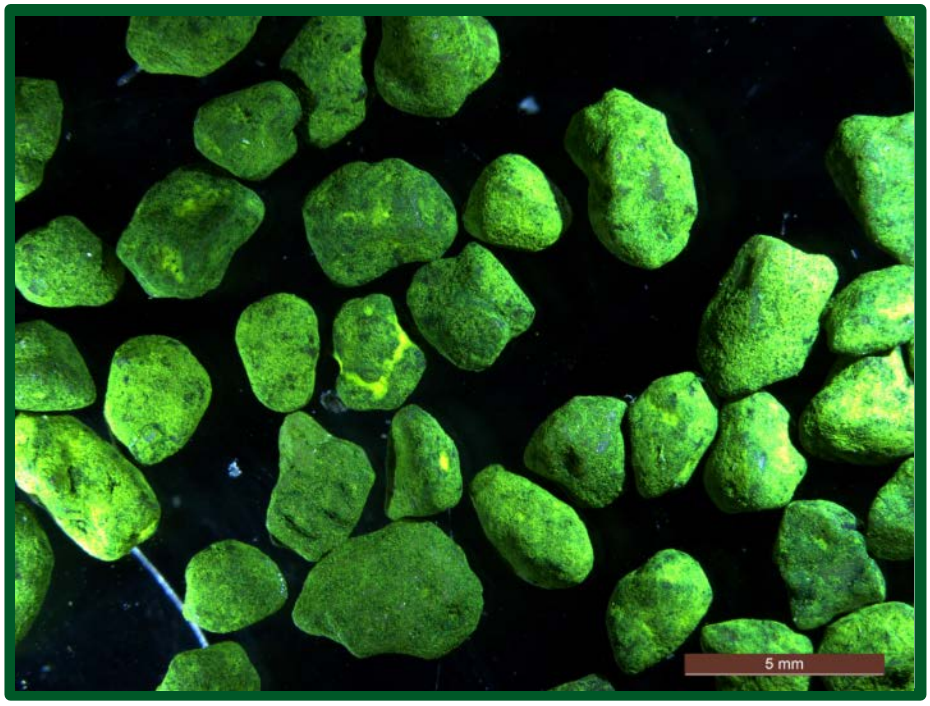
ESTCP
Cost and Performance Report

(ER-201214)



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

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14. ABSTRACT
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.

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ACRONYMS AND ABBREVIATIONS

λ	wavelength
µm	micrometer(s)
ADCP	Acoustic Doppler Current Profiler
cm	centimeter(s)
d_{50}	diameter of particle at 50% of the particle size distribution
DoD	Department of Defense
DZ	tracer deployment zone
ESTCP	Environmental Security and Technology Certification Program
ft	foot/feet
g	gram(s)
HPS	Hunters Point Shipyard
kg	kilogram(s)
L	liter(s)
mg	milligram(s)
NBSD	Naval Base San Diego
nm	nanometer(s)
Partrac	Partrac, Ltd. (Glasgow, Scotland)
PSD	particle size distribution
r^2	coefficient of determination
SPAWAR	Space and Naval Warfare Systems Center Pacific
TMDL	total maximum daily load
TSS	total suspended solids

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1.0 INTRODUCTION

1.1 BACKGROUND

Source control (i.e., the reduction of contamination from an 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 and following delivery into waterways, through time and across space. It is a relatively straightforward methodology which involves the introduction of particulate tracers into a water body. These particulate tracers are labeled with one or more signatures so 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 in order to provide actual field data for model validation. 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. Black et al. (2007) provide a comprehensive overview of the historic evolution of these differing approaches to tracer studies.

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 Department of Defense (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. All the performance objectives for this project that are listed in Section 3 Table 1 have been judged as successfully passed in Section 6.

1.3 REGULATORY DRIVERS

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 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 Section 303(d) list and water cleanup plans or total maximum daily loads (TMDLs) must be developed to bring the water body back into compliance.

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2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

The technology to be demonstrated uses proprietary tracers called dual signature tracers (Figure 1), which means that each particle (grain) of tracer has two signatures which are used to unequivocally identify the particle 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 tracers 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 grams per cubic centimeter (g/cm^3; i.e., mineral density) whereas fixed grain density for artificial particles can be adjusted through a range of 1.01 to 3.75 g/cm^3. Coated particle grain sizes range from 20 to 5000 micrometers (µm) 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. While 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 with a density of ~2.6 g/cm^3 was used at each of the demonstration sites. A second artificial particle tracer was used at the second demonstration site to simulate the activated carbon amendment at the cap site.

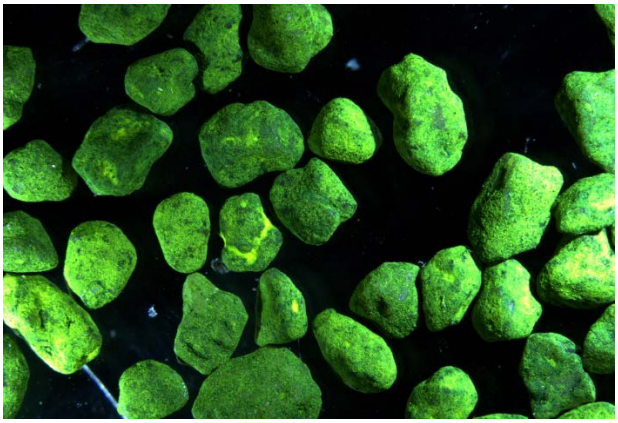

Figure 1. Photomicrograph of Coated Sand (mineral kernel) Fluorescent-magnetic Tracer Grains.

