data sets).

The direction of transport is determined via the quantity of tracer recovered from the sampling grid, best described as a percentage of the total tracer mass recovered, not the total tracer mass deployed (e.g., > 50 % of tracer recovered was found to the south of position X). As transport of sediment is often multidirectional, the dominant transport pathway, and receptor area, is determined by the presence of the greatest quantity of tracer. However, care must be exercised, as these results only reflect the conditions observed within the study.

A principle of tracing studies is normalization of the data to represent tracer mass/concentration within the surrounding area (White 1998; Vila-Concejo et al. 2004a; Black et al. 2007). This was first described by Inman and Chamberlain (1959b) who concluded that the mass of tracer recovered from a sample point (S_x) is representative of the mass of tracer in a rectangular shape around the point of the sample, with the boundaries of the rectangle being midway between sample points. To compute the tracer content within each area of the sample grid, the volume (V_{ri}) of the area (A_{ri}) represented by each core sample can be calculated:

$$V_{ri} = A_{ri} h \tag{1}$$

Where h is the height of the tagged layer.

A multiplying factor (T_{mi}) used to extrapolate the tracer concentration of the core (C) to the entire represented area can then be calculated by dividing C by the volume of the core (C_{vol}).

$$T_{mi} = \frac{C}{C_{vol}} \tag{2}$$

The tracer concentration of the represented area (M_i) is then calculated by multiplying the T_{mi} by the representative volume.

$$M_i = T_{mi} V_{ri} \tag{3}$$

Extrapolation, though often necessary, must be used with caution and the sampling frequency (i.e. distance between sample points) must be appropriate (Black et al. 2007).

The transport rate of tracer through the environment can be described through the advance of the tracer front and determination and tracing of the mass center of tracer distribution (e.g., White and Inman (1989); Vila-Concejo et al. (2004a); Carrasco et al. (2013)). In this approach the average transport velocity is calculated from the distance moved by the mass centroid of tracer divided by the time between introduction and sampling (White 1998). Assuming that all samples collected have been sampled throughout the active transport layer, following the enumeration of tracer content from each sampling point, the location (Y) of the mass center of the tracer distribution can be determined:

$$y = \sum M_i D_i / \sum M_i \tag{4}$$

Where Mi is the mass of tracer at each grid node and the average grain mass (usually obtained using mean grain size values from the area of interest), and Di is the distance from the introduction point.

Additional Control Measures

During a tracing study a number of quality control measures should be undertaken to ensure the study objectives are met. These measures may include but are not limited to the following:

Calibration of Equipment

The only items of equipment that typically need to be calibrated in a conventional sense are the spectrofluorimeters used for *in situ* sampling and for laboratory analysis of tracer dry mass/concentration. Calibration for *in situ* sampling will comprise a series of laboratory tests in which the mass concentration of tracer is known and varied, and the response of the spectrofluorimeter recorded. Error analysis will provide boundaries on the estimate of true values. A similar procedure will be used where spectrofluorimeters are used for tracer enumeration, but neat dye will be used to support the calibration process.

The (use of) magnets for tracer collection require no calibration but it is generally useful to deploy for 24 hours prior to release to assess quantitatively the presence of magnetic (non-fluorescent) particulates within the system. The capture efficiency of the magnets under differing tracer concentrations and flow conditions has been investigated in the laboratory and reported in the ESTCP Final Report (Section 6).

Quality Assurance Sampling

As part of the quality assurance (QA) program a number of QA samples should be utilized. During any field efforts a number of field duplicate samples should be collected (1 for every 20 samples collected). In addition the laboratory analysis of tracer is associated with a set of QA samples, including blanks (1 run every 10 samples tested), spikes (1-5% of total sample numbers) and sensor drift checks (every morning and evening). Where particle size and particle density analyses are run, reference materials data are provided with all results.

Decontamination Procedures

Equipment retrieved from the seafloor with contaminated sediment should be rinsed with surface water. During sample collection, all magnetic particles are either bagged or jarred, and any residual sediment material collected from the site will be placed into containers for proper disposal after the survey. Sediment collection equipment will be decontaminated between sampling sites using standard operating procedures including surface water washing followed by a clean water rinse. Laboratory toxicity testing has shown there is no toxicity issues associated with the tracer material (see Appendix 4 Tracer Toxicity Testing Report).

Sample Documentation

A standard labelling system should be used to clearly identify samples and to track them from the point of collection to the generation of results data. The system should isolate the following parameters:

- Location
- Type (magnet/water/sediment)
- Platform (marine/vessel)
- Primary/Duplicate/Calibration/QA
- Depth
- Time
- Date

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ESTCP Project ER201214 Appendix 4

Partrac Tracer Biological Effects (Toxicity) White Paper

US Navy - ESTCP

Project Number: ER-201214

Demonstration of fluorescent magnetic particles for linking sources to sediments at DoD sites

Partrac Tracer Material Toxicity 'White Paper'

Version 2b, April 2014

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DOCUMENT CONTROL

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Changes from the Previous Version	
n/a	Original version
V02	Inclusion of ecotoxicology test data
V02b	Correction to concentration units and inclusion of additional method tables, results figures, and references for bioassay section

