New Methodology Helps to Identify Sources of Pollution

NESDI Program's Pollutant Source Tracking Effort Supports the Proper Attribution of Contaminant Loads

WHEN A BODY of water is deemed contaminated by the U.S. Environmental Protection Agency (EPA), the polluters are responsible for initiating cleanup. However, when multiple entities share that body of water, the responsibility becomes difficult to assign. This is worsened when contamination is the result of historical discharges of unknown origin. Sediments and water may contain potential contaminants of concern (COC) from multiple sources as well as non-point sources (land runoff, precipitation, etc.). The complexities of such COC mixtures confound assignment of responsibility for mitigation.

Under section 303(d) of the Clean Water Act, states and territories are required to develop lists of waters that are too polluted or otherwise degraded to meet water quality standards. The law requires that these jurisdictions establish priority rankings for waters on the lists and develop Total Maximum Daily Loads (TMDL) for these waters. A TMDL is a calculation of the maximum amount of a pollutant that a water body can receive and still safely meet water quality standards.

Although the TMDL determines how much of a pollutant is in the water and associated sediment, it is only an indication of how much contaminant the water can accept from all sources while still meeting the stated criteria. In the absence of defensible source information, the Navy, often considered a high profile discharger by the civilian sector, can be held responsible for a disproportionate share of the source pollutant burden, even if that amount of pollutant did not originate from the Navy.

A Challenging Problem

Recognizing and unraveling multiple sources of contamination requires advanced chemical fingerprinting data of large numbers of samples, which can be cost-prohibitive. Thus, the need exists for a cost-effective process by which naval facilities can collect the data needed to recognize and distinguish between different sources of contamination in sediments and water proximal to former or existing Navy facilities.

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In 2006, the Navy Environmental Sustainability Development to Integration (NESDI) program co-sponsored a project aimed at solving this problem. The project's goals were to identify, review, demonstrate, and validate pollutant source tracking technologies, and to develop a

cost-effective technical framework for Navy water program managers to work with.

The project team from the Space and Naval Warfare Systems Center Pacific (SSC Pacific) received leveraged assistance from NESDI, the Strategic Environmental Research and Development Program (SERDP), and the Environmental Security Technology Certification Program (ESTCP).

As a starting point, the team consulted a process outlined in a previous Navy report (Stout et al., 2003). This project dealt with polyaromatic hydrocarbons (PAH), a commonly found organic contaminant at Navy facilities. Many aspects of this process are transferable to use with metals, bacteria, and other organic contaminants such as polychlorinated biphenyls (PCB).

Using this process and a suite of environmental forensic techniques, the team demonstrated and validated a Pollutant Source Tracking (PST) process for metals, bacteria, and organics, and compiled technical guidance for Remedial Project Managers and others to use.

Environmental Forensics

The general approach followed a process outlined in *Environmental Forensics* by Robert Morrison (2000). Dr. Morrison coined the term "environmental forensics" and defines it as "the review and interpretation of scientific data for the purpose of identifying the source and age of contaminant releases." The techniques used in this process may include aerial photograph interpretation, underground storage tank corrosion models, a literature review to identify the date when a chemical or additive became commercially available, association of a particular chemical with a manufacturing process, chemical profiling (fingerprinting), chemical degradation models, and contaminant transport modeling. The technical guidance produced by the project team focused primarily on chemical fingerprinting, but also touched on other key forensic techniques as needed.

PST is broadly applicable to many types of classes of environmental contaminants such as metals, organics, biologicals, and other inorganics, though the approach for specific contaminants can be different. The contaminants studied by the project team in the case studies include copper, bacteria, and PCBs, although only copper and PCBs had sufficient data for case studies. These substances were both high-priority contaminants and good candidates for source tracking.

