
Application of Passive Sampling in The State and Regional Water Boards for Water Quality Monitoring Programs

White Paper

February 1, 2021
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Executive Summary

Passive sampler devices (PSD) have been available for use for the last two decades. PSDs provide a time-weighted average concentration of pollutants indicating the average conditions of the waterbody during deployment periods (Alvarez 2010, Booij et.al, 2016). Their use by the State Water Resources Control Board or the Regional Water Quality Control Board (collectively, Water Boards) is very limited. The Water Boards need to increase passive sampler monitoring capacity to be efficient in water quality monitoring.

Upon encouragement of the Office of Information Management and Analysis (OIMA) management, interested State and Regional Water Board staff formed a workgroup to evaluate PSD sampling methodology and share the benefits to other programs and upper management. The intent of this whitepaper is to encourage the Water Boards to systematically develop monitoring projects for PSDs in order to expand our knowledge base and increase sampling efficiency. This whitepaper provides general descriptions of PSDs, summaries of PSD benefits and drawbacks (as compared to conventional grab sampling), discussions of Water Board programs utilizing PSDs and those that could benefit through the application of PSDs, and recommendations for special projects to assist in expanding the use of PSDs in other Water Boards programs.

Passive sampling has sufficiently progressed in the past several years and has become an accepted sampling methodology in water quality monitoring and screening applications. However, additional resources must be developed for using this technology in concentration-based applications. Although some knowledge gaps remain, there is enough scientific knowledge and supporting resources available for the application of PSDs. Waiting for more scientific evidence or knowledge in practical application is unnecessary. There are many passive samplers available in the market and new sorbents are continuously coming out.

The implementation of passive samplers should proceed using two monitoring designs simultaneously. It would be beneficial for ongoing surveillance monitoring of contaminants of emerging concern (CEC), current use pesticides, and similar ambient monitoring efforts. PSDs could be incorporated with relatively minimal effort. Such presence/absence monitoring requires minimal staff training, equipment, and sorbents for the target compounds.

For projects requiring concentration data, an integrated and flexible monitoring design should be developed to meet the following goals:

- validating the performance of PSDs in determining the concentration of compounds
- developing statewide standard operating procedures (SOPs)

- developing sampling rate (Rs) values for a wide range of compounds for calculating time-weighted averages (TWA)

Introduction

The Water Boards currently sample water, sediment, and tissues, and utilize biological and physical measurements to evaluate the status, trends, and compliance of waterbodies in California. The selection of sampling methods for these analyses has scientific and cost implications for monitoring projects. The Regional Water Boards water quality objectives, Statewide policies (including federal policies), and many other water quality evaluation thresholds are developed by using the conventional grab sampling methods. Except for biological assessments, which depend on sampling a segment of stream length, grab sampling methods provide a snapshot of a specific time and location. In general, grab samples are assumed to be representative of the waterbody under assessment, but are often inadequate to accurately characterize the daily, weekly, monthly, or yearly status of a waterbody.

In most cases, grab sampling targets peak concentrations with seasonal flux. For example, the best sampling time for detecting concentration peaks of pesticides (due to excessive application) is after heavy rainfall within, or just after the application period. Similarly, stormwater sampling is utilized after a heavy flush of rain. Generally, the appropriate time and frequency of sampling is determined by the program and objectives of the monitoring project. Composite samples (i.e. 24 hours to one week) might be employed by some programs to detect both representativeness and peak concentrations of seasonally-variable compounds or for determining the background conditions of sites, but several samples have to be collected in defined time intervals to create composite samples, which significantly increases sampling costs.

Sampling and analytical techniques for water quality monitoring have made significant progress in the last two decades, and the Water Boards should use new techniques to do effective regulatory work. PSDs have shown much promise as tools for measuring average concentrations of a wide range of compounds in water.

Overview of Passive Samplers

PSDs are manufactured sorbents capable of accumulating chemicals and used to monitor pollutant(s) in an environmental medium. They are composed of a deployment housing canister, sorbent holding disk, and a lid. They do not require power to operate and sample over a prolonged duration (hours to days to months). Left in a water body for a specified number of days, PSDs are capable of remaining stationary in water. The compounds of interest diffuse from the water and accumulate on the receiving sorbent. When the PSD is retrieved, the sample is analyzed for compounds with no additional intermediate procedures between field and lab analysis. Because there is no set volume

of water sampled, the concentration found does not directly represent the concentration of the compound per volume of water ($\mu\text{g/L}$). Rather, the concentration is measured by the average accumulated compound per time or days of deployment ($\mu\text{g/day}$).

Figure 1: Example PSD components using Chemcatcher deployment kit



Deployment Housing

Sorbent Holding Disks

Passive Sampler Types

Passive sampling methods are generally classified as either adsorptive or absorptive (Ahrens et al. 2005). Adsorptive methods take advantage of the retention of compounds by surface binding, while absorptive methods involve both surface binding and compound permeation into a sequestering medium. Depending on their physicochemical characteristics, compounds accumulate in a suitable PSD medium, which may be a solvent, chemical reagent, or adsorbent. The mediums may or may not be covered by a porous or non-porous diffusion membrane for sampling. The mediums have several variations of design, with the most common samplers being flat or tube-like in shape.

The accumulation and uptake rate of the compounds depends on the passive sampler's sorbent material, sampler design, physicochemical properties of the compounds, and environmental conditions, such as pH, temperature, and hydrodynamic factors such as turbulence (Allan et al. 2009). PSDs are commonly evaluated by the capacity of the sorbent medium to accumulate mass of the compounds and the TWA concentration of each compound. There are a wide range of sorbents used for monitoring, from custom-built to commercially manufactured. The choice of which PSD to use for monitoring primarily depends on the physicochemical properties of the compounds targeted for monitoring, and a given target compound could potentially be compatible with two or three PSDs, providing options and flexibility with regard to study design. In general, if

the intent of a monitoring project is to obtain the largest range of compounds possible, a combination of two or three PSDs may be necessary.

A large list of passive samplers is shown in the Tables 2 and 3 include PSDs for organic and inorganics compounds, while Table 4 lists PSDs for nutrients (Vrana et al., 2005; Imbrigiotta et al., 2020). Five PSDs that are commonly used for both legacy pollutants and CECs and have the potential to be candidates for Water Boards projects are discussed below.