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CONTENTS

1. INTRODUCTION

1.1 Background

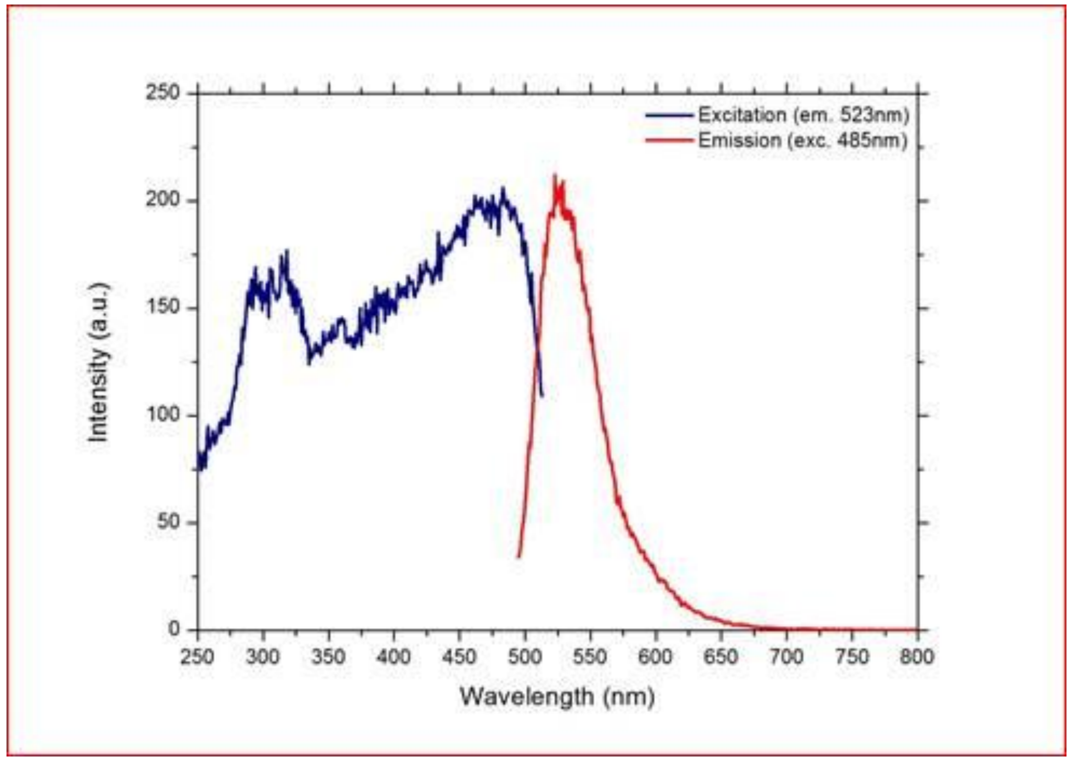
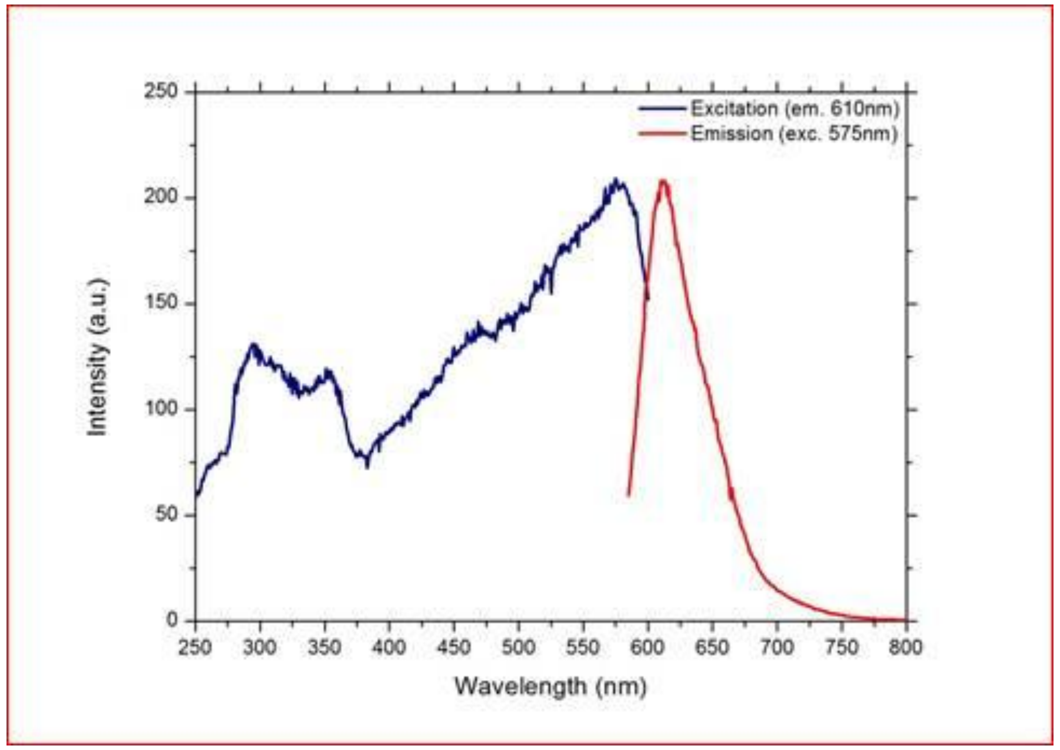
Within the Action Items that resulted following the November 2012 SERDP/ESTCP In-Progress Review of the ESTCP funded project 'Demonstration of Fluorescent Magnetic Particles for Linking Sources to Sediments at DoD Sites' (Project Number: ER-201214) Action Item 3 was a request to provide ESTCP with a white paper that discusses the toxicity and biodegradation pathways of the dyes used in the demonstration. In addition, Material Safety Data Sheets (MSDS) were requested for the dye compounds that have some estimate of toxicity to aquatic organisms. Finally, as requested, we provide an estimate of the dye mass at the initial point of release.

The following document has been compiled in response to the Action item request and contains all of the toxicological information that is currently available for the tracer material. Version 1 of this white paper was submitted in February 2013, but there were additional questions as to whether any additional toxicity data were available. This Version 2 of the white paper is being submitted to address these additional questions. Section 4 has been amended to include an estimate of the amount of tracer that might typically be released. Since no additional requested toxicity information could be obtained from the dye manufacturer, Section 5 has been added to include laboratory toxicity testing for several different common marine test organisms and endpoints (Mysid Shrimp survival, and embryo-larval development for Mussels and Echinoderms).

2. MANUFACTURED TRACER MATERIAL SPECIFICATIONS

Table 1 displays the average specifications of the manufactured tracer material expected to be deployed during the ESTCP Study

Table 1 Actual specification of manufactured tracer material

Specific metrics	Green material	Red material
Particle Labeling	Fluorescent color (green) and magnetic signature	Fluorescent color (red) and magnetic signature
Quantity used in Study (kg)	To be determined in the Demonstration plan development	To be determined in the Demonstration plan development
Particle Size (d_{50})	0.04-0.05 mm	0.04-0.05 mm
Constituents (% of total)	Natural Sand/Silt grains (silicon dioxide, or SiO_2) = 80% Dye Pigment (8%) Magnetite (5%) Polyester Resin Binding/Coating agent (7%)	Natural Sand/Silt grains (silicon dioxide, or SiO_2) = 80% Dye Pigment (8%) Magnetite (5%) Polyester Resin Binding/Coating agent (7%)
Specific Gravity	To be determined expected to be ~1500 kg m^{-3}	To be determined expected to be ~1500 kg m^{-3}
Bulk Density (kg m^{-3}) dry weight	To be determined expected to be ~2600 kg m-3	To be determined expected to be ~2600 kg m^{-3}
Spectral properties of fluorescent dye	Shade: Brilliant BSR-CH227 Chartreuse Peak emission frequency (λ)is λ_{green}=~530 nm  The fluorescence excitation spectrum (blue line) is obtained by fixing the fluorescence detector wavelength at 523nm and then scanning the excitation wavelengths. Inversely, the fluorescence emission spectrum (red line) was obtained by fixing the excitation wavelength at 485nm and then scanning the emission wavelengths.	Shade: Brilliant BSR-RD213 Red Peak emission frequency (λ)is λ_{red}=~610 nm  The fluorescence excitation spectrum (blue line) is obtained by fixing the fluorescence detector wavelength at 610nm and then scanning the excitation wavelengths. Inversely, the fluorescence emission spectrum (red line) was obtained by fixing the excitation wavelength at 575nm and then scanning the emission wavelengths.

3. SAFETY PROCEDURES FOR MATERIAL USE AND TRACER EMPLACEMENT

3.1 Material Safety

The material that is manufactured is natural quartz sand and/or silt that has a fine layer of a magnetic and fluorescent coloured pigment coating applied to each of the individual particles using a polyester resin binding agent. The material and coatings are non-toxic and benign when placed into an aquatic environment such as intended for the present study.

3.1.1 Sand / Silt

The tracer product contains 80% by volume of naturally occurring sand and/or silt (dependent on the size distribution of the material required). The sand/silt is predominantly composed of naturally occurring silicon dioxide (SiO_2). The sand/silt is inert and non-toxic.

3.1.2 Dye pigments

The tracer product contains 8% by volume of fluorescent dye pigment that is either Brilliant BSR-CH227 Chartreuse Green or Brilliant BSR-RD213 Red.

Brilliant™, the manufacturers of the dye pigments, indicate within their technical literature that through independent laboratory toxicity testing, the BSR fluorescent coloured pigments used in the tracer product are “essentially non-toxic.” The literature describes that the pigments have the following specifications:

- insoluble in water,
- 100% solid by weight
- 3 to 5 microns average particle size
- Non Hazardous, and as such they contain no reportable hazardous ingredients.

The MSDSs, produced by Brilliant™ for the dye pigments in June 2012, show that with regard to regulatory information the following apply:

U.S. FEDERAL REGULATIONS

TSCA (TOXIC SUBSTANCE CONTROL ACT): ALL COMPONENTS OF THIS PRODUCT ARE INCLUDED ON THE TSCA INVENTORY IN COMPLIANCE WITH THE TOXIC SUBSTANCES CONTROL ACT, 15 U.S.C. 2601 ET. SEQ.

CERCLA (COMPREHENSIVE ENVIRONMENTAL RESPONSE COMPENSATION, AND LIABILITY ACT): THIS IS NOT A REGULATED MATERIAL UNDER 40 CFR 117.302. NOTIFICATION OF SPILLS IS NOT REQUIRED.