Metals Source Tracking

There are many explanations for the presence of metals in an aquatic environment. There are natural sources, including leaching from minerals with high metal concentration, atmospheric transport, and deposition of metal-laden particles. There are also anthropogenic (synthetic or man-made) sources such as industrial and municipal effluent discharges, stormwater runoff, or leaching from antifouling paints.

Metal concentration gradients can help identify trends in seawater for estuaries and harbors that result from both anthropogenic and natural geologic sources. In San Diego Bay, environmental concentration monitoring has indicated the presence of elevated copper levels in the water. Though some amount of copper is present in all bodies of water, elevated levels increase the regulatory pressure for capturing and treating stormwater.

The Basics About the NESDI Program

THE NESDI PROGRAM seeks to provide solutions by demonstrating, validating and integrating innovative technologies, processes, materials, and filling knowledge gaps to minimize operational environmental risks, constraints and costs while ensuring Fleet readiness. The program accomplishes this mission through the evaluation of cost-effective technologies, processes, materials and knowledge that enhance environmental readiness of naval shore activities and ensure they can be integrated into weapons system acquisition programs.

The NESDI program is sponsored by the Chief of Naval Operations Energy and Environmental Readiness Division and managed by the Naval Facilities Engineering Command (NAVFAC) out of the Naval Facilities Engineering and Expeditionary Warfare Center in Port Hueneme, California. The program is the Navy's complement to ESTCP which conducts demonstration and validation of technologies important to the tri-Services, U.S. Environmental Protection Agency and Department of Energy.

For more information, visit the NESDI program web site at www.nesdi.navy.mil or contact Leslie Karr, the NESDI Program Manager at 805-982-1618, DSN: 551-1618 or leslie.karr@navy.mil.

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Compliance related to the TMDL process is expected to further impact capturing and treating stormwater.

In an effort to identify the source of the elevated copper levels, the project team performed a case study in San Diego Bay. Using an extensive collection of water samples collected for a previous SERDP project (CP-1156: "Fate and Ecological Effects of Copper and Zinc in Estuarine Environments: A Multi Disciplinary Program"), the team evaluated the distribution of many different metals, focusing on concentration gradients. They then looked for associations with sources of the metals identified, and used various statistical analyses to make sense of the data. Finally, the team used isotopic ratios to map metal sources. The team was able to identify an anthropogenic source for the copper (antifouling coatings) as well as a geological source (natural silty sediments). The copper from antifouling coatings can be attributed to several sources including hull coatings on pleasure craft and Naval vessels.

Bacteria Source Tracking

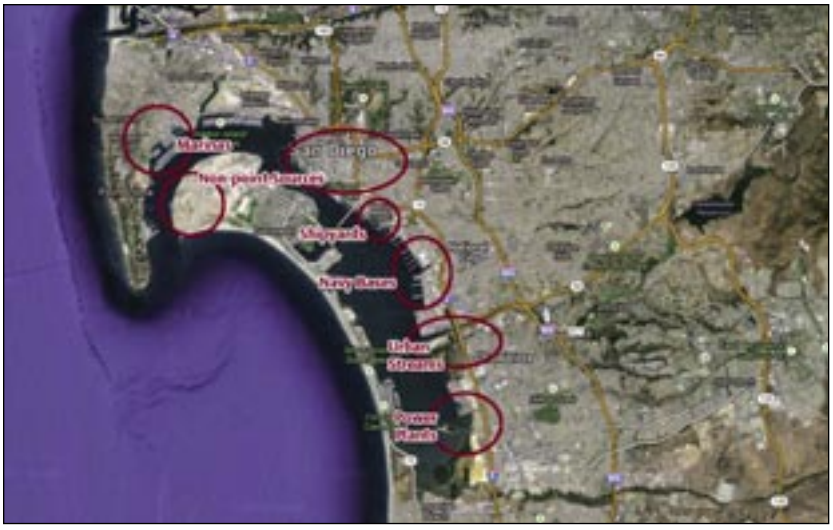
The process of identifying sources of bacterial pollution is a difficult one but one that is necessary to resolve compliance issues and target complete remedial actions. Certain bacteria and viruses serve as indicators for a wide range of pathogens, and these organisms are those targeted for microbial (bacterial) forensics (EPA, 2002b). The most likely use of microbial source tracking by Navy managers is during TMDL implementation, and involves the identification of fecal bacteria.