- **Polar Organic Chemical Integrative Sampler (POCIS):** A POCIS is one of the more widely used samplers. They are designed to sample the more water-soluble organic compounds with a log K_{ow} less than three. This includes most pharmaceuticals, illicit drugs, polar pesticides, phosphate flame retardants, surfactants, metabolites and degradation products. There are two kinds of sorbent mediums used in POCIS: one is used for sampling pesticides, and the other is used for sampling pharmaceuticals. Both apply solid phase extraction (SPE) methods for analyses. The difference between the two POCIS mediums is the solid sorbent (i.e. the component that traps the sampled compounds) utilized in the POCIS design (Alvarez 2010), which are discussed in detail below.
 - **POCIS – A:** The sorbents are a triphasic admixture of Isolute[®] ENV+ and Ambersorb[®] 1500 or 572 carbon dispersed on S-X3 BioBeads[®]. These sorbents are used to monitor pesticides, natural and synthetic hormones, many wastewater-related compounds, and other water-soluble organic compounds.
 - **POCIS – B:** The sorbent is hydrophilic-lipophilic balanced (HLB) and is comprised of a specific ratio of two monomers: hydrophilic N-vinylpyrrolidone and lipophilic divinylbenzene. HLB is typically considered a universal sorbent in environmental analyses and has been used to extract a wide range of chemical classes from water. This sorbent is mostly used to sample pharmaceuticals, personal care products, and other drug residues.
- **Chemcatcher:** Chemcatchers consist of a disk as receiving phase with or without a limiting diffusion membrane sealed into a polycarbonate or polytetrafluoroethylene holding plate and capped. Several SPE disks with a broad-spectrum extraction material (without specificity and polymer disk) have been developed (Gong et al. 2018). The various SPE disks within Chemcatchers can be used with membranes composed of cellulose acetate, low density polyethylene (LDPE), polysulfone, polyethersulfone, or without any membrane at all. The strength of the Chemcatcher is that the design allows field crews to deploy up to three combinations of disks,

increasing the opportunity to sample a range of contaminants with different physicochemical properties, both polar and non-polar.

- **C18 Disk:** A silica sorbent covered with an LDPE membrane that is the most used receiving phase to sample hydrophobic compounds. One design is used for non-polar organics with log K_{ow} values greater than four, while another design is used for sampling polar organic compounds. More designs are being developed for a range of emerging contaminants, including alkylphenoles, pharmaceuticals, steroids, flame retardants, and pesticides.
 - **HLB Disk:** A widely used POCIS sampler. Refer to POCIS-B above for description.
 - **SDB-RPS (styrenedivinylbenzene-reverse phase sulfonated) and SDP-XC (styrenedivinylbenzene-exchange) Disks:** Poly copolymer sorbent. They consist of 100% copolymeric particles that are spherical, porous, and are suitable for polar and low polarity compounds.
- **Semi-Permeable Membrane Devices (SPMD):** SPMDs consist of a sealed, flat tube of thin-walled, nonporous LDPE containing a thin film of liquid receiving phase. Triolein is conventionally used as receiving phase because it is the major storage lipid found in most organisms and it has low permeability through LDPE membranes. Other advantages of triolein include the similarity in magnitude to, and good correlation of, triolein-water and n-octanol-water partition coefficients, and low triolein-LDPE interfacial tension. SPMDs are generally used for sampling neutral organic compounds with a log octanol-water partition coefficient K_{ow} greater than three. Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides, polybrominated diphenyl ethers (PBDEs), dioxins, and furans are all commonly measured using SPMDs.
- **Silicone Rubber (SR) Strips:** SR strips are polymer sheets comprised of polydimethylsiloxane and are suitable for sampling hydrophobic compounds with a log K_{ow} greater than three. They are cheap and robust and can be reused several times (Ahren et al. 2015). SR strips have been used to detect legacy compounds such as PBDEs, PCBs, DDTs, and Phenols.
- **Diffusion Gradient Thin films (DGT):** DGT is a popular PSD for inorganic compounds such as trace metals. The design is comprised of a diffuse gel that controls compound uptake, and a binding gel for sequestering compounds. The variation organic-DGT (o-DGT) medium expands the use for pharmaceuticals and

pesticides. It includes both HLB binding gel and diffusing gel. All gels can be made from agarose. According to Challis et al. (2016), the advantage of this device is it significantly reduces the need for laborious sampler calibrations because one can accurately estimate compound concentration based strictly on a measured or modeled diffusion coefficient (D). Measurement of temperature-specific diffusion coefficient through gel is relatively well established and simple to do, thus determination of sampling rates with temperature is simpler as it accounts for temperature differences between laboratory and field deployment.

- **Continuous Low-Level Aquatic Monitoring Device (CLAM):** CLAM devices are small, submersible extraction samplers that continuously draw water through the extraction media at a rate of approximately five to 60 milliliters per minute. The device is housed in a clear, high-impact polycarbonate sealed sphere that is 5 inches in diameter. The device itself consists of a micro-pump, a volume data acquisition system, and a rechargeable lithium-ion battery. The device utilizes U.S. EPA-approved SPE to detect pesticides, herbicides, PAHs, total petroleum hydrocarbons, and other trace organics in water. The SPE media is housed in disks and attaches to the CLAM device by lure fittings. The micro pump can provide high volume extractions of up to 100 liters (sample aliquots), and is connected to the volume acquisition data system, which is referred to as the “Volume Totalizer.” This system tracks sampling activities, including the total volume of sample collected through the sample media. The Volume Totalizer may be used to determine concentrations of the extracted analyte.

Advantages and Limitations of Using Passive Samplers

PSDs operates in a well-defined diffusion principles and partition properties of compounds in water. It provides an equilibrium concentration of compounds in water (source) and sorbent (receiving phase) as a TWA of chemicals over a deployment period. The sorbent materials used in construction have uniform composition and provides consistent samples for analysis and allows compound quantification among different environments in reproducible manner. The fact that it provides an average of the freely dissolved concentration (bioavailable fraction) over a period of deployment is a better representative than a grab measurement in reflecting the risk posed to aquatic organisms. PSDs have a higher sensitivity for a greater range of compounds, as well as improved stability of compounds within the sample and therefore do not require additional treatments (Taylor et al. 2019). This is because PSDs use compounds that are pre-concentrated and preserved in the sample receiving materials. Thus, labs run the analysis without intermediate processing of the sample.

Using grab samples, a chemical’s effect on aquatic species is evaluated by correlating the dissolved or total concentration of compounds to survival and sub-lethal endpoints.

This underestimates the concentration of compounds present and includes forms that are not bioavailable. PSD analyses directly yield the freely dissolved fraction of the compounds that are toxic to aquatic organisms, and the bioavailable fractions of the compounds are directly measured (Booij et al. 2016), thereby providing significant improvement in this regard.