SARA TITLE III (SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT): THIS PRODUCT CONTAINS NO KNOWN CHEMICALS CONTAINED ON THE LIST OF TOXIC CHEMICALS SUBJECT TO THE REPORTING REQUIREMENTS OF SECTION 313 OF THE EMERGENCY PLANNING & COMMUNITY RIGHT TO KNOW ACT OF 1986 & OF 40 CFR372.

311/312 HAZARD CATEGORIES: NONE KNOWN

313 REPORTABLE INGREDIENTS: NONE KNOWN

STATE REGULATIONS: CALIFORNIA PROPOSITION 65: WARNING: THIS PRODUCT CONTAINS A CHEMICAL KNOWN TO THE STATE OF CALIFORNIA TO CAUSE CANCER.

INTERNATIONAL REGULATIONS:

CANADA DSL: ALL COMPONENTS OF THIS PRODUCT ARE INCLUDED ON THE DOMESTIC SUBSTANCES LIST.

EEC EINECS: ALL COMPONENTS OF THIS PRODUCT ARE INCLUDED ON THE EUROPEAN INVENTORY OF EXISTING CHEMICAL SUBSTANCES (EINECS) IN COMPLIANCE WITH COUNCIL DIRECTIVE 67/548/EEC AND ITS AMENDMENTS.

Copies of the MSDSs are attached to this document.

3.1.3 Magnetite

The tracer product contains 5% by volume of naturally occurring magnetite. It is sourced from Minelco (now LKAB Minerals Norden) from mines located in Kiruna and Malmberget in the northern part of Sweden.

Magnetite, Fe_3O_4, is a black ferri-magnetic naturally occurring iron oxide and a member of the spinel group. Magnetite is inert and non-toxic.

3.1.4 Polyester Resin Binding/Coating Agent

The tracer product contains 7% by volume of a polyester resin that is used as a binding agent for the magnetite and dye pigment for coating of the individual sand/silt particles. This polyester material is the same as found within standard industrial water purification systems.

4. DYE MASS AT THE INITIAL POINT OF RELEASE

As is apparent from Table 1, the mass of the dye pigment at the initial point of release will be 8% of the total mass of the amount of tracer material released. For example, in 100 kilogrammes (kg) of tracer material released, the dye mass would be 8 kg. For comparison to the toxicity results in the following section, if 100 kg of tracer material is released from an outfall, a concentration of 0.1 gram/Liter (g/L) would be expected in a well mixed box of 10 meters per side (a volume of 1 million Liters of seawater). If the tracer is not immediately homogenously mixed, it might be expected to be at higher concentrations so the toxicity tests were conducted over a range of concentrations from 0.1 up to 10 g/L.

5. TOXICITY TESTING

Acute and chronic bioassays were performed to evaluate the toxicity of the tracer product in response to concerns about potential toxicity issues related to the typical use of the tracer product. Tests were performed using purple sea urchins (*Strongylocentrotus purpuratus*), Mediterranean mussels (*Mytilus galloprovincialis*), and mysid shrimp (*Americamysis bahia*) in accordance with standard methods (ASTM 1999, USEPA 1995, USEPA 2002, USEPA and USACE 1998).

5.1 Materials and Methods

5.1.1 Test Material

Using standard elutriate test methods (USEPA and USACE 1998), the tracer material was added to an excess of clean fresh water to “wet” the tracer material to ensure complete transfer of the tracer into 1 L beakers to produce a slurry. The excess fresh water was decanted off and the remaining slurry was brought up to volume using 0.45-µm filtered San Diego Bay seawater (salinity approximately 34 parts per thousand). These tests used a range of tracer concentrations that would be expected to be present in typical tracer experiments (0.1, 1.0, and 10 grams of tracer per Liter of seawater). For elutriate tests, the different concentrations of tracer were kept agitated in seawater on a shaker table for 30 minutes and then allowed to settle for 1 hour. Samples of the overlying seawater were then siphoned off, with the samples split into filtered and unfiltered stocks to look for any effects of fine particles that might remain in the overlying water.

5.1.2 Chronic and Acute Screening Methods

Testing was conducted in accordance with methods published in US EPA (1995), US EPA (2002), and ASTM (1999). The purple sea urchin (*S. purpuratus*) and mussel (*M. galloprovincialis*) embryo-larval development test, and mysid shrimp (*A. bahia*) survival test condition summaries are provided in Tables 2 through 4, along with the test specifications for each species.

Table 2. Purple Sea Urchin Larval Development Toxicity Test Specifications.

Test period	10/29/2013 – 11/2/2013
Test endpoint	Embryo-larval development
Test organism	*Strongylocentrotus purpuratus* (Purple sea urchin)
Test organism source	Field collected in San Diego, CA
Test solution renewal	None
Feeding	None
Test chamber	30-mL scintillation vial
Test solution volume	10 mL
Test temperature	15 ± 1°C
Control/ Dilution water	Filtered (0.45 µm) natural seawater (Source: San Diego Bay)
Test concentrations	0.1, 1, 10 (g/L); Filtered and Un-Filtered
Number of organisms/chamber	250 eggs, appropriate sperm density to provide > 90% fertilization success (determined in a pre-test trial)
Number of replicates	4
Photoperiod	16 hours light/8 hours dark
Test Protocol	EPA 600/R-95/136, 1995 West Coast Manual
Test acceptability criteria for controls	≥ 80% normal development, < 25 % Minimum Significant Difference (MSD)

Table 3. Mussel Embryo-Larval Development Toxicity Test Specifications.

Test period	10/29/2013 – 10/31/2013
Test endpoints	Embryo Development Rate (Proportion Normal) & Combined Survival and Development Rate (% Normal Alive)
Test organism	*Mytilus galloprovincialis* (Mediterranean mussel)
Test organism source	Carlsbad Aquafarms; Carlsbad, CA
Test solution renewal	None
Feeding	None
Test chamber	30-mL scintillation vial
Test solution volume	10 mL
Test temperature	15 ± 1°C
Control/ Dilution water	Filtered (0.45 µm) natural seawater (Source: San Diego Bay)
Test concentrations	0.1, 1, 10 (g/L) ; Filtered and Un-Filtered
Number of organisms/chamber	200 eggs, appropriate sperm density to provide >95% fertilization success (determined in a pre-test trial)
Number of replicates	4
Photoperiod	16 hours light/8 hours dark
Test Protocol	EPA 600/R-95/136, 1995 West Coast Manual
Test acceptability criteria for controls	≥ 70% normally developed larvae relative to initial number of embryos , < 25 % Minimum Significant Difference (MSD)

Table 4. Mysid Shrimp Acute (96-h) Survival Toxicity Test Specifications.

Test period	6/19/2013 – 6/23/2013
Test endpoint	96-hour survival
Test organism	*Americamysis bahia* (mysid shrimp)
Test organism source	Aquatic Biosystems; Fort Collins, CO
Test organism age at initiation	4 days
Test solution renewal	None
Feeding	*Artemia* nauplii during holding time and 2 times daily
Test chamber	400 mL plastic cup
Test solution volume	200 mL
Test temperature	20 ± 1°C
Control/ Dilution water	Filtered (0.45 µm) natural seawater (Source: San Diego Bay)
Test concentrations	0.1, 1, 10 (g/L); Un-Filtered only
Number of organisms/chamber	5
Number of replicates	2
Photoperiod	16 hours light/8 hours dark
Test Protocol	EPA 821/R-02/012
Test acceptability criteria for controls	≥ 90% survival

5.2 Results

A thorough review of the data and test procedures did not identify any likely or foreseeable impacts on test results; therefore, all data presented were deemed acceptable for reporting purposes. All tests performed had controls that met acceptability criteria for their respective endpoints. All tests were conducted within the required 36-hour holding time from sample delivery, and water quality measurements taken throughout the testing period were within recommended ranges.