Bacterial source tracking is much more complicated than metals tracking because the science is much less mature. Even in the best case scenario, bacterial source tracking mechanisms are only accurate about sixty percent of the time.

Because of the data gaps in this area, the team did not perform a demonstration. Instead, they recommended the formation of a user group to perform the following steps:

- Study current research and development (R&D) efforts across the field
- Choose two or three of the most promising R&D efforts
- Fund efforts to establish a knowledge management system
- Fund laboratories to perform R&D on several fronts

At the conclusion of this process (approximately two to three years) the group would pick one methodology and seek funds to support a five to 10 year project.



The Navy has a large presence on the water, but there are numerous other sources of discharge.
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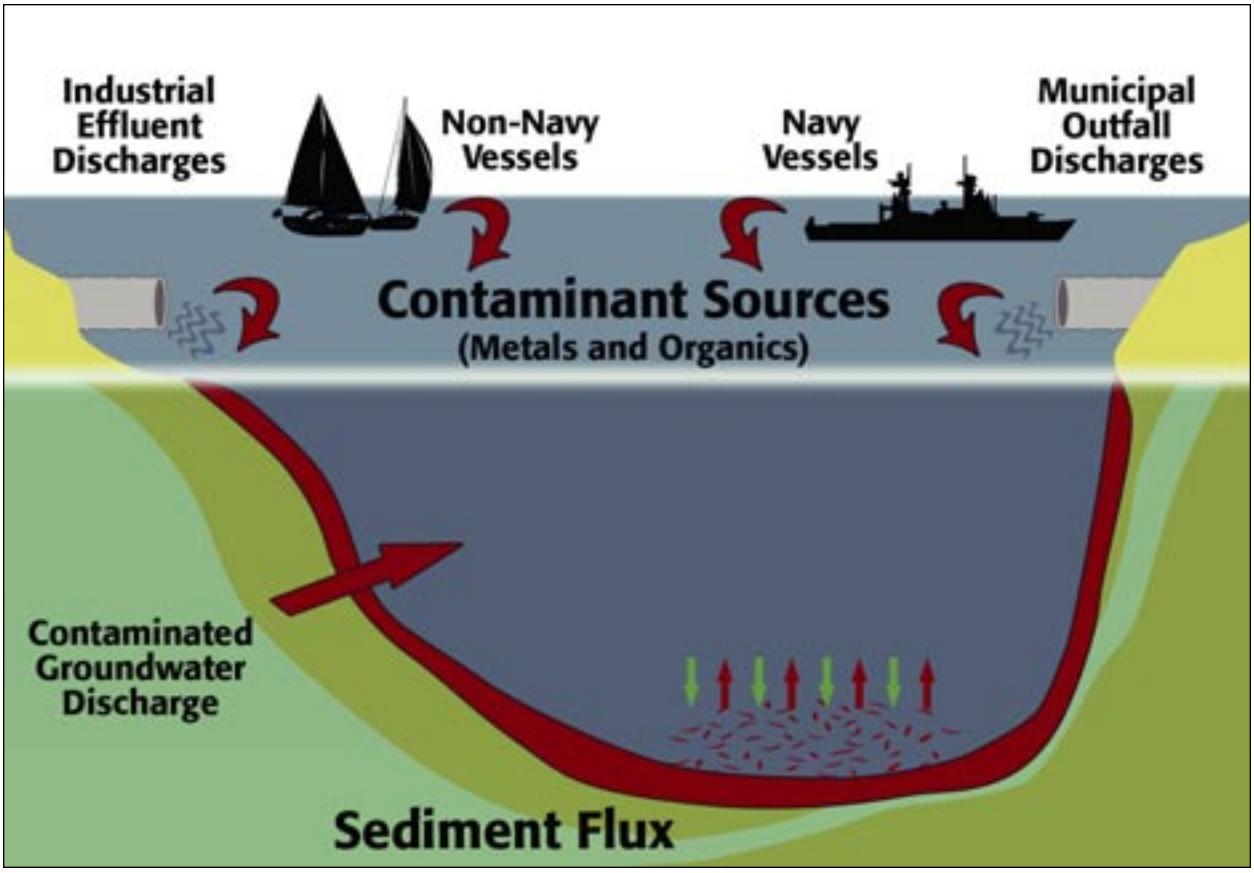
Organics Source Tracking