The grains pictured are ~ 150 - 200 µm in size.

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).

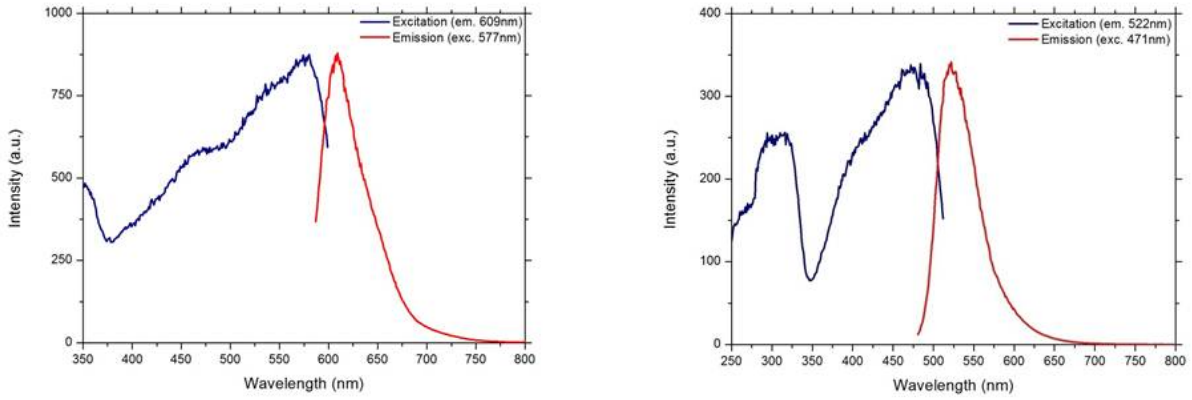

Figure 2. Excitation – Emission Spectra for Pink (left) and Green (right) Pigment Tracer Particles.

The fluorescence excitation spectrum (blue line) is obtained by fixing the fluorescence detector wavelength at 523 nm and then scanning the excitation wavelengths. Inversely, the fluorescence emission spectrum (red line) was obtained by fixing the excitation wavelength at 485 nm 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; 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.

2.1.1 TECHNOLOGY DEVELOPMENT

Conducting a tracer study involves a specific set of steps which include: conducting a background study and tracer manufacture; tracer introduction; tracer sampling; and enumeration of tracer from environmental samples (Black et al., 2007). A more complete description of these steps in given in Sections 5.1 and 5.2. 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, Ltd. (Glasgow, Scotland; 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 for both sand-sized and finer grained sediments. This is important because it is often these finer grained sediments that carry a larger proportion of the contaminant loads. At the Duwamish Superfund site, much of the finer silt sized material left the immediate area where the contaminant sources were located, but the utility of *in situ* magnets as (point, passive) sampling devices was demonstrated (Sloan and Gries, 2009). The magnet collection of tracers demonstrated that the fine grained sediments (along with their contaminant loads) were being transported from the source areas to downstream sediment depositional sites.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

2.2.1 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 or filtration), and manual inspection. *In situ* magnets avoid these processes entirely as tracer separation *from* the environment occurs *within* the environment (Figure 3). 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 for easy tracer collection.

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). 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; it is here that the magnetic character of the dual signature tracer provides substantial benefit in terms of time and cost.

2.2.2 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, also termed 'hydraulic matching', is the process in which the physical attributes of the manufactured tracer (e.g., size, density) are compared quantitatively to those of the native particles. Figure 4 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. Black et al. (2007) developed a set of tolerances for the hydraulic matching process to ensure tracers behave similar to native particles.