The uptake of compounds by aquatic species and by PSDs is similar. Studies have shown a correlation between the concentration of compounds analyzed from PSDs and toxic effects to aquatic animals (Andrade 2014). For example, a strong correlation has been observed between lipid-based concentrations of organochlorine pesticides, PAHs, and PCBs, and equilibrium concentrations for amphipods (Golding et al. 2008) and bivalves (Meloche et al. 2009).

There are some challenges when deploying passive samplers that primarily originate from environmental variables occurring during the deployment period. Water turbulence affects the diffusion of the compound(s) from water to the receiving sorbent. Similarly, biofouling affects transfer and limits diffusion because biofilms increase thickness and block the pores of the membrane and the sorbents. Water turbulence may also move a PSD from its original location or wash it away altogether, making it difficult to recover the equipment. In addition, the equipment is exposed to vandalism and theft.

To estimate the TWA concentration of compounds, PSD calibration is required before deployment to determine the sampling rate (R_s) for the class of compounds or each target compound. The sampling rate is significantly affected by fluctuating environmental variables such as water temperature, pH, flow velocity, and biofouling. These factors are site-specific and affect the estimation of R_s and subsequent compound concentration estimates in water. Calibration can be conducted in the laboratory or field, as needed. A lab calibrated R_s is commonly used because it is easier, cheaper, and water parameters such as pH, conductivity, and temperature are controlled. Moreover, a large list of calibration data developed in laboratories are available. For the Water Boards to further refine these R_s lists for constituents of emerging concern and legacy contaminants, a special R_s study must be conducted. A draft study plan is provided in the appendix. USGS (2010) has developed R_s list and a tool to calculate TWA for hydrophilic compounds.

Advantages and Limitations of Using Grab Sampling

Conventional grab sampling techniques for water, sediment, and aquatic species are widely used in Water Board monitoring programs as the procedures are established, and its limitations are well understood. Moreover, Federal and State regulations are based on grab sampling values, and numerical thresholds for evaluating the status of

water quality are readily available in Regional Basin Plans, as well as statewide plans and policies.

Grab sampling is a labor-intensive field effort but enables safe data collection in a variety of locations (receiving water, end of pipe, confined space). It allows for integrated analysis of site conditions when analytical data is paired with field observations and measurements. The sampler can adaptively respond to dynamic sites conditions and can re-sample or supplement an existing sample if unusual conditions are observed.

However, grab sampling techniques have known limitations for reliably characterizing water quality data. Pollutant mobilization and transport is a function of discharges and many environmental factors, and these factors may differ during dry weather conditions,¹ storm conditions,² and snow (melt) conditions. Extensive research has indicated that grab sampling is inadequate for capturing episodic discharge events, while ponding and water stagnation that may occur during particularly low-flow conditions has been known to cause matrix interference (false positive and false negative detections). Stormwater flows are also highly variable. Pollutograph sampling has shown that the first flush and rising limb of a hydrograph can significantly change between samples, whereas the return of the baseflow tends to be more homogenous. A grab sample can only characterize a snapshot of data.

For hydrophobic compounds, freely dissolved concentrations are difficult for laboratories to measure directly in a grab sample as some portion of the substance will bond to dissolved organic carbon, from which it cannot be easily isolated, and some may adsorb to filters, lowering the measurement of the freely dissolved fraction. As a result, the bioavailable concentration is underestimated using conventional grab sample analyses.

In addition to missing a discharge pulse, the small volume of water collected for grab samples means that only a fraction of the discharge is being characterized. In order to reach sufficiently low detection limits for hydrophilic compounds, large volumes of water must be collected and processed, which may cause some technical difficulties when filtering samples.

¹ Pollutant mobilization by non-storm (dry weather) discharges may be influenced by factors like volume of flow, rate of flow, season, MS4 configuration, or water source (natural rising groundwater, permitted discharges, unpermitted anthropogenic).

² Pollutant mobilization by rainfall-driven runoff may be influenced by factors like storms size, storm duration, storm intensity, number of antecedent dry weather days, total impervious surface, or pollutant source.

Efforts are taken by the Water Boards and the regulated community to collect the most representative grab samples, and/or the most environmentally protective grab samples. Monitoring programs may require grab sample collection shortly after storm-associated discharge begins, or they may require a higher frequency of sampling (temporally or geospatially). Storm event grab sampling can also be required hourly during a portion of the hydrograph (or window of time); dry weather sampling requirements may be separated by days, weeks, months or seasons.

Monitoring programs may alternatively require composite sampling. This is when discrete aliquots are collected and then pooled into a composite sample. The composite is analyzed to compensate for the deficiencies of one-time-grab sampling, giving a more temporal and/or spatially representative sample. Increasing the frequency of sampling, however, increases costs significantly by requiring additional labor and/or additional equipment. Automated sampling equipment may be purchased or rented to increase the frequency of aliquot sample collection and minimize sample handling during an event.

Table 1. Summary of pros and cons of PSD and grab sampling methods.

Evaluation parameters	Passive Sampler		Grab Sampling	
	Pros	Cons	Pros	Cons
Sample Size	Samples large volumes of water without need for transporting large volumes			Sample small volume, usually 1 liter, analysis is conducted from small sample size
Sample Purity	No matrix interference	Biofouling interference		Potential for matrix interference
Sample Representativeness	Time-weighted average (average of many days and months) integrates temporal variation	Does not measure peak concentration	Snapshot concentration for peak event	Several grab samples must be collected to average temporal variation
Detection Limits	Relatively low detection limits on all samples because of high volume of water sampled			Potential to need large sample volumes to achieve environmentally relevant detection limits
Infrastructure Availability	Non-mechanical and easy to deploy	Feasible installation may be limited by site conditions	Non-mechanical and easy to collect samples	Laborious for sediment and toxicity. Particularly toxicity involves upkeep of test animals
Maintenance		Cleaning may be required to prevent biofouling; frequent inspections for biofouling required	Simple cleaning of collection equipment	
Sampling Environment	Applicable in a range of environments, at sites with limited security, and which are remote with little/no infrastructure	In populated areas, potential for vandalism or theft	Applicable in a range of environments and no risk of vandalism or theft	
Energy Requirement	Not needed		Not needed	
Quantitation of Concentration	Concentration estimated by applying models	Does not use known volume of environmental matrices	Concentration estimate by known volume from environmental matrices	
Sampling Medium	Manufactured sorbents	Indirect, not environmental matrices; may require batch QA testing to confirm no background contribution (sorbent blank)	Direct measure of water, sediment, and tissue	
Compound Concentration and Data Generated	Consistent data across environmental matrices as devices are manufactured from same materials	Will require standards and protocols to be established		Inconsistent data set because of the inherent variability within and among sampling matrices
Special Requirement Before Deployment		Requires training to ensure each type of PSD is installed correctly, and inspection to ensure no defects in PSD prior to deployment, calibration to determine Rs is required to calculate concentration	Grab sampling protocols generally do not change	

