

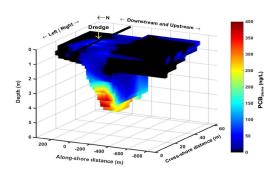




The OPTICS tool (U.S. Patent No. 11079368) integrates commercial, off-the-shelf, *in situ* optical, physical, and water quality sensors, discrete surface water samples, and a multiparameter statistical model to provide high-resolution characterization of surface water chemicals of concern (COCs) (Chang et al. 2018a, b). The OPTICS methodology is effective for addressing a wide range of questions at contaminated sediment and surface water sites, including:

- What is/are the source(s) of COCs and what is its fate?
- Is erosion of the sediment bed leading to the exposure of buried contaminants?
- Are contaminants being redistributed and/or moved offsite by sediment transport and water movement?
- Will natural processes lead to the burial and isolation of contamination by relatively clean sediment?
- If a site is actively remediated, could sediment transport lead to recontamination?
- Are control measures effective at reducing contaminant transport?

The novel use of optically-based *in situ* monitoring for high-resolution, robust derivation of chemical properties allows for quantification of surface water COC concentrations over unprecedented temporal and spatial scales.



Chemical contaminant concentrations at scales that are unattainable through traditional sampling

OPTICS Technology

- Provides surface water chemical contaminant concentration at significantly higher resolution relative to traditional methods
- Integrates data from commercially available aquatic sensors with discrete water sample data using a multiparameter statistical prediction model
- Applicable for baseline assessment, source control evaluation, remedial implementation monitoring, and remedy performance evaluation

Advantages Compared to Traditional Sampling

- Environmental monitoring costs reduced by as much 99%
- Contaminant concentrations at resolution that supports flux and mass loading quantification
- Chemical concentrations at suitable resolution for interpretation in the context of biophysical processes

Best Suited For

- Surface water COCs
- Hydrophobic COCs at concentrations detectable using analytical laboratory procedures
- Freshwater, estuarine, or marine aquatic environments with water depths ranging from 1 meter to hundreds of meters

Pearl Harbor, Honolulu, Hawaii, Sediment Site

The Pearl Harbor Sediment Site (at Joint Base Pearl Harbor-Hickam, Hawaii) was listed by the U.S. Environmental Protection Agency as a contaminated site in 1992, primarily due to pollutants from naval and surrounding land activities. Recent investigations, facilitated by support from the Environmental Security Technology Certification Program (ESTCP), focused on Decision Unit N-2, a 10.8-hectare area along the harbor's eastern bank, where elevated PCB levels near the Oscar 1 Pier outfall suggest ongoing contamination. Using OPTICS technology, Integral completed a study from November 2022 to March 2023 to examine stormwater contributions of PCBs, employing high-resolution, *in situ* monitoring. Data from this study aids in assessing PCB dispersal patterns and informs targeted remediation efforts for long-term site recovery.

This ESTCP project demonstrated the use of OPTICS for source control evaluation and stormflow plume characterization at Oscar 1 Pier outfall, Decision Unit (DU) N-2, Pearl Harbor Sediment Site, Honolulu, Hawaii (Oahu), between November 2022 and March 2023.

- OPTICS technology was demonstrated at DU N-2, Pearl Harbor Sediment Site ("Site"), Honolulu, HI (Oahu). DU N-2 is impacted by PCBs, which were hypothesized, but had not been previously shown to be delivered during stormflow to surface water and ultimately, site sediment, via the Oscar 1 Pier outfall.
- Two stationary OPTICS systems were deployed for 4 months in winter 2022/2023 and provided near-continuous data at 20 minute intervals.
 A mobile OPTICS system was deployed from a vessel during baseline (November 2022 and March 2023) and stormflow conditions (February 2023) as it transited throughout DU N-2.
- OPTICS statistical prediction modeling enabled derivation of high resolution PCBs. Model results were compared to discrete water sample data and statistical metrics were compared to the same metrics calculated for water sample field duplicates.
- OPTICS provided robust PCB data at sufficient resolution to evaluate that
 Oscar 1 Pier outfall is a source of contamination to DU N-2, and that PCBs are
 discharged from the outfall, remain in suspension, and dispersed throughout
 the site before settling.

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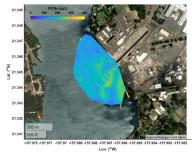
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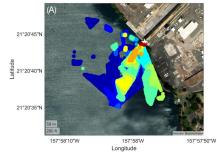
The Environmental Security Technology Certification Program (ESTCP) is the U.S. Department of Defense's environmental technology demonstration and validation program. The program's goal is to identify and assess innovative technologies that address DoD's high-priority environmental requirements efficiently and cost-effectively.