Figure 3. *In situ* Capture of Tracer Using a Submersible Magnet

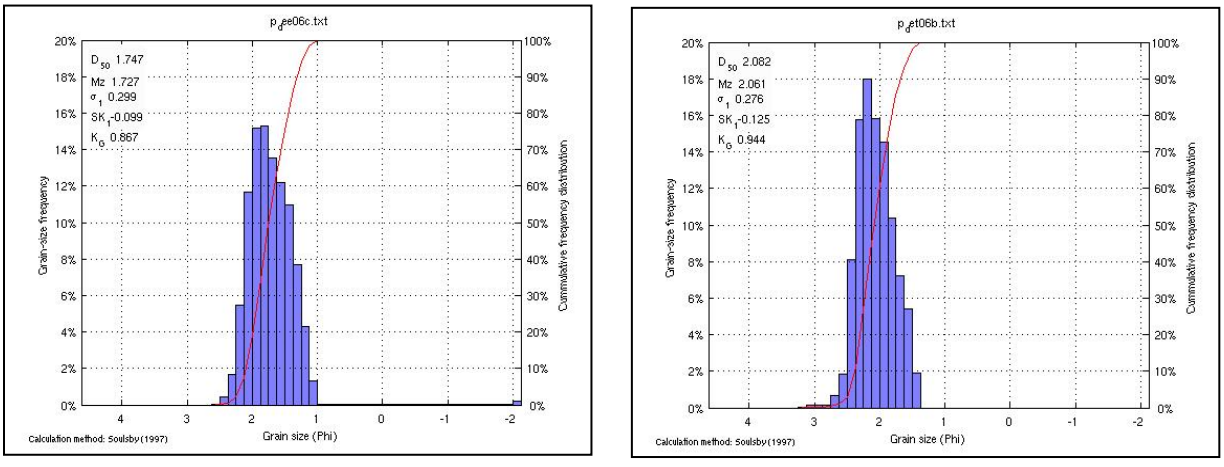

Figure 4. Example of Nearly Equivalent Grain Size Spectra for (a) Native and (b) Tracer Particles Derived from Settling Velocity Determinations.

3.0 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} - $\rho_{tracer}/\rho_{native} \leq \pm 6\%$, with overlapping standard deviation values.	Section 6.1
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
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 6.3
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 6.4
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 6.5
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 6.6
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 6.7

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4.0 SITE DESCRIPTION

4.1 NAVAL BASE SAN DIEGO

The first site selected for this demonstration project was Naval Base San Diego (NBSD) located in San Diego, California. 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 is available for the site (Katz et al., 2006; 2011; 2014), and 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. Figure 5 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 Katz et al., 2011 for further discussion). The target outfall/discharge area for this Environmental Security and Technology Certification Program (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.

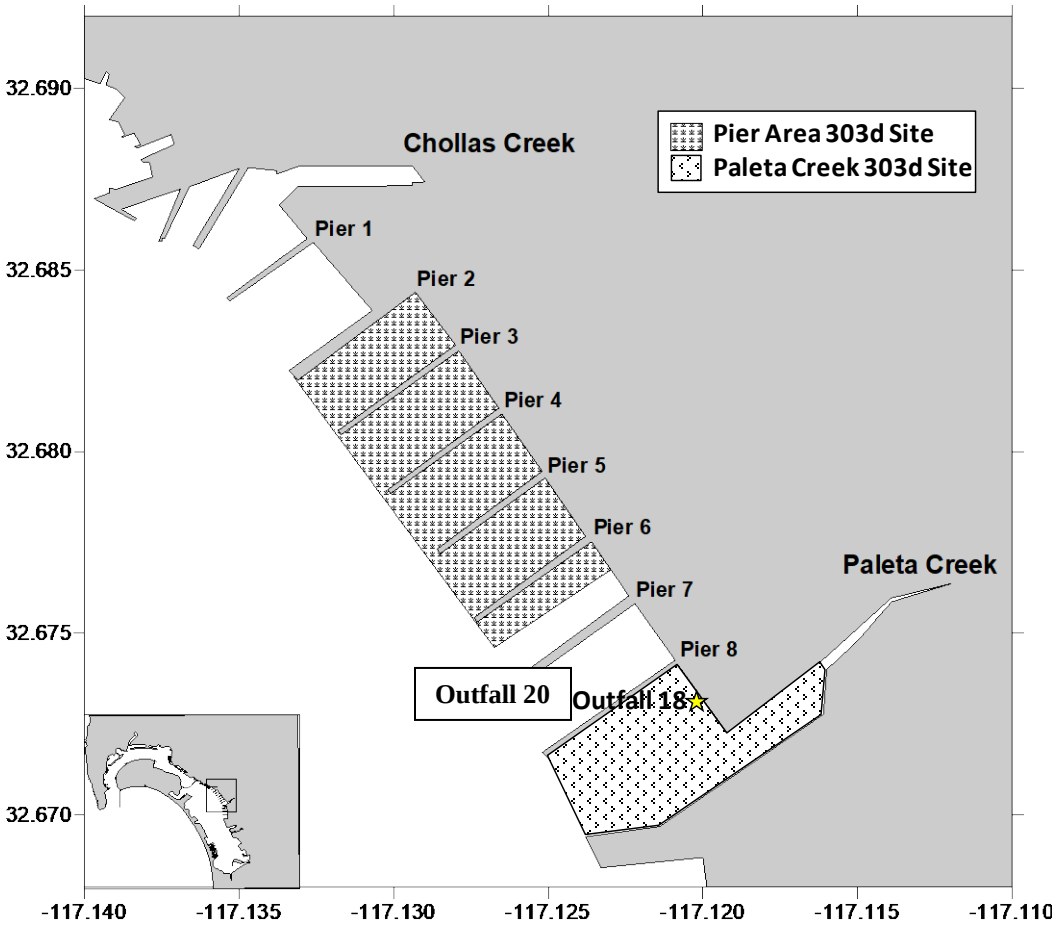

Figure 5. The NBSD Demonstration Site is at Outfall 20 Located Between Pier 8 and Paleta Creek on the East Side of San Diego Bay, CA (from Katz et al., 2011).

4.2 HUNTERS POINT SHIPYARD

The second demonstration site that was selected for this project was Hunters Point Shipyard (HPS) located in San Francisco, California (Figures 6 and 7). 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.