The Feasibility of Application of Passive Samplers in Water Boards

The programs in Water Boards are so diverse and the compounds they are monitoring and, the water quality objectives are variable. PSDs can be utilized for most waterbody types the waterboards routinely monitors including rivers, lakes, estuaries, bays, and ocean. They also apply to widely monitored chemicals including metals, nutrients, pesticides, and pharmaceuticals. The choice of PSD depends on the physiochemical characteristics of the target compounds to monitor. Thus, a one-size-fits-all approach across programs is not practical. In the short-term, PSDs are best suited for screening and determining the presence or absence of chemicals. Over the long term, PSDs can be utilized for compliance monitoring by making supportive technical resources available and amending regulatory requirements.

Passive samplers measure only the chemical constituents of the waterbody and determine their average concentrations; they do not allow for the determination of peak concentrations of chemicals in each water event. Field physiochemical characteristics (temperature, pH, specific conductivity, dissolved oxygen, etc.) cannot be measured by PSDs alone. For these metrics, supplemental equipment needs to be deployed alongside these devices.

In addition, the application of PSDs depends on the waterbody's conditions and the chemicals being monitored. If the waterbody is ephemeral or with occasional seasonal flow, PSDs may not be usable because they need to be completely submersed in water for the entire deployment. Similarly, if there is no appropriate sorbent available on the market for the chemical of interest, PSDs would not be appropriate tools.

The Water Boards regulate water quality in their programs using statewide policies, Basin Plan objectives, maximum contaminant levels, and drinking water standards, among other water quality metrics. Generally, most water quality is evaluated using grab samples to determine compliance with regulatory programs or to determine impairment of a water body. In addition to the fact that this only provides a snapshot of water quality, grab samples may miss certain constituents if they are below detection limits or absent in that specific sampling event. PSDs provide utility in better characterizing the conditions in a water body over a longer period of time.

Programs need to conduct their own assessment whether PSDs are a viable alternative or supplemental sampling method to their current grab sampling regimen. Programs will need to evaluate their data quality objectives and analyze the sampling goals, target analytes, hydrologic conditions, and relevant regulatory requirements before they consider using PSDs.

In general, many programs at the Water Board could benefit from complementing their sampling protocol of grab samples with passive samplers. PSDs have the potential to

be used in regulatory programs and be included in the monitoring requirements of waste discharge requirements. Some of the programs that may benefit include stormwater, wastewater, cleanup, the Irrigated Lands Regulatory Program, and drinking water. In these programs, the constituents of concern do not always have consistent concentrations in the water body and have the potential to change in concentration based on storm events, spring melt, and anthropogenic events. PSDs are better suited to evaluate water quality changes over a longer time scale than ambient and episodic grab sampling.

PSDs can also be used in for Total Maximum Daily Loads, the Surface Water Ambient Monitoring Program, citizen monitoring, and non-point source programs. When used jointly with conventional monitoring, passive samplers can better characterize long-term improvements by providing a more thorough sample set. They can evaluate the presence or absence of a multitude of chemical constituents and, with additional effort, quantification of the pollutants. This data can inform the 303(d) List of Impaired Waters, determine restoration success, evaluate ambient conditions, and further vet constituents of emerging concern to prioritize regulatory and enforcement actions. This data can also be used to inform future climate change policies and related actions taken by the Water Boards.

Depending on the program, the successful implementation of PSDs involves many different steps and requirements. These include identification of passive sampler type, deployment and retrieval of the equipment, use of supplemental equipment, and field maintenance. Some compliance monitoring programs may even need legal counsel approvals if time-integrated average concentrations of the chemicals are used as acceptable values.

PSDs apply to a wide range of chemicals including metals, nutrients, current and legacy pesticides, and pharmaceuticals. Tables 2, 3, and 4 provide a list of PSDs used for various chemicals, as well as a short explanation of each.

Table 2: Overview of Passive Sampling Devices for Organic Contaminants

Sampler	Full name	Construction	Analytes	Sampling purpose	Typical deployment period	Advantages	Drawbacks	Sample preparation for chemical analysis
Ceramic dosimeter	Ceramic dosimeter and toximeter	Ceramic tube (5 · 1 cm) filled with a solid-phase sorbent material, closed with PTFE lids	PAHs, BTEX, chlorinated hydrocarbons	Integrative sampling in groundwater		No need for extensive laboratory calibrations. Robust design, suitable for long-term monitoring. Sorbent material of the "Toximeter" variant can be tested in contact bioassays	Low sensitivity	Solvent extraction or thermal desorption
Chemcatcher	Universal passive sampler using Empore disk	A housing made of inert plastic (e.g., PTFE), containing a disk of solid receiving phase bound in a porous polymer, and a disk of diffusion-modulating membrane.	Polar and non-polar organics	Integrative		Selectivity of the sampler can be adjusted using appropriate combination of membrane and Empore disks. Calibration data available for many chemicals		Solvent extraction
Dosimeter		Activated carbon receiving phase in a perforated acrylic housing	BTEX and atrazine	Integrative				Solvent extraction
Ecoscope	A sampler based on solvent-filled dialysis membranes and chelating sorbent discs	A plastic housing containing a chelating sorbent disc for sampling metals and dialysis membrane filled with solvents	Non-polar organics	Qualitative screening				
Gaiasafe		Paper or fabric strips impregnated with a solution of binding agent	Metals, anions, organic compounds	Screening				Solvent extraction
Gore-Sorber		Various sorbent materials filled in a carrier hose made of Gore-Tex	BTEX, MTBE, PAHs, VOCs, SVOCs	Equilibrium	14 days			Thermal desorption
LDPE and silicone strips	Low-density polyethylene or silicone strips	Hydrophobic organic compounds		Integrative	2 month	Simple construction, inexpensive, simple sample processing and calibration data available for many analytes classes	Smaller sampling capacity than SPMDs	Solvent extraction
MESCO	Membrane-enclosed sorptive coating	PDMS-coated stir bar used in SBSE or a PDMS rod enclosed in a membrane made of regenerated cellulose or low-density polyethylene	PAHs, PCBs organochlorine pesticides	Integrative				
nd-SPME	Negligible depletion-solid phase microextraction	A fiber coated with liquid (polymer), a solid (sorbent), or a combination of both	Hydrophobic chemicals, including PAHs, PCBs, petroleum hydrocarbons, organochlorine pesticides, aniline, phenols	Equilibrium	Hours	Negligible depletion extraction, a cheap, disposable device	Low sensitivity	Thermal desorption in GC inlet