In 2006, NAVFAC issued a TMDL Prioritization Report listing the main COCs for their compliance program, and PCBs topped the list. PCBs are a class of chlorinated organic compounds that were produced commercially by Monsanto from 1930 to 1977 under the trade name Aroclor. PCBs were used in a wide



Examples of point and non-point sources of copper in San Diego Bay, CA. Point sources are those with well-defined physical discharges, while non-point sources are not physically well defined. In this figure, non-point sources include runoff from urbanized/industrialized areas, both civil and military.

array of industrial applications. Their stability results in a long environmental life, and they are often found residing in sediments. The standard approach to compliance and cleanup has been to assign blame to the source closest to the contamination, which may or may not be accurate.

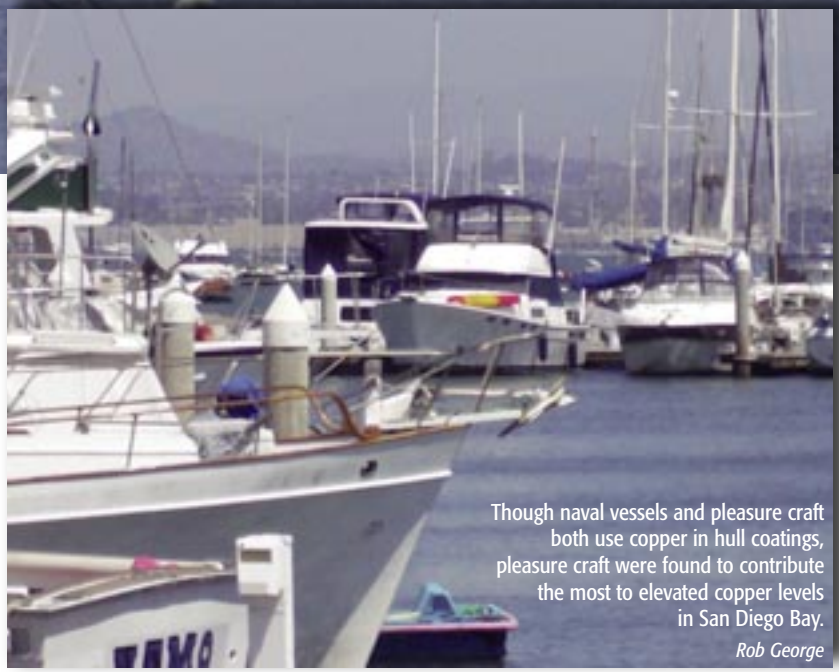
Studies aimed at identifying the sources of PCB contamination in sediments have been conducted for the past decade or so, utilizing some form of multivariate statistical analysis.

For this study, the project team chose the now-shuttered Hunters Point Shipyard south of San Francisco. Due to the regulatory Remedial Investigation (RI) and Feasibility Study (FS) associated with the base closure, there was a large amount of PCB data available to leverage for this project. The team utilized data and information generated under an ESTCP project entitled "Integrated Forensics Approach to Fingerprint PCB Sources using Rapid Sediment Characterization (RSC) and Advanced Chemical Fingerprinting (ACF)." RSC is a way to quickly characterize contaminated sediments at marine sites. Advanced chemical fingerprinting identifies a unique chemical pattern in the data to help determine its specific PCB composition. This, in turn, helps narrow down its source.