For the all species tested, no significant adverse responses (p-values < 0.05) were observed for any of the elutriate test concentrations compared to their respective controls (Figures 1-4). There was one case where a statistically significant difference was observed (using a two-tailed t-test) for mussel larval development, but the difference suggested a very slight increase (i.e. not an adverse effect) in the percentage of normally developed larvae, and is attributed to very low variability among replicates for that treatment rather than anything of toxicological meaning.

Initial concern was expressed regarding fine particles of the tracer product remaining in suspension and its potential to cause artifacts leading to toxicity; however, there was no notable differences in normal development between the un-filtered and filtered elutriate samples tested for either the sea urchin or bivalve development tests.

Mussel embryo development success test results were expressed in two ways, which often show very similar results, as they did in these tests. Both were provided, as some studies suggest that the combined endpoint (% normal alive) is more comprehensive than the % normal development endpoint.

Summaries of results are provided in Tables 5 through 7. Raw test data are summarized in Tables 8 through 10.

Figure 1. Mean Purple Sea Urchin Embryo Development (% Normal ± 1SD).

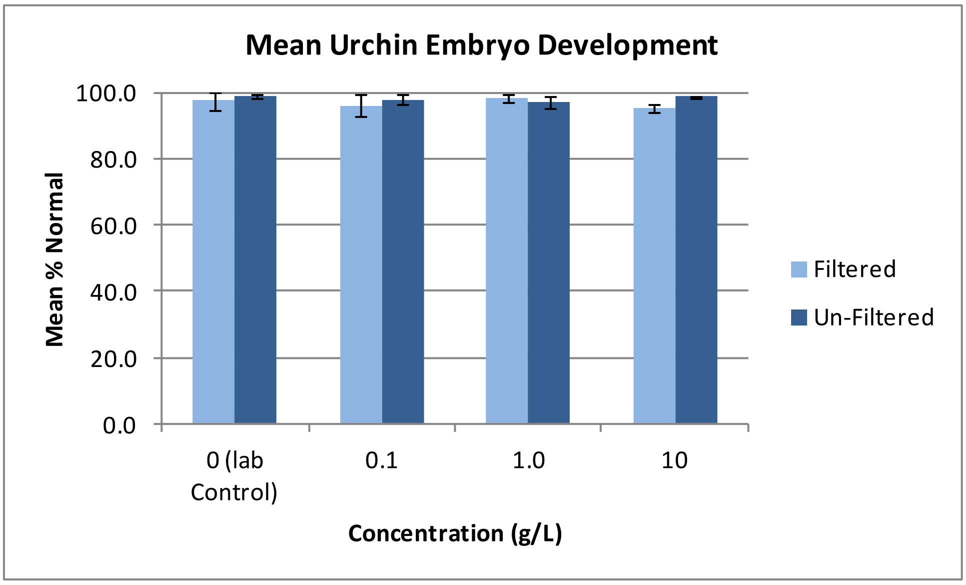


Figure 2. Mean Mussel Embryo Development (% Normal ± 1SD).

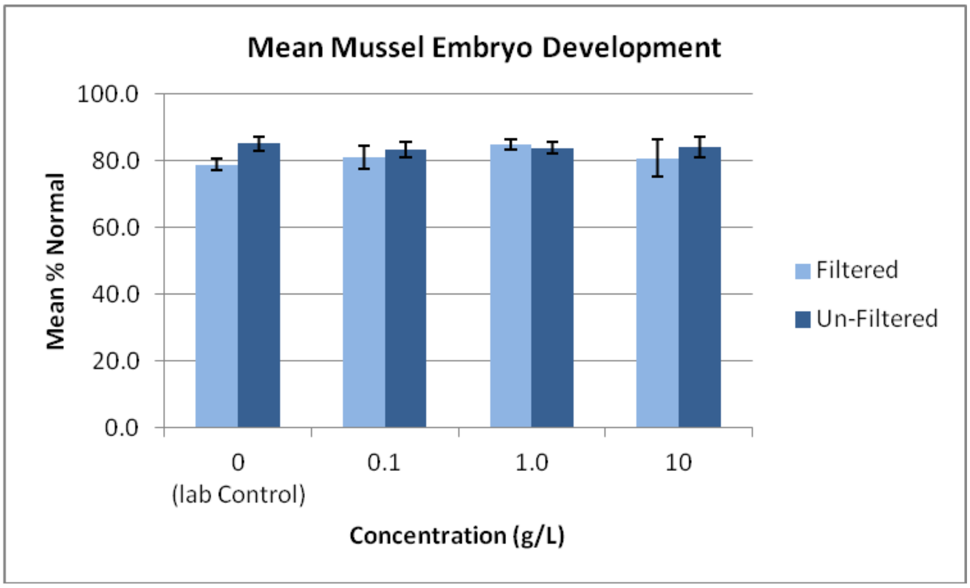


Figure 3. Mean Mussel Embryo Combined Development (% Normal Alive ± 1SD).

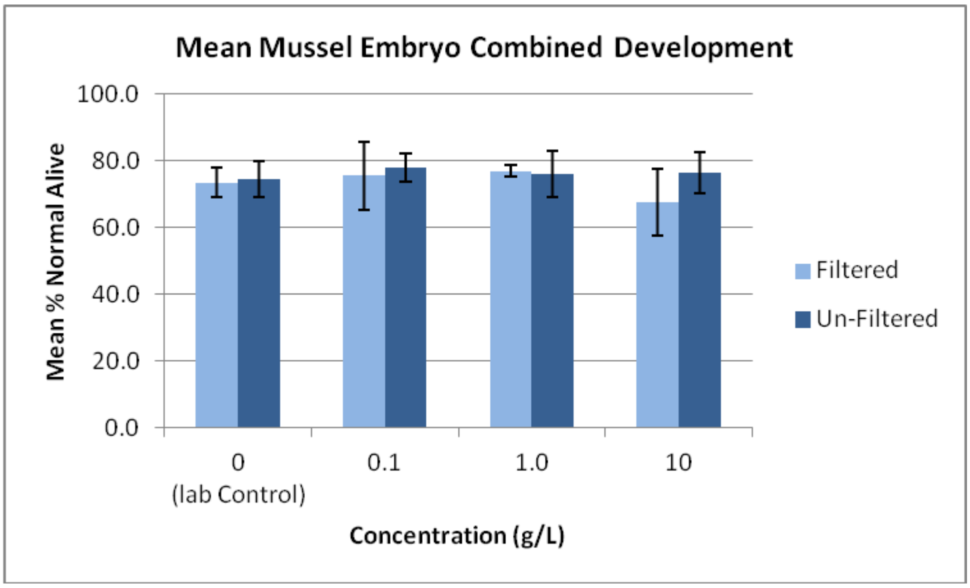


Figure 4. Mean Mysid Survival (96-h acute exposure).