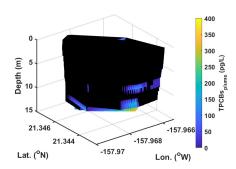
OPTICS instrumentation system deployed at the base of Oscar 1 Pier Outfall in DU N-2, Pearl Harbor.



OPTICS-derived TPCB (total PCB) concentrations at midwater column are higher near the outfall and toward the south during ebb tide conditions.



TPCB concentrations in exceedance of baseline were observed near the water surface closest to the outfall and dispersed throughout the site at deeper depths.



3D volumetric plot of TPCB concentrations in exceedance of baseline throughout DU N-2 show that PCBs are discharged from the outfall, remain in suspension, and dispersed throughout the site before settling (the outfall is toward the back of the figure).



Understanding PFAS Behavior in Sediment

By Jarrod D. Gasper, Senior Consultant

Per- and polyfluoroalkyl substances (PFAS) have vaulted to the forefront of interest for manufacturers, water utilities, regulators, litigators, and the wider public. With diverse applications, PFAS are in hundreds of products for residential, commercial, and industrial use. As a result, they are ubiquitous in the environment, and they are increasingly regulated by the Environmental Protection Agency and state agencies.

Contrary to "old guard" contaminants—such as PCBs and dioxins/furans—many PFAS do not sorb strongly to sediment. Nonetheless, they cause concern to the contaminated sediment practitioner due to their diversity. The expanse of PFAS, particularly larger ones, brings four notable characteristics as they relate to sediment:

- **1.** Certain designed characteristics of larger PFAS can vastly increase their potential to sorb to sediment compared to simpler, smaller PFAS.
- 2. Larger PFAS compounds may incorporate or contain one or more basic PFAS, such as perfluorooctanoic acid (PFOA) or perfluorooctane sulfonic acid (PFOS). The degradation of these larger PFAS can release the incorporated PFAS into the environment.
- **3.** Transformation- or degradation-type reactions generate different PFAS. For example, the degradation of fluorotelomer alcohols (FTOHs) forms compounds such as perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), and PFOA.



4. Analytical methods for PFAS fail to measure precursors that eventually transform into the analyzed PFAS. They also fail to detect the presence of specific PFAS when it incorporated into a larger PFAS.

Because of these characteristics, PFAS can be released into the environment in forms that are highly sorptive (#1), contain other PFAS and PFAS precursors (#2 and #3), and remain undetectable by current analytical methods (#4). This implies that sediment can



become enriched in PFAS that are "invisible" (i.e., not measured by standard methods) until they degrade and subsequently release known, detectable, and less sorbable PFAS. Essentially, PFAS visibility and sorbability are driven by molecular changes, and a basic understanding of these changes can help explain PFAS fate and transport.

As an example, one of the largest PFAS applications is for coatings to impart water- and stain-resistant properties onto a material. Understanding the functionality of these surface applications, by way of their molecular structure, is key to understanding the potential for PFAS accumulation in sediment. Consider a common class of PFAS fabric treatments—a type of polymer, known as a side-chain fluorinated polymer, comprising three parts:

- **PFAS moiety:** The moiety is the source of the functional characteristics of stain- and water-resistance. The type of moiety is defined by the functional group (carboxylic acid or sulfonate) and chain length. Examples include a short-chain sulfonate, such as perfluorobutanesulfonic acid (PFBS), and a long-chain carboxylic acid, such as PFOA.
- **Polymer backbone:** This part provides adhesion to the fabric to ensure the durability of treatment. The polymer backbone is typically a urethane or acrylate polymer with numerous PFAS moieties attached to it.

• **Linkage:** The linkage provides the chemical bond between the PFAS moiety and the polymer backbone. The linkage-moiety combination often includes a PFAS precursor. Examples include FTOHs, such as 8:2 FTOH, and perfluorooctanesulfonamide (PFOSA).

These polymers have high molecular weights— 10,000 Da or higher—that allow them to sorb or settle into sediment and biosolids. (After all, the purpose of the polymer backbone is to ensure adhesion to a textile surface.) Over time, however, these compounds degrade in the environment. The degradation rates are variable, with half-lives ranging from years to decades. Degradation rates are affected by pH and organic carbon content. Higher rates of degradation occur at high pH and at lower organic carbon content. Regardless, as these compounds degrade, PFAS or their precursors are released from the degrading structure. The base carboxylic or sulfonate molecules (e.g., PFOA and PFOS) represent the degradation endpoints. They are highly stable, readily identifiable, and substantially less sorptive than the original polymeric molecules.