Sampler	Full name	Construction	Analytes	Sampling purpose	Typical deployment period	Advantages	Drawbacks	Sample preparation for chemical analysis
Passive	Sampler according to Lee and Hardy	Silicone polycarbonate permeation membrane and an adsorbent receiving phase	Chlorobenzenes, nitrobenzenes and nitrotoluenes	Integrative	Up to 1 day			Solvent extraction
PDB	Passive diffusion bag samplers	Dialysis membrane or a low-density polyethylene bag filled with distilled water	Polar organic compounds, VOCs, metals, trace elements	Equilibrium sampling in groundwater	2 weeks	Relatively inexpensive, and sample recovery is rapid	Not suitable for sampling semi-volatile organic compounds	Conventional analysis of the receiving water phase
PISCES	Passive in situ concentration extraction sampler	Hexane in a polyethylene membrane	PCB	Integrative	2 weeks			Volume reduction of the receiving phase
POCIS	Polar organic chemical integrative sampler	Solid sorbent receiving phase material enclosed in a polyethersulphone membrane	Herbicides and pharmaceuticals with log K _{OW} < 3	Integrative	Up to 2 months	High sensitivity; capacity of the sampler can be adjusted using appropriate sorbent materials, membrane has low susceptibility to biofouling, and calibration data available for many chemicals		Solvent extraction
Porous	Sampler according to De Jonge and Rothenberg	A water permeable porous sampler that acts as a semi-infinite adsorptive sink	Wide range of contaminants	Fluxproportion a l sampling in soil and groundwater	1 month			Solvent extraction
Stainless steel housing	Sampler according to Kot-Wasik	A stainless steel housing, containing organic solvent in a chamber separated from water by a membrane	Phenols, acid herbicides, triazines	Integrative	1 month	A sample of the receiving phase solvent can be taken without affecting the integrity of the sampler	Low-sensitivity, receiving phase solvent may diffuse out of the sampler during field deployment	Analysis of a sub-sample of solvent is taken and analysed without further clean-up steps
Solvent filled dialysis membranes		Non-polar solvent immiscible with water filled in a cellulose dialysis membrane	Hydrophobic organic compounds	Integrative	1 month	Not prone to biofouling	Low sensitivity for very hydrophobic compounds, and solvent diffuses out of the sampler during deployment	Volume reduction of the receiving phase
SPATT	Solid phase adsorption toxin tracking	Porous synthetic resin filled polyester fabric sachets	Polar phytotoxins	Integrative	1 week			Solvent extraction
SPMD	Semi-permeable membrane devices	Flat tube of LDPE filled with triolein	Hydrophobic semi-volatile organic compounds	Integrative	1 month	Widely used method, commercially available, well-established standard operation procedures, and calibration data available for many analyte classes, and high sensitivity	Complicated sample cleanup, susceptible to biofouling	Dialysis in organic solvents, size exclusion chromatography

Sampler	Full name	Construction	Analytes	Sampling purpose	Typical deployment period	Advantages	Drawbacks	Sample preparation for chemical analysis
TLC plate	Thin-layer chromatography plate		Organophosphates	Screening	1 month	Good sensitivity because of a large surface area		Solvent extraction
TRIMPS	Trimethyl-pentane containing passive sampler	2,2,3-Trimethylpentane filled in a low-density polyethylene membrane	Pesticides	Integrative	1 month	Simple sample clean-up and analysis	Receiving phase solvent diffuses out of the sampler during field deployment	Direct analysis of the receiving phase solvent
TWA-SPME	Solid phase microextraction applied for determination of TWA concentrations	A fiber coated with a liquid (polymer), a solid (sorbent), or a combination of both	BTEX	Integrative	A few minutes	No need for extensive laboratory calibrations, and sampling rates can be estimated using empirical mass-transfer models	Short-term sampling only, and fiber susceptible to damage or fouling in the field	Thermal desorption in GC inlet

Table 3: Overview of Passive Sampling Devices for Inorganic Contaminants

Sampler	Full name	Construction	Analytes	Sampling purpose	Typical deployment period	Advantages	Drawbacks	Sample preparation for chemical analysis
Chemcatcher	Comprises an immobilized chelating acceptor resin on a PTFE base and a cellulose acetate membrane filter acting as a thin diffusion layer		In situ sampling, integrative, speciation Cd, Cu, Ni, Pb and Zn	14 days – 1 month	Selectivity of the sampler can be adjusted using appropriate combination of membrane and Empore disks, and calibration data available for many chemicals		Acid extraction	
DGT	Diffusion gradients in thin films	Two layers of acrylamide gel mounted in a holder device, one containing an acceptor phase, the other acting as a thin diffusion layer	55 metallic elements including the common heavy metals, phosphorous, sulfide and ⁹⁹ Tc	Integrative, speciation, screening, mimicking biological uptake	1 week	Versatile, well documented	Complicated preparation of device	Acid extraction
PIMS	Passive integrative mercury sampler	LDPE lay-flat tubing	Neutral Hg species	Pre-concentration, screening	Weeks–months	Membrane characteristics may be altered for control of sampling rates	Further development necessary for aquatic conditions	Direct analysis of the receiving phase
PLM	Permeation liquid membrane	Microporous hydrophobic support separating test solution from receiving solution	Cu, Pb	Bioavailable metal species	Hours	Selectivity of the sampler can be adjusted using appropriate combination of carrier media and receiving phase	Complicated preparation of device	Solvent extraction
SLM	Supported liquid membrane	A strip solution with strong complexing agent is separated from the test solution by a macroporous hydrophobic membrane	Doubly charged cations	Integrative field sampling, preconcentration of trace elements, mimicking biological membranes	Days	Versatile, selectivity of the sampler can be adjusted		Direct analysis, can be coupled on-line for real time monitoring
SLMD	Stabilized liquid membrane device	LDPE lay-flat tubing containing an acidic solution with high affinity for the target elements	Divalent metal ions	Pre-concentration, in situ sampling, determination of labile metal ions in grab samples	Days–weeks		Early development stage	Acid extraction