A large amount of pre-existing data is available for the site (Battelle et al., 2006; BAI, 2007), and this site served as an early demonstration site for activated carbon used for sequestration of sediment contamination (ESTCP Project ER-200510 [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 recently (June 2015) placed a larger one acre activated carbon cap in the South Basin (Figure 7) which will serve as the location for this demonstration.

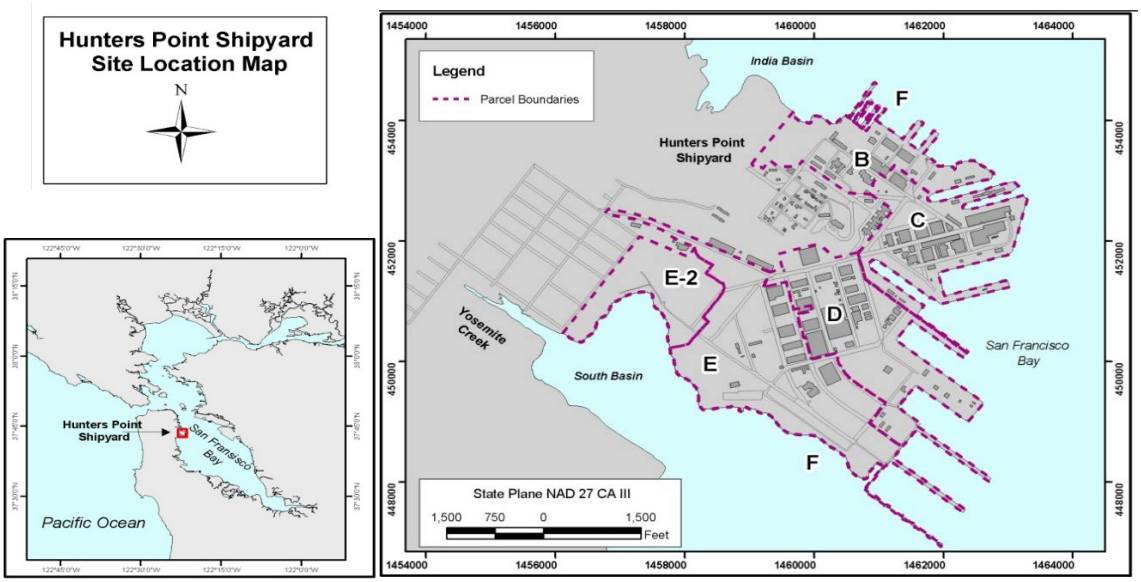

Figure 6. Map of HPS Including South Basin where ESTCP Demonstration Will Occur.