The example of the side-chain fluorinated polymer demonstrates the need to evaluate larger PFAS despite their "invisibility." There are three key strategies to do so:

Develop a strong conceptual model. Analysts
 can create a conceptual model that includes the
 potential for PFAS precursors and smaller PFAS from

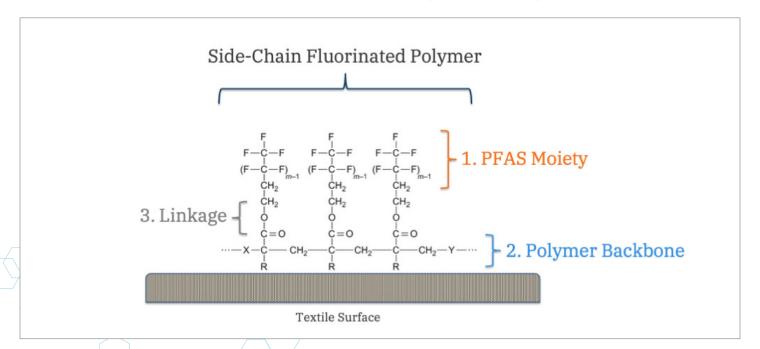


Figure 1. Side-Chain Fluorinated Polymer Molecular Structure

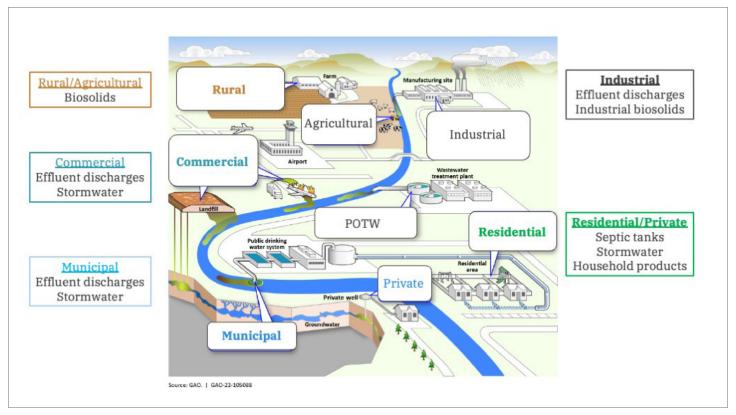


Figure 2. A comprehensive conceptual site model illustrates the potential for PFAS precursors and smaller PFAS from larger compounds.

larger compounds. Facilities commonly associated with these compounds include wastewater treatment plants, textile mills, and paper mills. Locations with biosolids are also notable.

• Use alternative methods to assess hidden PFAS.

Procedures to detect otherwise unmeasured

PFAS include a total oxidizable precursor (TOP)

assay or a measurement of total organic fluorine

(TOF). These methods, while less quantitative than

mass spectrometry, can indicate the presence of

precursors or PFAS-containing compounds.

• Consider fate and transport changes with structure. When PFAS-containing polymers or PFAS precursors are present, it is important to understand that their sorption and transport behavior can change as molecules degrade and transform.

Consider, for example, how these strategies explain spikes in PFAS in surface water following a reservoir

draw down. During the draw down, sediment is exposed to the atmosphere, allowing for PFAS degradation and oxidation of organic matter. When the sediment is then flooded, new PFAS—produced from degradation or released from oxidized organic matter—mobilize to create the concentration spikes. Because precursor and polymer degradation rates are often slow, sediment enriched in these compounds can be a long-term source of PFAS. Additionally, because regulatory thresholds for PFAS are low (e.g., the EPA maximum contaminant levels for PFOA and PFOS are each 4 ng/L), small sources of PFAS can be significant. It is only through nuanced investigative strategies that this phenomenon can be explained and, subsequently, mitigated.

Integral has experience with PFAS, particularly those in sediment, and has employed these investigative strategies on behalf of clients. Today, with PFAS discussions becoming increasingly relevant, Integral's role in addressing these compounds is vital.

Authors

GRACE CHANG, PH.D.

Dr. Grace Chang has more than 25 years of experience in the fields of limnology and oceanography. Dr. Chang has managed programs involving field operations, data processing and analysis, and numerical modeling for environmental characterization, observational monitoring, scientific research, and technology development in support of marine renewable energy, hydrodynamics and sediment transport, and oceanographic research programs. She is recognized for her continued advancement of analytical methods in hydrodynamics and particle characterization through optics and acoustics, as well as for environmental research and monitoring. Dr. Chang has more than 40 peer-reviewed publications and frequently is invited to review materials for professional journals and national funding agencies.

JARROD D. GASPER

Mr. Jarrod Gasper is a geochemist with 18 years of experience. His primary area of expertise is the analysis of the fate and transport of metals and organic chemicals in the environment, with a focus on mining and industrial sites. His experience includes the forensic analysis of contaminant sources, the geochemical analysis of sediments and water, prediction and modeling of physical limnology and water quality at proposed mine pit lakes, analysis and modeling of surface water quality, and remediation of contaminated groundwater. Mr. Gasper's background includes aqueous geochemistry, geology, and chemical engineering.

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