Table 4: Some Passive Samplers for Nutrients Monitoring

Chemicals	Passive samplers	Construction	Advantage	Drawbacks	Market availability
Nutrients (NO3, NO2, NH4, PO4)	Regenerated cellulose dialysis membrane sampler (RCDM)	Consist of deionized water-filled tube of high-grade regenerated cellulose membrane is tied in a knot at one end, and a valve is attached to other end. The membrane is then inserted into protective LDPE mesh, the tube is filled with deionized water, and the valve closed.	The samples they collect requires no field filtration, and they are disposable	Must be filled and kept immersed in deionized water prior to deployment and lend itself for possibility of leakage. They are biodegradable and cannot be left in water for extended period	available
	Rigid porous polyethylene sampler (RPP)	Thin sheets of foam-like porous polyethylene with pores sizes of 6-15um, The sampler is filled with deionized water closed at both ends; placed inside a mesh sleeve, which is subsequently attached to a deployment rope using cable-ties.	They can be used for a wide range of chemicals and are not biodegradable.	Must be filled and kept immersed in deionized water prior to deployment and lend itself for possibility of leakage	
	Nylon screen sampler (NS)	Polypropylene bottle filled with deionized water and with nylon screen placed across the opening and covered with a cap.	Low cost to construct	Need filtration and need to be immersed in deionized water between the time construction and deployment.	not available
	Downhole thief sampler (Snap)	Specialized containers that can be triggered to close and seal. Consists polytetrafluoroethene or stainless-steel module vial-sized bottle that is open on both ends. The device keeps the spring-loaded caps open while the device is deployed in water.	Has no membrane or		
	Dual membrane sampler (DM)	A long hollow cylindrical, perforated tube that forms a rigid sampler chamber. The chamber is wrapped by mesh nylon screen material and the bottom chamber is wrapped by LDPE membrane.	They are constructed of non- degradable materials	Relatively has small surface area compared to the internal volume of the dual membrane lengthen equilibration times.	

USGS: Imbrigiotta, T.E., and Harte, P.T., 2020, Passive sampling of groundwater wells for determination of water chemistry: U.S. Geological Survey Techniques and Methods, chap. 8, section D, book 1, 80 p

Factors to Consider

When staff evaluate the potential use of PSDs, it is important to consider several factors, such as whether the selected sampler is capable of collecting the chemical in question, and if the type of monitoring data collected will meet project goals (Table 5).

Table 5: Factors to Consider when Planning to Apply a PSD

Factors to consider	Conditions for use	Applicable	Not applicable
Purpose of sampling	Peak concentration		✓
	Average concentration	✓	
	Detect or not detect	✓	
Water body type	Perennial streams, lakes, estuarine, bay, ocean and groundwater	✓	
	Ephemeral streams, seasonal river		✓
Target Chemicals	Organics	✓	
	Inorganics	✓	
	Nutrients	✓	
	CECs, pharmaceuticals, PFAS, and others	✓	
	Pesticides	✓	
Frequency of sampling	One time		✓
	More than once	✓	

Technical Capacity Building

Currently, passive sampling is not being used in compliance monitoring for regulatory programs at the Water Boards. The lack of guidance for PSD selection and field deployment protocol, the inability to generate concentration values, and data reporting and analysis limits for immediate acceptance of PSD in regulatory programs. As such, the following technical resources should be made available for statewide monitoring programs.

Guidance Documents

- **Passive sampler selection guidance**
This white paper provides a summary and overview of PSDs and potential uses of this technology; it is not designed to provide guidance. Necessary guidance would systematically go through the monitoring program's design process and identify the appropriate passive sampler for a given application. The selection of PSD types is an important process in applying passive samplers for effective monitoring. There

are many PSDs on the market with different designs and receiving phases (sorbents) that are dependent on the polarity of the target chemicals. The Water Boards programs have some common target chemicals they are monitoring. This commonality provides an opportunity to be consistent in the type of passive samplers to be used across programs. In order to limit inconsistencies and establish systematic PSD selection procedures, the Water Boards need to develop passive sampler selection guidance with the help of experts in the field. This may result in an approved technology list, similar to the Trash Amendment's full-trash capture technology.

- **Field Guidance - Deployment Protocol**
Preparation, deployment, retrieval, and associated quality control requirements vary among PSDs. General protocols that detail PSD anchoring techniques, cleaning procedures, and sample handling and transport must be made available. This guidance would provide potential users with the necessary insight to apply and adjust the various procedures to their own specific uses.
- **Field Data collection and data analysis guidance**
Each type of PSD has technology-specific field data needs to properly assess outputs. This guidance would identify appropriate data to be recorded in the field upon deployment and upon retrieval. Recommended data quality guidelines and paired data needs (field flow measurements, field parameters, photos, etc.) would also be established, along with proper data entry procedures for Water Boards-managed databases. By establishing valid values and data types, the Water Boards would be able to ensure PSD data are reported consistently and in a manner that makes them broadly usable for monitoring programs and the public.

Develop Statewide R_s values

The major challenge in the application of PSDs is the calibration necessary to determine TWA accurately. To avoid inconsistencies and reduce the burden of performing a calibration study for each project, the development of statewide R_s values for targeted chemicals is an essential step in facilitating statewide usage of PSDs.

Compound-specific R_s values for appropriate sorbents can be calculated either in the lab or the field, but laboratory calibration is more widely used because it significantly controls environmental variables. However, lab calibrated R_s values must be corrected to properly infer field conditions and produce inconsistent estimated concentration results. To save cost and time, some passive sampler projects use lab calibrated R_s values from literature to calculate concentrations, yet literature reports do not provide detailed calibration procedures, resulting in incomplete information how the R_s values were produced.

Additionally, there are several ways to perform laboratory calibrations, and R_s values can vary widely if calibration is not performed consistently.

Field calibration procedures require extensive data collection for each applicable environmental condition but produces more accurate, environment specific R_s values to calculate concentrations. The Water Boards have the capacity to develop a reliable, robust and well-defined calibration system for statewide use. There are extensive field-generated datasets collected in the past two decades that can be used to develop field-calibrated R_s values for a wide range of compounds and environments. This approach would have the following additional benefits:

- Validating the ability of PSDs to determine the concentration of compounds
- Developing statewide SOPs
- Establishing acceptable R_s accuracy limits
- Comparing costs between grab and passive sampling methods

A detailed scope of R_s study is presented in the Appendix.

Passive Sampler Monitoring Projects at the Waterboards

Several programs at the State and Regional Water Boards have conducted or are planning to conduct monitoring studies using PSDs. The following are summaries of PSD studies that have been completed or are currently being planned by the Water Boards as of September 2020.