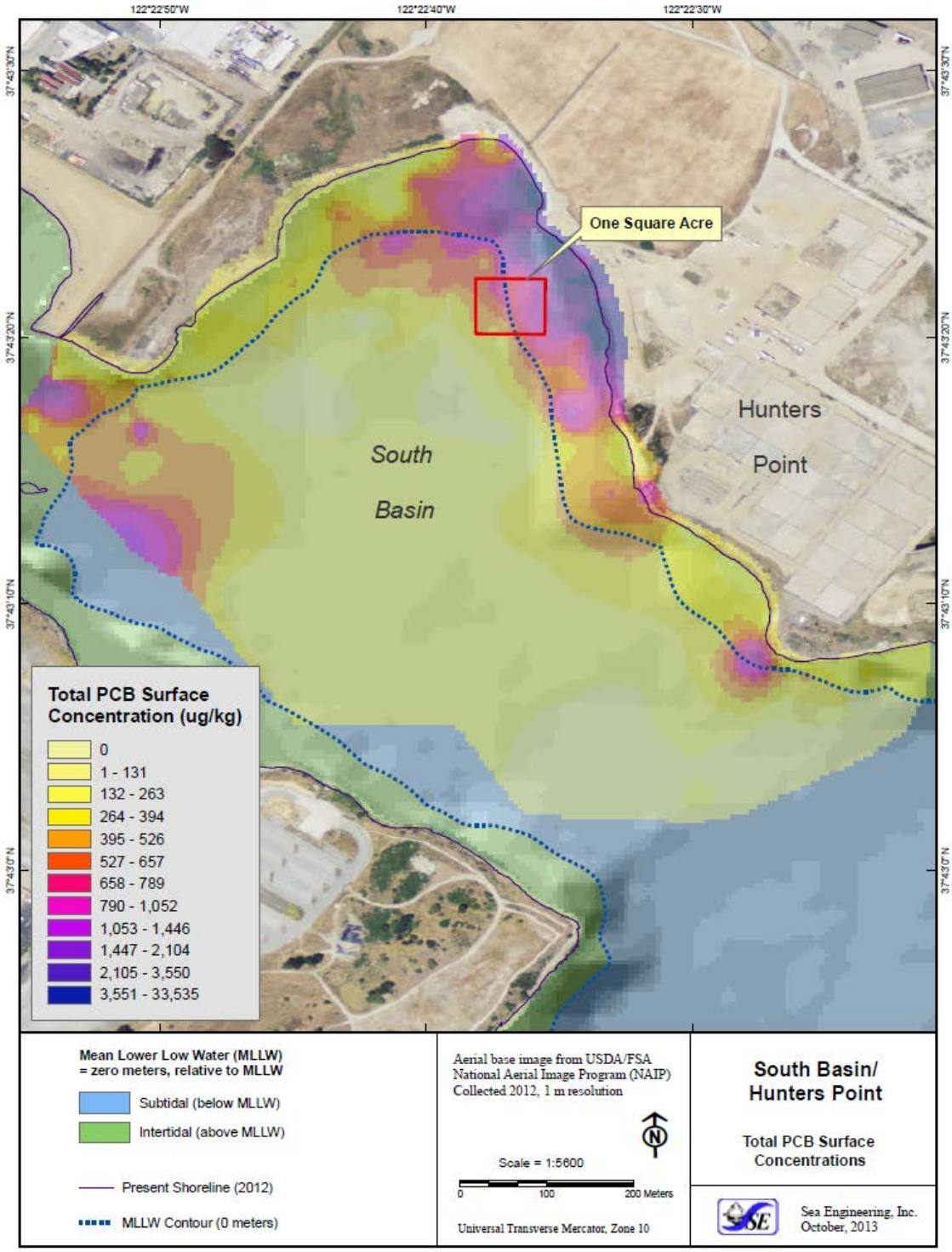

Figure 7. Location of One Square Acre Amendment Study Site Along the Mean Low Low Water Contour in South Basin for the Second ESTCP Demonstration.

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5.0 TEST DESIGN

This section contains a 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 2.1.1, conducting the particle tracking demonstration and validation study involves a specific set of steps. These steps are: 1) conducting pre-demonstration background studies; 2) demonstration setup and introduction of tracer material; 3) magnetic collection of tracer; and 4) data analysis and reporting results. The first three of these tasks are described below in Section 5.1.2 and the final analysis task is described in Section 5.1.3.

5.1.2 FIELD TESTING

The field testing at NBSD occurred at Outfall 20 between Pier 8 and Paleta Creek (Figure 5) during the week of 15 September 2014. Several ship movements in the area delayed the start of field work until 17 September 2014 and all field work was completed by 21 September 2014.

5.1.2.1 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 two depths were collected and analyzed for the same.

5.1.2.2 Setup and Introduction of Tracer

The fixed magnets were deployed on Thursday, 18 September 2014, the day prior to introduction of the tracer. 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 Doppler Current Profiler (ADCP) over the demonstration period which provided data that 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, 19 September 2014 with local low tide at 1300) to capture both ebb and flood tide conditions. The tracer release was done from a 40-foot (ft) vessel which was anchored in front of Outfall 20 with the vessel moved periodically from 10-50 meters out from the quay wall in front of the outfall. The tracer was introduced with a pumped seawater system in the discharge zone outside the outfall. Figure 8 shows the delivery system setup and a plume of the tracer near site T3-2 buoy located 30 meters in front of the outfall. With a high-pressure pump (flow of 3000 liters [L] per minute), the total tracer load of 800 kilogram (kg) was delivered in approximately 8 hours with an average TSS of 555 milligrams (mg)/L which is close to the modeled TSS value of 500 mg/L found in outfalls at the site.

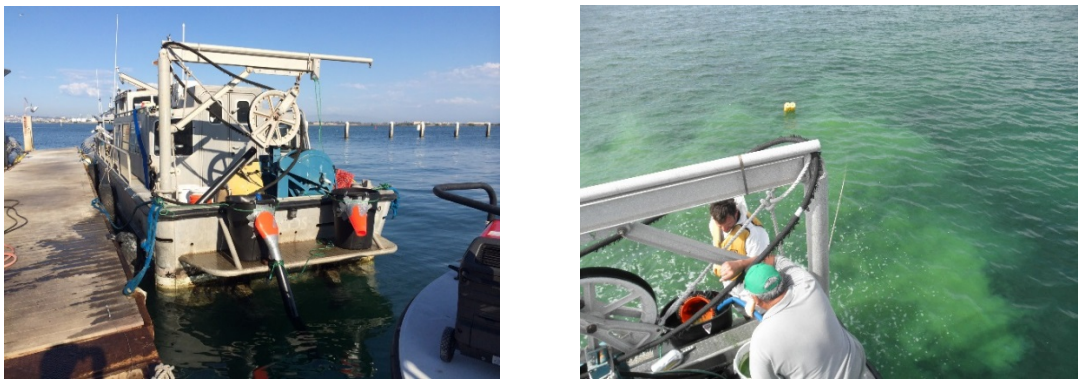

Figure 8. (Left) Setup for Tracer Release Done from Stern Swim Platform with a 32 Gallon Mixing Container with Overflow Through a 4-inch Polyvinylchloride Pipe so the Tracer Released Just Below the Water Surface.

(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).

5.1.2.3 Magnet Collections of Tracer

Magnets located 1 meter from the sediment surface were sampled one day after tracer release (Saturday 20 September 2014) and sediment grabs were collected two days after release (Sunday 21 September 2014). 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 9). 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 used to measure the concentration of tracer directly beneath the sensor head (see method and results in Final Report Appendix 1 NBSD Field Report).

Figure 9. (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.