This combined RSC and ACF approach was used at Hunters Point. The preliminary RSC (field screening) indicated that two types of Aroclor, located in two distinct areas, were responsible for most of the contamination. Advanced chemical fingerprinting helped to identify possible sources of the contamination. It was determined that the two sources were different mixtures of Aroclor 1254 and 1260 emanating from old sewer outfalls and a former landfill.

The User's Guide

The main goal of this project was the creation of a user's guide that would help program managers address the cleanup and compliance issues related to contaminants in the marine environment. The guide outlines the



Though naval vessels and pleasure craft both use copper in hull coatings, pleasure craft were found to contribute the most to elevated copper levels in San Diego Bay.
Rob George

various steps and processes that may be needed for successful identification of each class of contaminant. As there are many possible contaminant formulations, there are nearly as many specific approaches to identifying them. This user's guide will help managers clearly understand the suite of tracking technologies currently available, their strengths and weaknesses, and how those technologies can be used to develop management decisions for compliance issues. This scientifically defensible approach will help prevent arbitrary and burdensome regulatory decisions and actions that negatively impact the Navy.

The user's guide assists managers with answering such questions as:

- What are possible Navy sources of contamination?
- What alteration mechanisms should I be aware of?
- What rapid screening tools are available?
- What analytical chemistry methods are available?
- What is the best way to analyze/process my data?
- What are the data/technology gaps?

(Note: Alteration mechanisms include advection, dispersion, and adsorption which can contribute to the spatial and temporal changes in contaminant concentrations observed in the marine environment.)

Lessons Learned

Lessons learned during the two case studies above are included in the user's guide, along with a summary of an earlier bacterial source tracking study. Synopses of these case studies are included below.

Virginia Beach

In 2007, a TMDL investigation was instigated to determine the reason for elevated bacteria levels at Naval Air Station Oceana, Virginia Beach, Virginia. This study determined that horse manure from a stable on-base was the main culprit, contributing 92 percent of the contaminant. Monthly sampling was performed over a

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10-month period and intensive sampling was performed three times a week in historical wet months. The user's guide summarizes and analyzes the lessons learned as the result of this project. Suggestions for best management practices regarding fertilizer were discussed as were weaknesses such as insufficient sampling and the wisdom of performing the intensive sampling only during the wet months.

Hunters Point

The Hunters Point project was a success because researchers were able to pinpoint two distinct source areas of PCB contamination, using methods that will serve as a framework for program managers facing similar situations. These methods can quantitatively apportion contaminants among multiple sources, but this often requires historical site information that is hard to obtain. However, the project illustrated the importance of experienced forensic technicians and high-quality data.

The former Hunters Point Shipyard is located in South San Francisco.

And perhaps even more importantly, illustrated the need for presenting the results in a fair, accurate, and easy-to-understand format.

San Diego

The team identified various tracking and fingerprinting approaches for the identification of the original source of metals, in the aquatic environment, including:

- Concentration gradients
- Association of the metal with a specific source
- Differentiation of sources using statistical analysis
- Application of fate and transport models for the elucidation of sources and effects
- Fingerprinting the sources with isotopic ratios (although this technology is immature and there are important data gaps in this area).

The successful application of any of these approaches is determined by the characteristics of the area of study.

What's Next

Along with the second demonstration site, in the Ashtabula River in Ohio, the PCB fingerprinting case studies can be investigated further on the ESTCP web site by visiting www.serdp-estcp.org and entering "200826" in the search box.

The PST process was included in the 2013 Remediation Innovative Technology Seminar series, and in other seminars and webinars. The user's guide is available directly from SSC Pacific and will be available for download soon. ⚓

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