Chemical Contaminant Monitoring by Passive Sampler

Region 5

Phase 1: The Region 5 Forest Activities Program first deployed PSDs in partnership with the California Fish and Wildlife Water Pollution Control Lab in Battle Creek following the Ponderosa Fire in 2013. This initial study focused on the viability of detecting pesticides and herbicides used in commercial forestry with PSDs. The original CLAM devices were deployed 26 times, with each deployment and subsequent elution containing at least one pesticide with the herbicide hexazinone. Due to the size of the Battle Creek watershed, staff was unable to trace the detection of pesticides to commercial forestry.

Phase 2: The Region 5 Forest Activities Program then partnered with the United States Geological Survey (USGS) Pesticide Fate and Transport Laboratory in 2015 through 2017. This second phase of the study was intended to determine the effectiveness of PSDs for detecting herbicides used in commercial forestry, as well as pesticides and insecticides commonly used in illegal cannabis grows. This phase of the study primarily focused on developing the sampling and analysis methodology for Chemcatchers. The sampling and

analysis methodology developed by USGS is modified U.S. EPA method 3535A, and it is now in the process of being verified by ELAP for use in the Statewide Chemistry Contract.

Phase 3: The Forest Activities Program partnered with USGS again to deploy Chemcatchers in eight mid-elevation Sierra Nevada streams from November 2018 to December 2019 to assess the presence of pesticides in surface waters. Chemcatchers were deployed with multiple solid phase extraction disk packages concurrently to determine an optimal disk configuration for measuring current-use pesticides. Extracts from the PSDs were analyzed for 155 pesticides. Twenty-two out of the 155 pesticides analyzed were detected in streams sampled with herbicides hexazinone and dithiopyr, the insecticide methoxyfenozide, and the fungicide azoxystrobin being the most frequently detected compounds

Region 6

In 2016, the Lahontan Water Board performed a toxicity study in the Susan River, in Lassen County. This study was performed because the Susan River was placed on the 303(d) List of impaired waters in 1990 due to U.S. EPA testing that found toxicity to larval fish and duckweed (although the cause was never determined). This data is unrecoverable as it is pre-2006 before an administrative record capturing this information was required. The Susan River was then segmented in a later listing cycle, resulting in the impairment being applied to all three segments of the river. A supplemental study was performed in 2003 and 2004 at four sites on the Susan River, and sampling was conducted monthly from spring to fall for both years. These samples were tested with a larval fish (fathead minnow), a cladoceran zooplankton species (*Ceriodaphnia dubia*), and a duckweed (*Lemna minor*). The data showed that the magnitude of toxicity to larval fish and *Ceriodaphnia dubia* was relatively low. At the time, there was no standard procedure for identification of chemical cause(s) of toxicity in duckweed that was published. Experiments conducted by the UC Davis Aquatic Health Program Laboratory (AHPL) strongly implicated additive/synergistic effects of Transline and surfactants (nonyphenol and nonyphenol ethoxylate) in Transline formulations as the causes of duckweed toxicity. Transline was used in Lassen County at the time for rights-of-way, and its application was mostly restricted to June through September.

The study conducted in 2016 was a follow-up to these initial studies (Transline is no longer used). Three sites were sampled along the Susan River to capture different land uses. Sites were sampled three times in the spring during the highest runoff (although it was a drought year). CLAM PSDs were deployed, and samples were collected for analysis by AHPL. A statistically significant reduction in the survival of the amphipod *Hyalella azteca* was observed at the forested site on April 6, 2016, and a statistically-significant reduction in *C. dubia* reproduction, and the cell density of the algae *Selenastrum capricornutum* was observed at the site below Susanville on May 10, 2016. The toxicity observed was at low enough levels that Toxicity Identification Evaluations were not conducted. Analytical

chemistry on the CLAM PSDs demonstrated the presence of the herbicide Hexazinone in every sample collected during the study, although concentrations were not able to be quantified and fell well below those documented to cause acute toxicity. Hexazinone is applied to control grasses, broadleaf, and woody plants.

This was the first time the Lahontan Water Board experimented with the CLAM to complement toxicity testing. There were also few samples collected due to budgetary constraints, but this information could lead to more directed toxicity sampling in the future and guide the development of a TMDL.

The CLAM samplers were moderately easy to use but did require a significant amount of staff time when the monitoring location required overnight travel. The Susan River turbidity levels led to clogging of the intake valves which had to be monitored and cleaned regularly. In the future, CLAM samplers might be a good option for a stream close to the office with lower turbidity.

DWQ

The information regarding DWQ experience with passive sampling is representative of the CEC program perspective and is based on recommendations of a science advisory panel and experience associated with a CEC pilot study.

Science Advisory Panel Recommendations

State Water Board convened an Advisory Panel for Aquatic Ecosystems in 2009 (Advisory Panel I) and a final report with recommendations for CEC monitoring was issued in 2012. The 2012 final report provided several recommendations, including a recommendation to look into the use of passive sampling devices as they can be calibrated to operate under rapid update or equilibrium conditions, take advantage of preferential partitioning into the device from the media of origin (e.g., water) and offer a range of benefits over conventional sampling and lab concentration protocols (Anderson et al. 2012). The report indicates that PSD technology could be particularly advantageous for screening for biological activity since it offers the advantage of accumulating substances over longer periods of time and to higher mass. The panel recommended standardized guidance on the use and application of PSD results, particularly as they pertain to CECs in water, sediment, and tissue matrices.

The Advisory Panel was reconvened in 2020 (Advisory Panel II) and will update recommendations submitted in 2012 to improve the understanding of CECs to protect public health and the environment. Additional information and recommendations regarding PSD technology for CEC monitoring will be incorporated in the statewide CEC management and monitoring program, as appropriate.

CEC Pilot Study Using PSDs

A multiagency CEC pilot study was conducted as part of the National Mussel Watch Monitoring of the California Coast (Alvarez et al. 2014; Maruya et al. 2014). The pilot study was initiated in 2009 as part of a collaborative effort between the State Water Board, Southern California Coastal Water Research Project Authority, San Francisco Estuary Institute, U.S. Geological Survey, and the National Oceanic and Atmospheric Administration. The study was designed to answer multiple questions with regard to CECs, including what CECs are detectable in the water column using PSDs and what is the relationship between CEC accumulation by PSDs and bivalve tissues. PSDs that target water soluble and hydrophobic analytes were deployed at seven of 68 stations where native *Mytilus* were collected and analyzed, and PSDs were also co-deployed with caged *Mytilus* at four additional stations, two of which were located in urban watersheds in close proximity to publicly owned treatment works out-falls, one location was associated with a large agricultural land use component, and the fourth location was not attributed to a specific land use type.