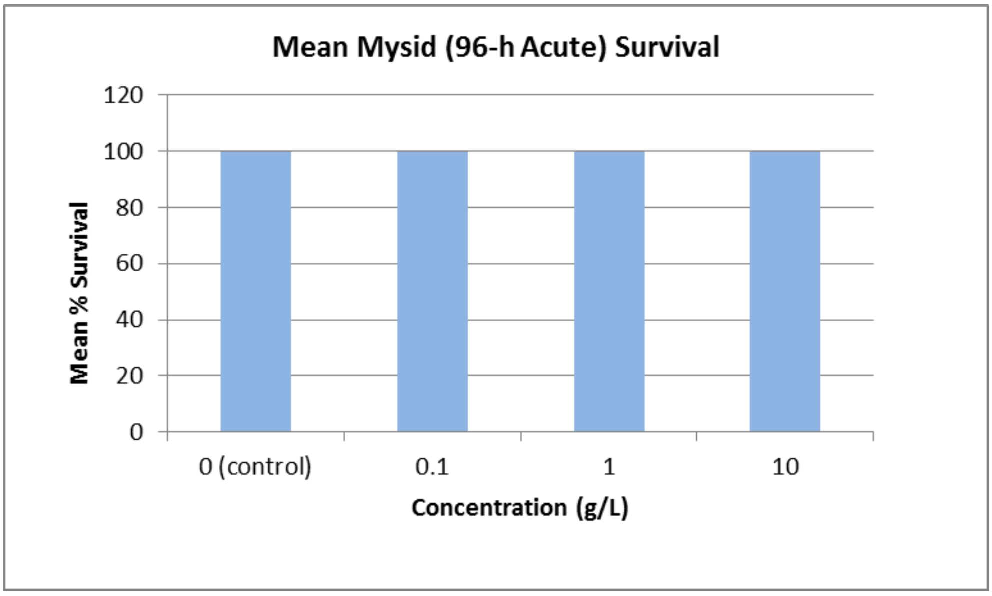


Table 5. Results Summary for Purple Urchin Embryo Development.

Test Concentration (g/L)	Purple Urchin Mean 96-hr Development (Mean % Normal)	
	Filtered Elutriate	Un-Filtered Elutriate
0 (Lab Control)	97.5	99.0
0.1	96.3	98.0
1.0	98.5	97.3
10	95.5	98.8

Table 6. Results Summary for Mussel Embryo-Larval Development and Combined Survival and Embryo-Larval Development (% normal alive).

Test Concentration (g/L)	Mediterranean Mussel Mean 48-hr Development			
	Filtered Elutriate		Un-Filtered Elutriate	
	Mean % Normal	Mean % Normal Alive	Mean % Normal	Mean % Normal Alive
0 (Lab Control)	78.9	73.4	85.2	74.5
0.1	81.1	75.6	83.4	77.9
1.0	85.0	77.0	84.0	76.1
10	80.8	67.7	84.2	76.3

Table 7. Results Summary for Mysid Survival.

Test Concentration (g/L)	Mysid Shrimp Mean 96-hr Survival
	Un-Filtered Elutriate
0 (Lab Control)	100
0.1	100
1.0	100
10	100

5.3 Raw Data

Table 8. Raw Toxicity Data for the Purple Urchin Embryo Development Test conducted on 10/29 – 11/2/2013.

Treatment ID		Rep	Number Counted	Number Normal	% Normal	Mean % Normal	*p*-Value
Filtered	1 Control	A	100	97	97	97.5	-
		B	100	94	94		
		C	100	99	99		
		D	100	100	100		
	2 (0.1g/L)	A	100	92	92	96.3	0.591
		B	100	98	98		
		C	100	95	95		
		D	100	100	100		
	3 (1g/L)	A	100	99	99	98.5	0.531
		B	100	100	100		
		C	100	98	98		
		D	100	97	97		
	4 (10g/L)	A	100	94	94	95.5	0.240
		B	100	96	96		
		C	100	95	95		
		D	100	97	97		
Un-filtered	1 Control	A	100	98	98	99.0	-
		B	100	99	99		
		C	100	100	100		
		D	100	99	99		
	2 (0.1g/L)	A	100	96	96	98.0	0.329
		B	100	100	100		
		C	100	98	98		
		D	100	98	98		
	3 (1g/L)	A	100	95	95	97.3	0.133
		B	100	99	99		
		C	100	97	97		
		D	100	98	98		
	4 (10g/L)	A	100	98	98	98.8	0.624
		B	100	99	99		
		C	100	99	99		
		D	100	99	99		

Table 9. Raw Toxicity Data for the Mussel Embryo Development Test conducted on 10/29 – 31/2013.

Treatment ID		Rep	Number Counted	Number Normal	Number Abnormal	% Normal	Mean % Normal	*p*-Value	% Normal Alive	Mean % Normal Alive	*p*-value
Filtered	1 Control	A	208	165	43	79	78.9	-	76	73.4	-
		B	202	161	41	80			74		
		C	206	165	41	80			76		
		D	190	145	45	76			67		
	2 (0.1g/L)	A	175	133	42	76	81.1	0.314	61	75.6	0.712
		B	216	177	39	82			82		
		C	194	163	31	84			75		
		D	221	182	39	82			84		
	3 (1g/L)	A	197	166	31	84	85.0	**0.002**	77	77.0	0.206
		B	205	171	34	83			79		
		C	186	162	24	87			75		
		D	197	168	29	85			78		
	4 (10g/L)	A	169	127	42	75	80.8	0.537	59	67.7	0.352
		B	169	132	37	78			61		
		C	199	175	24	88			81		
		D	185	152	33	82			70		
Un-filtered	1 Control	A	194	162	32	84	85.2	-	75	74.5	-
		B	175	147	28	84			68		
		C	198	175	23	88			81		
		D	190	161	29	85			74		
	2 (0.1g/L)	A	216	180	36	83	83.4	0.296	83	77.9	0.348
		B	204	164	40	80			76		
		C	204	172	32	84			79		
		D	186	159	27	85			73		
	3 (1g/L)	A	214	185	29	86	84.0	0.437	85	76.1	0.723
		B	196	162	34	83			75		
		C	180	149	31	83			69		
		D	194	163	31	84			75		
	4 (10g/L)	A	198	167	31	84	84.2	0.622	77	76.3	0.665
		B	214	172	42	80			79		
		C	174	146	28	84			67		
		D	200	176	24	88			81		

Table 10. Raw Toxicity Data for the Mysid Shrimp Survival Test conducted on 6/19 – 23/2013.

Treatment ID	Number Exposed	96 Hour Survival	% Survival	Mean % Survival
1 Control	5	5	100	100
	5	5	100	
2 (0.1g/L)	5	5	100	100
	5	5	100	
3 (1g/L)	5	5	100	100
	5	5	100	
4 (10g/L)	5	5	100	100
	5	5	100	

5.4 References

ASTM 1999. Standard guide for conducting static acute toxicity tests starting with embryos of four species of saltwater bivalve mollusks. American Society for Testing and Materials, Annual Book of Standards 2000. E724-98.

USEPA, 1995. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms. EPA/600/R-95/136. Washington, DC, USA.

USEPA, 2002. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fifth ed. EPA 821/R-02/012. October 2002.

USEPA and USACE 1998. Evaluation of dredged material proposed for discharge in waters of the U.S.- Testing Manual. Inland Testing Manual. EPA/823/B/98/004. February 1998.