5.1.3 SAMPLING RESULTS

A full discussion of the results can be found in the Final Report, so only an example of the types of results that were obtained will be repeated here. Figure 10 shows a color-coded map of the results for the 24-hour magnet collections from 1 meter above the sediment surface. Most of the tracer was found close to Outfall 20, with decreasing tracer mass recovered farther away from the release area. A total of 668 kg of tracer recovered within the yellow highlighted area represents 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 11 shows model results for silt sized particles (10 to 60 microns) in a simulated stormwater release from Outfall 20. Results are similar to Figure 10, although there is more particle movement to the north along the quay wall and less to the west away from 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. Since the silt results from modeling efforts are confirmed with 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.). These types of tracer studies can only be done under a limited number of site conditions, so it is typically expected that modeling will be performed in tandem to explore the various other possible scenarios that need to be addressed.

Figure 10. Colored Post Map of Magnet Results 24 Hours After Tracer Release Near Outfall 20.

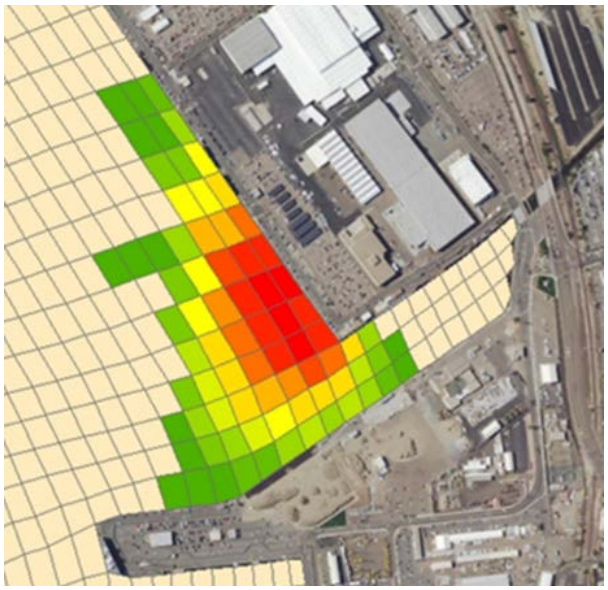

Figure 11. Modeled Release of Silt Tracer from Outfall 20.

(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, particle transport was observed in the direction of the prevailing current. As distance increased from the 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 meters of the release zone; and 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 modeling 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 2.1.1, conducting the particle tracking demonstration and validation study involves a specific set of steps. The first three of these tasks are described below in Section 5.2.2 and the final analysis task is described in Section 5.2.3.

5.2.2 FIELD TESTING

The field testing at HPS occurred over two weeks, starting the week of 12 September 2016. The objective was twofold: 1) to assess the stability against wave and tidal erosion of activated carbon cap amendment material; and 2) 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.

5.2.2.1 Background Studies

As discussed in Section 5.1.2, a similar set of background studies were performed.

5.2.2.2 Setup and Introduction of Tracer

On Wednesday 14 September 2016, a grid of sampling locations around the cap consisting of vertically oriented magnets were installed prior to the release of the two tracers. Presented below are the procedures for the setup and introduction of the tracer material on Thursday, 15 September 2016 for each of the two objectives:

1) Erosion from the Activated Carbon Cap Site

100 kg of pink tracer material was manufactured to mimic the physical properties (size, particle density (specific gravity), and settling velocity) of the activated carbon amendment. 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.

2) Recontamination from the Upland Sediments

200 kg of a green silt tracer was deployed in the intertidal zone north of the cap. The objective was to demonstrate if contaminated sediments were being remobilized (principally by wave action) and transported towards the activated carbon amendment cap.

5.2.2.3 Magnet Collection of Tracer

The sampling of the magnets was conducted during the midday high tide on Friday, 16 September 2016, and a second collection on the afternoon high tide of Wednesday, 21 September 2016. Powerful (high field) cylindrical rare earth magnets are encapsulated in plastic sheaths with end caps and attached to supporting plates (Figure 12) for the purpose of deployment on the sediment bed. Each plate had a small float attached with an identifying location mark.

The bottom sediments were sampled at the same time as the magnets using a smaller Petite Ponar grab. Very fine grain silty sediment was recovered at all sites with no signs of visible tracer (except in the deployment zone shown in Figure 13). The top 5 cm of sediments were sent back at the laboratory for the same dissolution and spectrofluorometric detection process used for the magnet samples.

Figure 12. The Magnet and Sheath Assemblies Attached to Baseplates and Placed on the Seabed.

Figure 13. 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.

5.2.3 SAMPLING RESULTS

Figure 14 shows an example post map for the green tracer on magnets and Figure 15 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.

