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Reliably Measuring Low-Level Persistent Organic Contaminants in Surface Water

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To understand the full picture of a site, sediment practitioners must consider the presence, sources, and pathways of persistent organic pollutants (POPs) in submerged sediment; surface sediment and water; biota; and drainage basins. Legacy contaminants, often at the heart of sediment cleanups, can cause long-term effects across every linkage in the food web. POPs are stable chemicals that can resist degradation for decades and even centuries, can travel far from their sources, and often occur at very low concentrations. Those ultra-low levels are hard to quantify confidently with traditional sampling and analytical methods. Understanding their nature and extent requires specialized sampling techniques and technologies.

Traditional surface water sampling involves filling a container with a sample of water (often 2 liters) and analyzing it for POPs dissolved in the water and bound to particles within that sample. Because POPs are hydrophobic and have low solubility, very few molecules may be present in a typical sample, making detection with standard analytical tools difficult. Further, a grab sample, or even a composite of grab samples, represents only a relatively limited spatial and temporal window.

Traditional water sampling is often insufficient for detecting and characterizing these contaminants because the analyst is working with a relatively small volume of water to characterize potentially widespread, low-level contamination. Enter high-volume, long-duration sampling technologies as an additional tool in the investigator's toolbox. These systems use pumps to actively and precisely move a known quantity of water through solid absorptive media, concentrating the POPs in a large volume of water within the sampling device.



Glass fiber filter (left) for solid phase analysis. Stainless steel column (right) contains resin beads for dissolved phase extraction.



Plastic absorptive resin beads for dissolved fraction sampling.

The solid media consists of a particle filter and a plastic resin column. The latter sorbs contaminants that are small enough to pass through the glass fiber filter. Because POPs adhere to plastics, plastic filters, and resins within the sampling device efficiently extract these chemicals from water. The filter and resin target different groups of POPs in the water: those associated with suspended particles and those dissolved within the water matrix, respectively.

The mass of compounds trapped on each material is analyzed separately and, in combination with the volume of water that passed through the media, can be used to calculate the concentration present in that water. Concentrating target analytes for extraction and measurement allows for significantly lower detection limits and greater confidence in quantifying contaminant concentrations. Sample representativeness relative to the environment being studied also increases with increasing sample volume.

Sample representativeness relative to the fluctuating stressor levels experienced by biota over one or more seasons also increases with sample collection duration. These sampling devices can be deployed over extended periods in dynamic systems, tracking the influence of short-term variabilities as well as longer trends.

Sample collection rate, controlled by the collection device, can be programmed to coincide with the behavior of the water body. In river systems, the river's flow rate can be monitored, and sample frequency can be proportional to flow allowing the filter and resin to capture dissolved POPs in proportion to the movement of contaminant mass through the system. Modelers can then use these data to calculate the mass of contaminants transported through the system over the sampling period.

From the risk assessor's perspective, the sampling protocol can also provide a better representation of the exposure conditions experienced by organisms bioaccumulating contaminants in these environments.

For 25 years, Integral (formerly Kinnetic Environmental) has been inventing, testing, and developing technology—from hardware to software—to continually improve deployment flexibility, data quality, resiliency, and efficiency at every level. These systems can be configured for location, duration, volume, and sampling rate. Robust enclosures allow independent monitoring in publicly accessible and remote locations such as river levees. The systems can be integrated with existing facilities, like flow meters at water treatment plants, to provide flow-weighted POP data for calculating facility contaminant loads from a determined sampling duration.

Open-water samplers are submerged and programmed to pump water at specified intervals, producing an integrated sample over the target duration. Adjusting pump and sample frequency variables allow for customizable deployment periods, from hours to weeks, so a representative sample can be captured across a broad range of conditions and interests.

Case Study: West Virginia

On a river in West Virginia, water analysis of dioxins was used to examine the effectiveness of a sediment cap under both high- and low-flow conditions. A hydrologic study was used to select transect locations where collected samples would be representative of conditions in the river. The sampling device's position and depth were maintained using live-boating.