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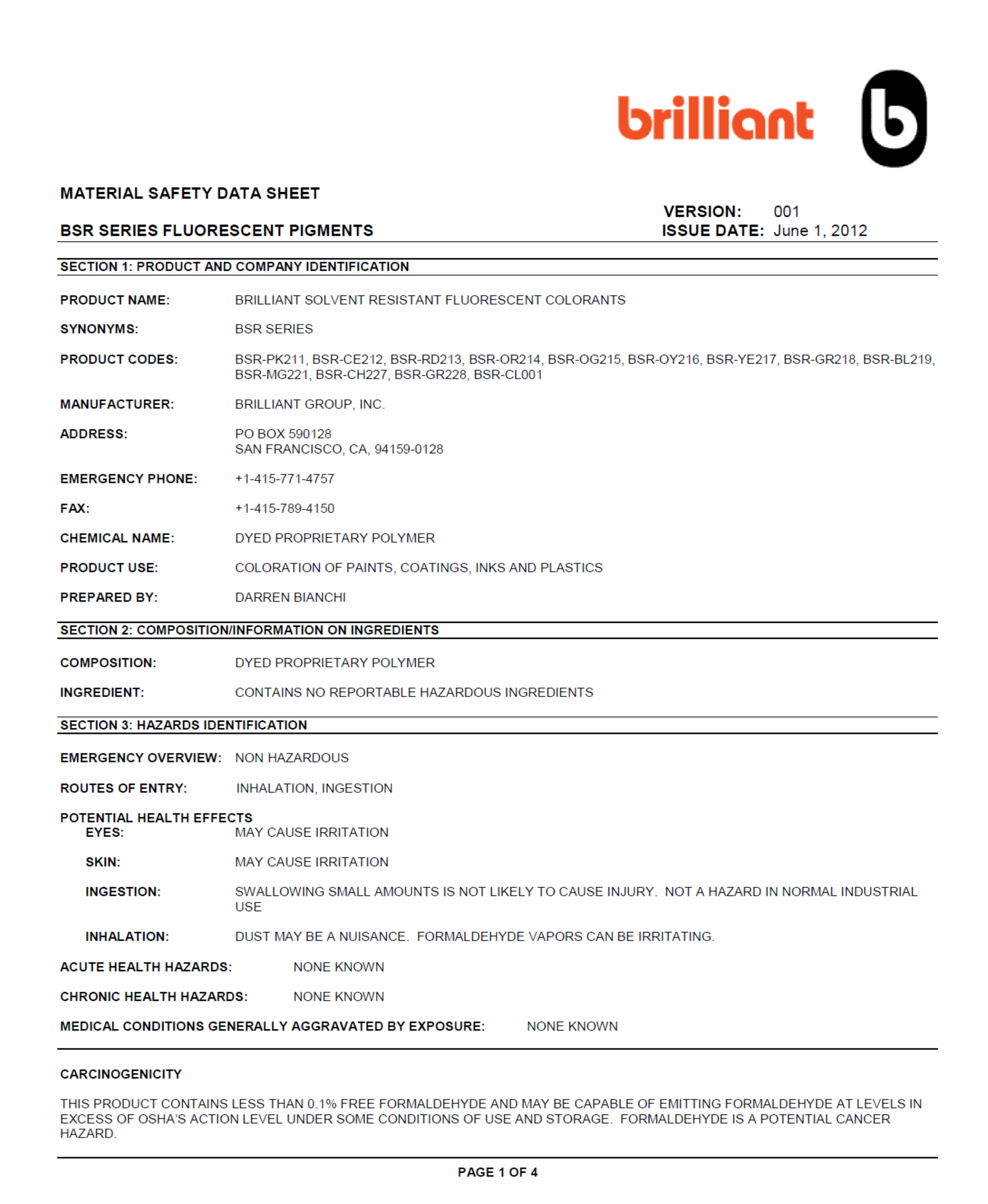
APPENDIX - BSR SERIES FLUORESCENT PIGMENTS MSDS



brilliant

MATERIAL SAFETY DATA SHEET

BSR SERIES FLUORESCENT PIGMENTS

VERSION: 001
ISSUE DATE: June 1, 2012

SECTION 1: PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME: BRILLIANT SOLVENT RESISTANT FLUORESCENT COLORANTS

SYNONYMS: BSR SERIES

PRODUCT CODES: BSR-PK211, BSR-CE212, BSR-RD213, BSR-OR214, BSR-OG215, BSR-OY216, BSR-YE217, BSR-GR218, BSR-BL219, BSR-MG221, BSR-CH227, BSR-GR228, BSR-CL001

MANUFACTURER: BRILLIANT GROUP, INC.

ADDRESS: PO BOX 590128
SAN FRANCISCO, CA, 94159-0128

EMERGENCY PHONE: +1-415-771-4757

FAX: +1-415-789-4150

CHEMICAL NAME: DYED PROPRIETARY POLYMER

PRODUCT USE: COLORATION OF PAINTS, COATINGS, INKS AND PLASTICS

PREPARED BY: DARREN BIANCHI

SECTION 2: COMPOSITION/INFORMATION ON INGREDIENTS

COMPOSITION: DYED PROPRIETARY POLYMER

INGREDIENT: CONTAINS NO REPORTABLE HAZARDOUS INGREDIENTS

SECTION 3: HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW: NON HAZARDOUS

ROUTES OF ENTRY: INHALATION, INGESTION

POTENTIAL HEALTH EFFECTS
- **EYES:** MAY CAUSE IRRITATION
- **SKIN:** MAY CAUSE IRRITATION
- **INGESTION:** SWALLOWING SMALL AMOUNTS IS NOT LIKELY TO CAUSE INJURY. NOT A HAZARD IN NORMAL INDUSTRIAL USE
- **INHALATION:** DUST MAY BE A NUISANCE. FORMALDEHYDE VAPORS CAN BE IRRITATING.