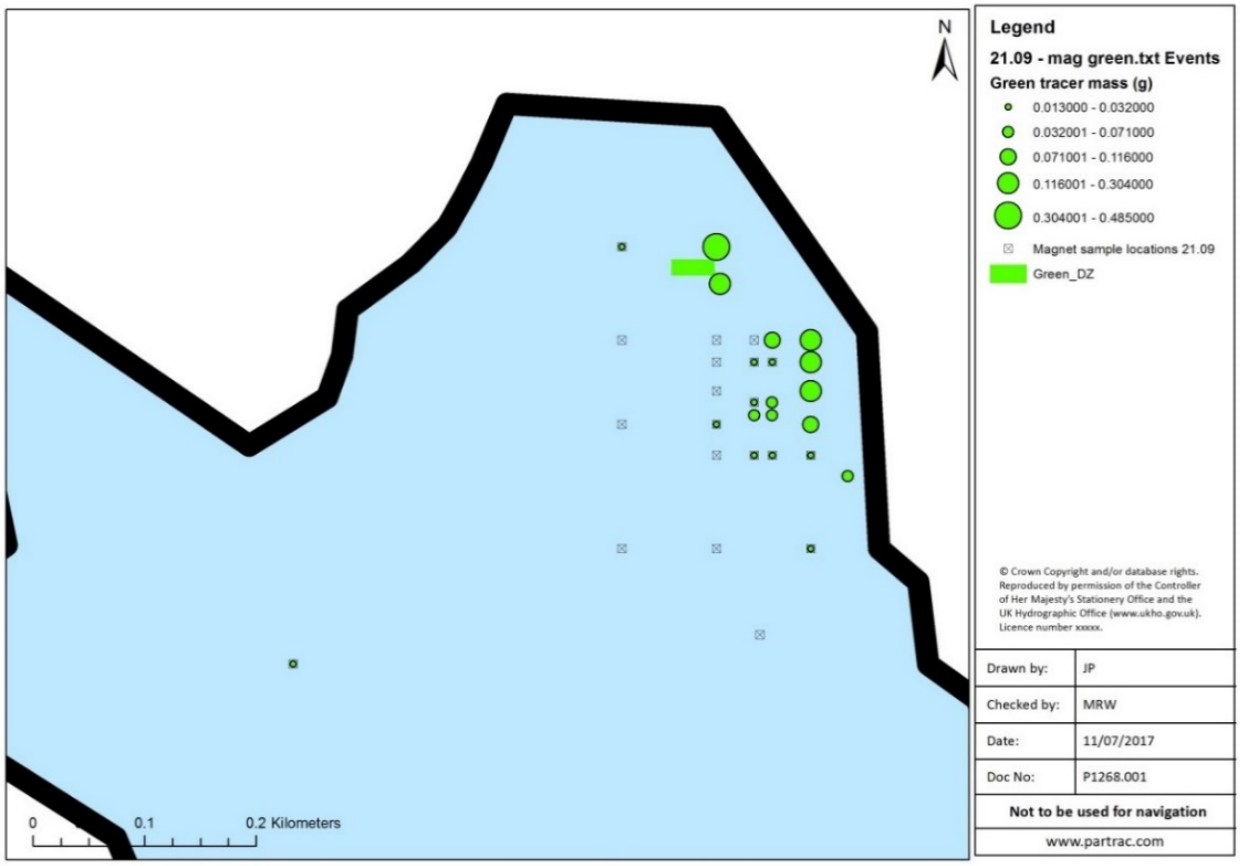

Figure 14. Green Tracer Results from Magnets after 6 Days.