Each sample was developed by passing 240 liters of water continuously through the media over an 8-hour period. A nearby U.S. Geological Survey river gauge provided flow-rate data, allowing contaminant concentrations to be converted to loads.



Live-boating on West Virginia river maintaining pinpoint location while sampling at prescribed depths based on previous hydrological study.

Case Study: Central Coast Long-Term Environmental Assessment Network (CCLEAN); Monterey Bay Area Governments, California

Integral has monitored the sources, loads, and effects of contaminants discharged into the Monterey Bay Marine Sanctuary since 2001. The mission of the project is to safeguard the beneficial uses of Monterey Bay's waters as defined by California regulations. Data are generated through the monitoring of the Bay's rivers, water treatment facility effluents, and receiving ocean waters, as well as the collection of coastal filter feeders (*Mytilus californianus*).

The study uses several high-volume, long-duration sampler configurations, including ocean moorings, river samplers, and effluent-installed devices, in five water treatment facilities. Across the ocean, river, and treatment-facility systems, absorbent POP resin filters collect contaminants from 250+ liters of water drawn through each device, producing an integrated 30-day contaminant concentration for each sample.

The river and treatment facility samplers are programmed for flow-weighted collection, allowing calculation of contaminant loads entering the Bay. The program covers 30 days during the dry season and 30 days during the wet season in every year since 2001. That long record makes it possible to examine trends and identify changes in contaminant sources and transport over time.

As with any broad-scale study, multiple sampling programs help refine the conceptual site model. Water grab and composite sampling are also performed to analyze per- and polyfluoroalkyl substances (PFAS), nutrients, current-use pesticides, and bacteria. Mussel samples are collected for bacteria and organic pollutants. Together, these efforts have identified major POP contributors to Monterey Bay and informed targeted interventions and regulatory actions. Regional collaboration among the various cities and agencies is critical to this comprehensive, coordinated effort.

Overall, POP loading to the Bay was found to be greater from rivers than from treatment facilities, indicating the need for targeted sampling and management in these rivers. After some flood events, samplers have shown unique signatures of DDT and related compounds, suggesting that these pesticides may have been stored in sediment and soil and were then mobilized by heavy precipitation and floodwaters. DDT's effects on bird shell failure persists, and tracing environmental reservoirs of this banned chemical remains critical to recovery efforts.

These studies also offer insight into how more frequent flooding linked to climate change affects ecosystems and food webs. High-volume sampling data show that DDT concentrations in the Pajaro River have not declined over time, and nearshore ocean waters still regularly exceed water quality objectives. Although levels are approximately 5 percent lower than in 1985, chemical distributions remain similar over time, providing insight into sources and pathways.

CCLEAN has also shown that Monterey Bay ocean water has exceeded water quality objectives for polychlorinated biphenyls (PCBs) in at least one integrated 30-day sample every year since 2001.

This highlights a persistent water-quality issue in the Bay that would have been very difficult to elucidate using traditional sampling methods alone.

Case Study: Washington State Department of Ecology

Lastly, the Washington State Department of Ecology is tracing a significant POP issue in the state's surface waters and has been consulting with us to develop its own system for extensive in-house processing and a statewide monitoring program. Scaling this technology statewide allows for consistent, highly representative data collection with a reasonable level of effort and cost.

Once deployed, these devices can operate independently for a range of durations and sampling rates at multiple locations throughout a watershed. They can also reduce the need to send field staff into the field during storm events or other episodic flow conditions, when identifying contaminant presence, transport, and loads may be particularly important.

Closing

Protecting the health of our water resources requires an understanding of aquatic stressors that can affect biota at very low levels and persist well beyond the time and place they were released. High-volume, long-duration water sampling devices provide researchers a way to connect the dots between offshore contamination, watershed sources, and ongoing transport pathways. By integrating contaminant concentrations over larger volumes and longer periods, these technologies provide detection and quantification capabilities that can complement—and in some applications, significantly improve upon—traditional surface water grab sampling.