ACUTE HEALTH HAZARDS: NONE KNOWN

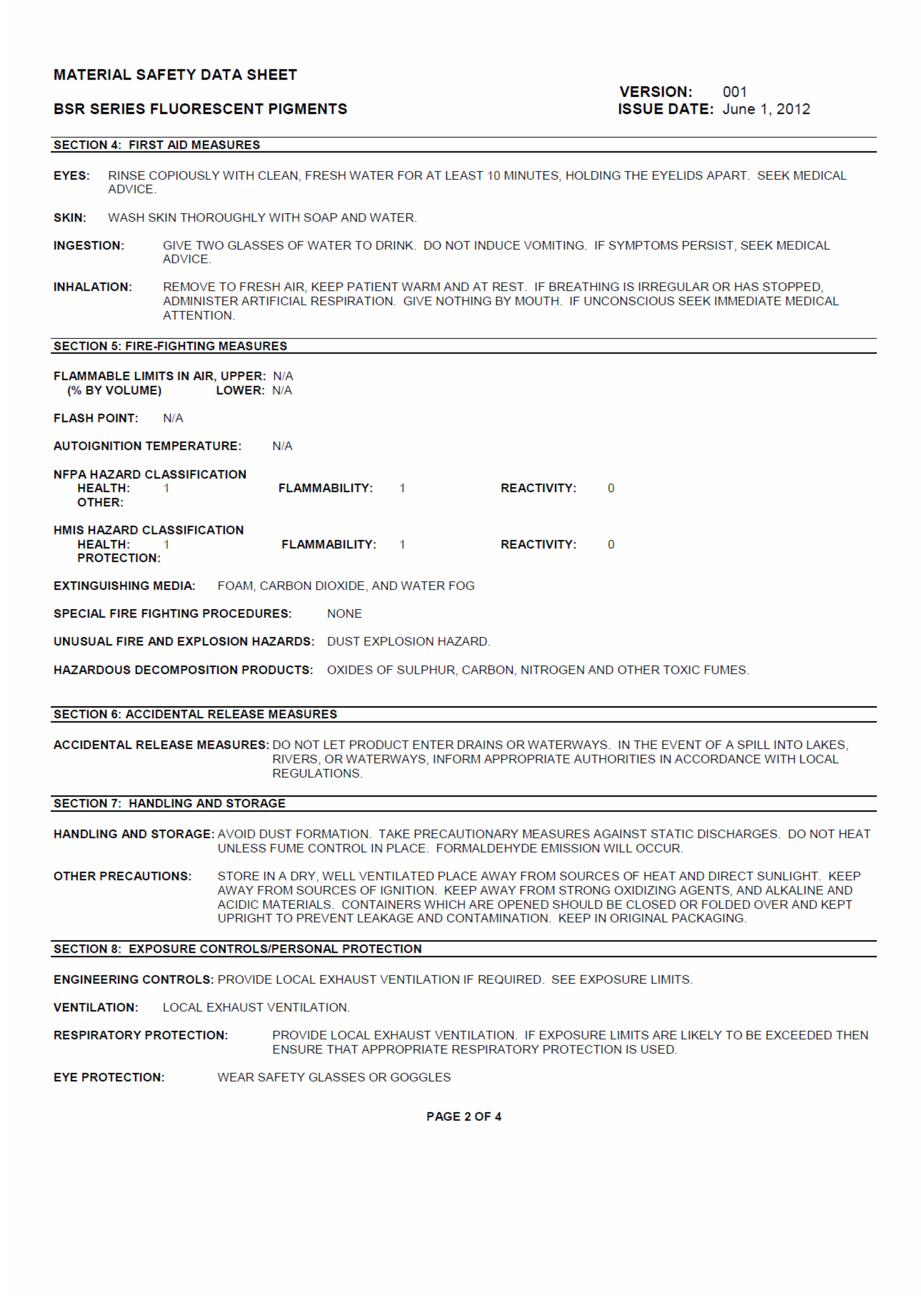
CHRONIC HEALTH HAZARDS: NONE KNOWN

MEDICAL CONDITIONS GENERALLY AGGRAVATED BY EXPOSURE: NONE KNOWN

CARCINOGENICITY

THIS PRODUCT CONTAINS LESS THAN 0.1% FREE FORMALDEHYDE AND MAY BE CAPABLE OF EMITTING FORMALDEHYDE AT LEVELS IN EXCESS OF OSHA'S ACTION LEVEL UNDER SOME CONDITIONS OF USE AND STORAGE. FORMALDEHYDE IS A POTENTIAL CANCER HAZARD.

PAGE 1 OF 4



MATERIAL SAFETY DATA SHEET

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SECTION 4: FIRST AID MEASURES

EYES: RINSE COPIOUSLY WITH CLEAN, FRESH WATER FOR AT LEAST 10 MINUTES, HOLDING THE EYELIDS APART. SEEK MEDICAL ADVICE.

SKIN: WASH SKIN THOROUGHLY WITH SOAP AND WATER.

INGESTION: GIVE TWO GLASSES OF WATER TO DRINK. DO NOT INDUCE VOMITING. IF SYMPTOMS PERSIST, SEEK MEDICAL ADVICE.

INHALATION: REMOVE TO FRESH AIR, KEEP PATIENT WARM AND AT REST. IF BREATHING IS IRREGULAR OR HAS STOPPED, ADMINISTER ARTIFICIAL RESPIRATION. GIVE NOTHING BY MOUTH. IF UNCONSCIOUS SEEK IMMEDIATE MEDICAL ATTENTION.

SECTION 5: FIRE-FIGHTING MEASURES

FLAMMABLE LIMITS IN AIR, UPPER: N/A
(% BY VOLUME) LOWER: N/A

FLASH POINT: N/A

AUTOIGNITION TEMPERATURE: N/A

NFPA HAZARD CLASSIFICATION
HEALTH: 1 **FLAMMABILITY:** 1 **REACTIVITY:** 0
OTHER:

HMIS HAZARD CLASSIFICATION
HEALTH: 1 **FLAMMABILITY:** 1 **REACTIVITY:** 0
PROTECTION:

EXTINGUISHING MEDIA: FOAM, CARBON DIOXIDE, AND WATER FOG

SPECIAL FIRE FIGHTING PROCEDURES: NONE

UNUSUAL FIRE AND EXPLOSION HAZARDS: DUST EXPLOSION HAZARD.

HAZARDOUS DECOMPOSITION PRODUCTS: OXIDES OF SULPHUR, CARBON, NITROGEN AND OTHER TOXIC FUMES.

SECTION 6: ACCIDENTAL RELEASE MEASURES

ACCIDENTAL RELEASE MEASURES: DO NOT LET PRODUCT ENTER DRAINS OR WATERWAYS. IN THE EVENT OF A SPILL INTO LAKES, RIVERS, OR WATERWAYS, INFORM APPROPRIATE AUTHORITIES IN ACCORDANCE WITH LOCAL REGULATIONS.

SECTION 7: HANDLING AND STORAGE

HANDLING AND STORAGE: AVOID DUST FORMATION. TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES. DO NOT HEAT UNLESS FUME CONTROL IN PLACE. FORMALDEHYDE EMISSION WILL OCCUR.

OTHER PRECAUTIONS: STORE IN A DRY, WELL VENTILATED PLACE AWAY FROM SOURCES OF HEAT AND DIRECT SUNLIGHT. KEEP AWAY FROM SOURCES OF IGNITION. KEEP AWAY FROM STRONG OXIDIZING AGENTS, AND ALKALINE AND ACIDIC MATERIALS. CONTAINERS WHICH ARE OPENED SHOULD BE CLOSED OR FOLDED OVER AND KEPT UPRIGHT TO PREVENT LEAKAGE AND CONTAMINATION. KEEP IN ORIGINAL PACKAGING.

SECTION 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

ENGINEERING CONTROLS: PROVIDE LOCAL EXHAUST VENTILATION IF REQUIRED. SEE EXPOSURE LIMITS.

VENTILATION: LOCAL EXHAUST VENTILATION.

RESPIRATORY PROTECTION: PROVIDE LOCAL EXHAUST VENTILATION. IF EXPOSURE LIMITS ARE LIKELY TO BE EXCEEDED THEN ENSURE THAT APPROPRIATE RESPIRATORY PROTECTION IS USED.

EYE PROTECTION: WEAR SAFETY GLASSES OR GOGGLES

MATERIAL SAFETY DATA SHEET

VERSION: 001
ISSUE DATE: June 1, 2012

BSR SERIES FLUORESCENT PIGMENTS

SKIN PROTECTION: WEAR GLOVES

OTHER PROTECTIVE CLOTHING OR EQUIPMENT: COVERALLS, LAB COAT, ETC. TO KEEP PRODUCT OFF CLOTHES

WORK HYGIENIC PRACTICES: STANDARD GOOD HYGIENE PRACTICES FOR THE SAFE HANDLING OF CHEMICALS SHOULD BE OBSERVED. DO NOT HEAT UNLESS FUME CONTROL IN PLACE.

EXPOSURE GUIDELINES:	SHORT TERM EXPOSURE LIMIT	LONG TERM EXPOSURE LIMIT
TOTAL INHALABLE DUST	10mg/m3	10mg/m3
RESPIRABLE DUST	5mg/m3	5mg/m3

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE: BRIGHTLY COLORED FINE POWDER

ODOR: SLIGHT CHARACTERISTIC ODOR

PHYSICAL STATE: FINELY DIVIDED POWDER

pH AS SUPPLIED: N/A

BOILING POINT: N/A

MELTING POINT:
F: 374
C: 190

FREEZING POINT: N/A

VAPOR PRESSURE (mmHg): N/A

VAPOR DENSITY (AIR = 1): N/A

SPECIFIC GRAVITY (H2O = 1): 1.3

EVAPORATION RATE: N/A

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES (con't)