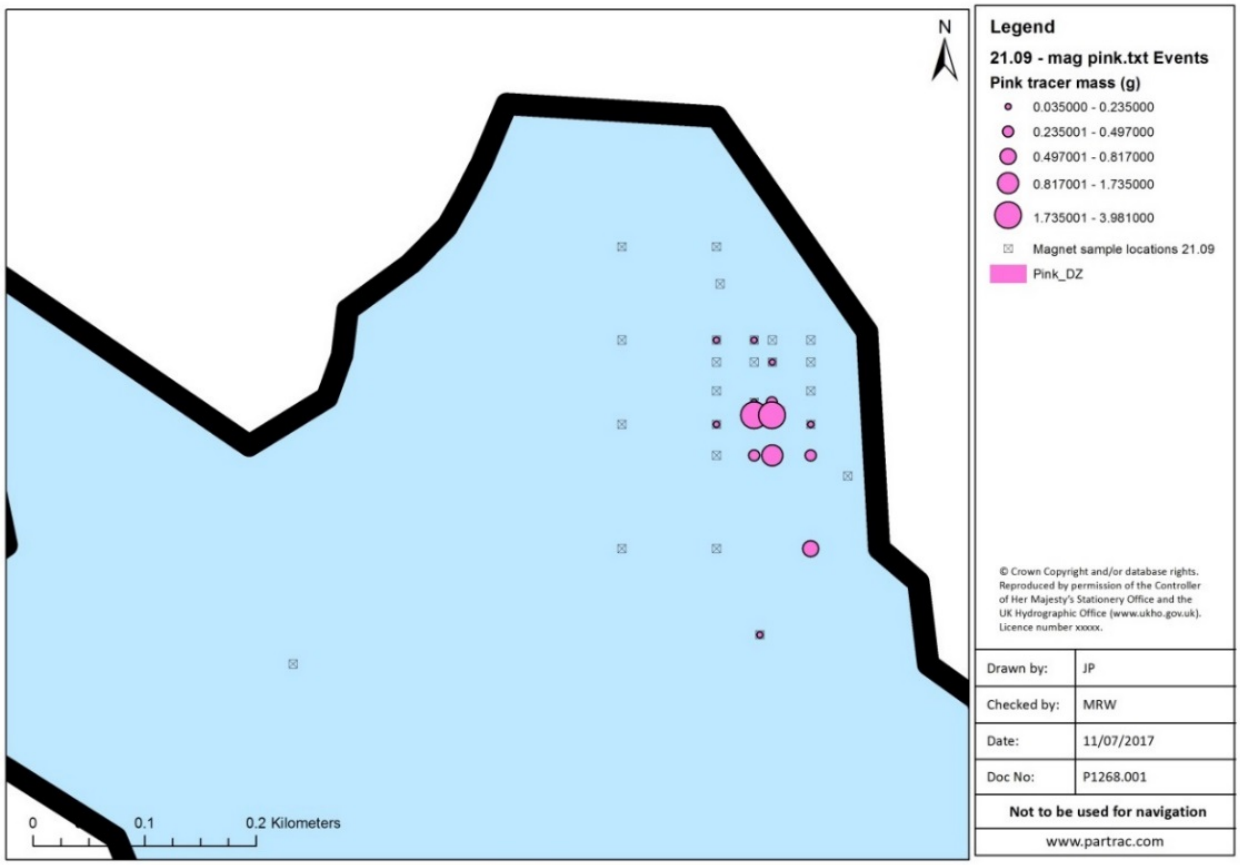

Figure 15. Pink Tracer Results from Magnets After 6 Days.

Overall, the HPS study demonstrated the following:

- 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 which included 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 and 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.
- This study demonstrated the use of, and applied methodology of, deploying two types of dual signature tracer at the same site.

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6.0 PERFORMANCE ASSESSMENT

6.1 HYDRAULIC MATCHING OF TRACER TO NATIVE PARTICLES

For the first performance objective, data from the Final Report Appendices showed comparable tracer characteristics to the field samples, so the performance objective was considered passed.

6.2 COMPARISON OF TRACER COLLECTION METHODS

For the second performance objective, data is presented from the laboratory testing conducted in the first year of the program. The efficiency of high field magnets for sampling suspended sediment is shown to be > 90% (Table 2). 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 L). The efficiency of traditional water sampling techniques and analyses (i.e., via filtration and gravimetric analyses) to determine the concentration of TSS, where correct procedures are followed, can be considered to be > 90%. Thus, the two techniques can be considered comparable in terms of efficiency.

Table 2. Efficiency of Magnet Sampler for Sampling Suspended Sediment.

Please note the 'sampling window' afforded by each 30 cm bar magnet is 1 L of water.

Mass of tracer in suspension (g)	Volume of water (L)	Concentration of tracer in suspension (g/L)	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

6.3 MAGNET RETENTION CAPACITY

For the third performance objective, data is 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. Measured current velocities ranged from ~ 0.01 – 0.1 meters per second (m/s) so retention capacity was greater than 90% and this objective passed (Table 3).

Table 3. The Magnet Retention Capacity Determined from Experiments Conducted in the Flume.

Flow velocity (m/s)	Initial Tracer on magnet (g)	Tracer retained on magnet after 1-minute 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

6.4 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. Table 4 presents data from a laboratory experiment designed to determine the sampling efficiency of a magnet frame.

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 exceeded about 80% recovery. Additional work to better design magnet bedframes is in progress, as the magnet bedframes did not perform as well as expected based on field performance of deposited tracer recovery from the sediment surface. The grab data at both field sites provided lower mass balance values compared to magnet results.

Table 4. 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 to settle for 1 hour, finest particles remained in suspension
Sediment grab	0.2	0.2	10	9.248	92	

6.5 PERFORMANCE OF SPECTROFLUOROMETRIC ANALYSIS METHODS

The spectrofluorometric analytical procedure was adapted and developed to exploit the fluorescent attribute of the tracer particles to directly provide a 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 Final Report Appendix 1 NBSD study report and Appendix 2 HPS study report). Table 5 presents the corresponding r^2 value for each reference standard developed (six in total). Table 6 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%.

Table 5. The Coefficient of Determination (r2 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 6. The Percentage Difference Between Each Data Point and the Line of Best Fit.

Data garnered from the six standard curves developed during the study program.

Data points (*N*)	Difference between scatter points and line of best fit (%)		
	Mean	Range	Std dev
54	4.9	0.0 – 29.5	7.1

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 six 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.

6.6 DEMONSTRATE MASS BALANCE

The evaluation of mass balance is based on the magnet data presented in Figure 10 and discussed in Section 5.1.3 for the first demonstration at NBSD. Assuming the tracer mass collected on each magnet represents collection of tracer over 1 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.

6.7 EASE OF USE

The evaluation of ease of use was based on comparisons to previous Space and Naval Warfare Systems Center Pacific (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. 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.

7.0 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. For comparison, Table 7 shows the size of the area of interest and total tracer mass deployed at the two demonstrations.

Table 7. 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. However, it is necessary 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 8 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 8. 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

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 more magnet sampling sites could have been used at both study sites. However, the 30-40 magnet sites were calculated in the above budget for one boat with four people to sample in a 10-hour workday. If the budget would have allowed, more magnets with higher sampling density near the release area at each demonstration site could have been used 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 8. 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. So while 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.

8.0 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 study design discussions 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 be included, so a standard operating procedure is provided in Appendix 3 of the Final Report. 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. 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 of the Final Report. 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 typically adds 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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