SOLUBILITY IN WATER: INSOLUBLE

PERCENT SOLIDS BY WEIGHT: 100%

PERCENT VOLATILE: 0%

VOLATILE ORGANIC COMPOUNDS (VOC): 0%

SECTION 10: STABILITY AND REACTIVITY

	STABLE	UNSTABLE
STABILITY:	X	

CONDITIONS TO AVOID (STABILITY): EXCESSIVE HEAT

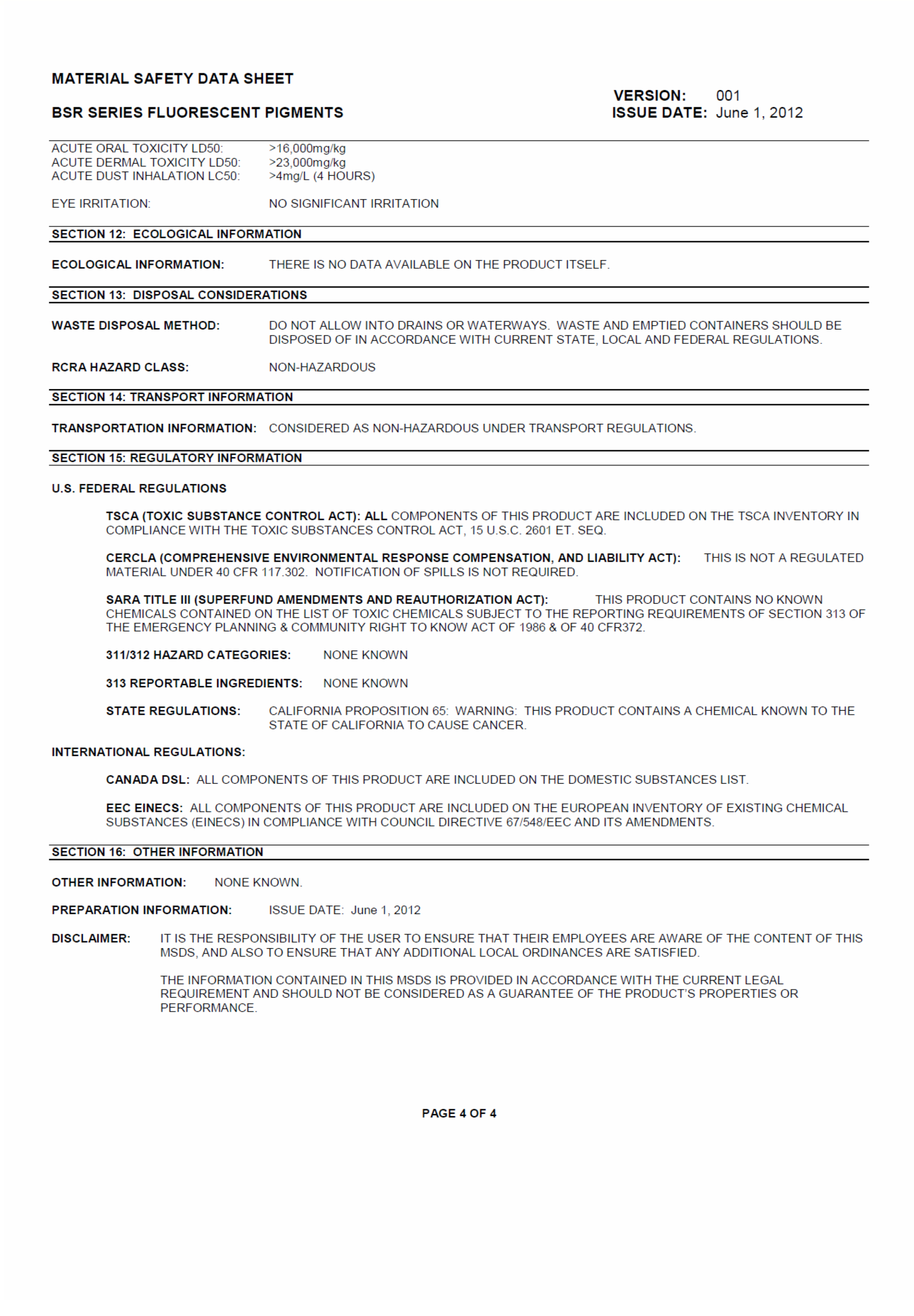
INCOMPATIBILITY (MATERIAL TO AVOID): STRONG OXIDIZING AGENTS, STRONG ALKALINE OR ACIDIC MATERIALS

HAZARDOUS DECOMPOSITION OR BY-PRODUCTS: FUMES MAY CONTAIN OXIDES OF SULPHUR, CARBON OR NITROGEN, OR OTHER TOXIC FUMES.

HAZARDOUS POLYMERIZATION: WILL NOT OCCUR

SECTION 11: TOXICOLOGICAL INFORMATION

TOXICOLOGICAL INFORMATION:



MATERIAL SAFETY DATA SHEET

BSR SERIES FLUORESCENT PIGMENTS

VERSION: 001
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ACUTE ORAL TOXICITY LD50:	>16,000mg/kg
ACUTE DERMAL TOXICITY LD50:	>23,000mg/kg
ACUTE DUST INHALATION LC50:	>4mg/L (4 HOURS)
EYE IRRITATION:	NO SIGNIFICANT IRRITATION

SECTION 12: ECOLOGICAL INFORMATION

ECOLOGICAL INFORMATION: THERE IS NO DATA AVAILABLE ON THE PRODUCT ITSELF.

SECTION 13: DISPOSAL CONSIDERATIONS

WASTE DISPOSAL METHOD: DO NOT ALLOW INTO DRAINS OR WATERWAYS. WASTE AND EMPTIED CONTAINERS SHOULD BE DISPOSED OF IN ACCORDANCE WITH CURRENT STATE, LOCAL AND FEDERAL REGULATIONS.

RCRA HAZARD CLASS: NON-HAZARDOUS

SECTION 14: TRANSPORT INFORMATION

TRANSPORTATION INFORMATION: CONSIDERED AS NON-HAZARDOUS UNDER TRANSPORT REGULATIONS.

SECTION 15: REGULATORY INFORMATION

U.S. FEDERAL REGULATIONS

TSCA (TOXIC SUBSTANCE CONTROL ACT): ALL COMPONENTS OF THIS PRODUCT ARE INCLUDED ON THE TSCA INVENTORY IN COMPLIANCE WITH THE TOXIC SUBSTANCES CONTROL ACT, 15 U.S.C. 2601 ET. SEQ.

CERCLA (COMPREHENSIVE ENVIRONMENTAL RESPONSE COMPENSATION, AND LIABILITY ACT): THIS IS NOT A REGULATED MATERIAL UNDER 40 CFR 117.302. NOTIFICATION OF SPILLS IS NOT REQUIRED.

SARA TITLE III (SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT): THIS PRODUCT CONTAINS NO KNOWN CHEMICALS CONTAINED ON THE LIST OF TOXIC CHEMICALS SUBJECT TO THE REPORTING REQUIREMENTS OF SECTION 313 OF THE EMERGENCY PLANNING & COMMUNITY RIGHT TO KNOW ACT OF 1986 & OF 40 CFR372.

311/312 HAZARD CATEGORIES: NONE KNOWN

313 REPORTABLE INGREDIENTS: NONE KNOWN

STATE REGULATIONS: CALIFORNIA PROPOSITION 65: WARNING: THIS PRODUCT CONTAINS A CHEMICAL KNOWN TO THE STATE OF CALIFORNIA TO CAUSE CANCER.

INTERNATIONAL REGULATIONS:

CANADA DSL: ALL COMPONENTS OF THIS PRODUCT ARE INCLUDED ON THE DOMESTIC SUBSTANCES LIST.

EEC EINECS: ALL COMPONENTS OF THIS PRODUCT ARE INCLUDED ON THE EUROPEAN INVENTORY OF EXISTING CHEMICAL SUBSTANCES (EINECS) IN COMPLIANCE WITH COUNCIL DIRECTIVE 67/548/EEC AND ITS AMENDMENTS.

SECTION 16: OTHER INFORMATION

OTHER INFORMATION: NONE KNOWN.

PREPARATION INFORMATION: ISSUE DATE: June 1, 2012

DISCLAIMER: IT IS THE RESPONSIBILITY OF THE USER TO ENSURE THAT THEIR EMPLOYEES ARE AWARE OF THE CONTENT OF THIS MSDS, AND ALSO TO ENSURE THAT ANY ADDITIONAL LOCAL ORDINANCES ARE SATISFIED.

THE INFORMATION CONTAINED IN THIS MSDS IS PROVIDED IN ACCORDANCE WITH THE CURRENT LEGAL REQUIREMENT AND SHOULD NOT BE CONSIDERED AS A GUARANTEE OF THE PRODUCT'S PROPERTIES OR PERFORMANCE.