A detailed summary of the study is published in the Marine Pollution Bulletin and is available to download at [Occurrence of contaminants of emerging concern along the California coast \(2009–10\) using passive sampling devices - ScienceDirect](#). The study design incorporated three PSDs including polar organic chemical integrated samplers (POCIS), polyethylene devices (PEDs) and solid phase microextraction samplers (SPME). The study results indicate that the most information on the presence of organic contaminants in the watershed is obtained by using a combination of PSDs (Alvarez et al. 2014), and the combination used in this study provided the opportunity to evaluate a broad range of analytes in coastal water (Maruya et al. 2014). Additionally, the concentration of persistent and bioaccumulative compounds were estimated using PSDs and found to be positively correlated with *Mytilus* tissue concentrations (Maruya et al. 2014). Additionally, PSDs such as the POCIS provided a means of measuring hydrophilic CECs that are otherwise challenging to measure in mussel tissue (Alvarez et al. 2014).

In summary, the study results indicate that PSDs can be used to monitor the occurrence of water-soluble CECs, and have the potential to serve as surrogates for bivalves when assessing bioaccumulation of persistent contaminants and to provide a means for evaluating locations where sentinel species are nonexistent and/or scarce. Biofouling of unprotected PSDs was noted as a possible concern in certain scenarios, however, corrections for attenuated exchange between the water column and the PSD sorbing phase can be made by incorporating performance reference compounds (Fernandez et al. 2012, as cited in Maruya et al. 2014).

OIMA

OIMA has conducted two PSD projects and has an additional research projects underway.

Water Quality Monitoring at a Delta Integrator Site: Fish Health and Behavior:

This is a collaborative project among three agencies: State Water Board, U.C. Davis, and the State and Federal Contractors Water Agency. The project is being conducted at the Department of Water Resources' (DWR) Hood real-time monitoring station. The site represents the integration of all tributary flows from the Sacramento River watershed prior to entering the Delta. The DWR station houses flow-through exposure tanks and records water quality parameters such as DOC, TOC, pH, DO, EC, turbidity, flow, temperature, and chlorophyll in real-time using automated systems. Meanwhile, water pumped from the Sacramento River is used in flow-through testing with *Oncorhynchus mykiss* (rainbow trout) and *H. azteca*, providing opportunity to analyze survival and sub-lethal endpoints, such as growth and swimming behavior. Chemical sampling for CECs is performed using a PSD deployed for the duration of the exposure. At the termination of the project, surviving *O. mykiss* will be preserved for sub-lethal biomarker endpoint analyses. The results of this study were used to evaluate the water quality of the Sacramento River, expressed in terms of fish health and behavior, and chemical pollutants accumulated in the passive sampler. This project was terminated due of lack of funding. The summary of the results is available at the [SWAMP – Constituents of Emerging Concern \(CECs\) in Aquatic Ecosystems](#) website.

Monitoring CECs:

The goals of this study are to utilize the Stream Pollution Trends (SPoT) Monitoring Program's network of sampling stations to determine if PSDs can provide enhanced information about CECs at these sites, and to compare concentrations determined by PSDs to those of water and sediment grab samples. Following the SPoT sampling plan, PSDs were deployed at the same time that sediment and water grab samples were collected. A second water grab sample was collected at the time of PSD retrieval at each site. The PSDs were retrieved 20 days after deployment. The long-term objective of OIMA is to start passive sampler monitoring in one of the statewide monitoring programs, and develop SOPs to help regulatory programs apply PSDs in their respective monitoring projects.

Cyanotoxin Monitoring by Passive Sampler

Region 1

The North Coast Region utilized SPATT passive samplers for the analysis of cyanotoxins under the North Coast Regional Water Quality Control Board Cyanobacteria Public Health Monitoring Program (2016-2019), and the Garcia River Watershed Conditions Monitoring Program (2018-2019). A total of 374 SPATTs were deployed at 30 sampling locations, and PSD deployment ranged from 24 hours to 14 days. The SPATTs were variably analyzed via enzyme linked immunosorbent assay (ELISA) or liquid chromatography-mass spectrometry for anatoxins, microcystins, nodularin, cylindrospermopsin, lyngbyatoxin, and saxitoxin. Detection rates varied throughout each sampling season (June 1 through-

October 31) and by station. Overall, microcystins were detected in 69% of samplers, anatoxin in 60%, nodularin in 58%, cylindrospermopsin in 16%, and saxitoxin in 3% of SPATT samplers. Lyngbyatoxin was not detected in 64 samples analyzed by SPATTs.

The North Coast Regional Water Board is currently evaluating the data collected during the implementation of the Cyanobacteria Public Health Monitoring Program to determine the efficacy of SPATTs, and to evaluate any economic advantages prior to recommending their continued use as a cyanotoxin monitoring tool for public health protection.

Region 3

The Central Coast Region deployed SPATT samplers at coastal confluence sites across three consecutive months during the 2011 dry season. Microcystin was detected in 20 of the 33 coastal confluences sampled. The PSD was successful in detecting microcystin in watersheds that are considered relatively pristine. This project supports the potential application of SPATT technology in routine ambient monitoring for toxins.

Region 4

The Los Angeles Region concurrently used traditional grab sampling methods and PSDs to screen for microcystins. A total of nine sites were screened for the presence of microcystins during the summer and fall seasons of 2018. Seven of these sites tested positive. During the summer and fall of 2019, along with the traditional grab sampling method, two PSDs, SPATT and o-DGT, were deployed concurrently for sampling microcystins. The goal of this project was to document the occurrence of microcystins in selected waterbodies (Pyramid lake, Castaic Lake, Huntington Harbor, and Clear Lake), and to compare the utility of passive sampling methods for measuring microcystin in freshwater. Microcystin was detected in all waterbodies, except Huntington Harbor. The result of this study indicated the potential of using o-DGT over SPATT due to the more quantitative nature of o-DGT. The o-DGT results indicated a comparable prevalence as the grab sample results when microcystins were detected at low levels (under 100 ng/L).

Region 9

The San Diego Region conducted a cyanotoxin screening using SPATT and discrete grab sampling procedures. Sampling was conducted in streams, lakes, reservoirs, and depression wetlands from 2011 through 2013. The cyanotoxin screening in streams included 120 samples that were collected in 2011 and 2012, throughout Southern California, using a random design. A smaller subset of SPATT samples was analyzed at U.C. Santa Cruz, using liquid chromatography with tandem mass spectrometry for microcystin, anatoxin, cylindrospermopsin, saxitoxin, nodularin, and lyngbyatoxin detection. Out of the 120 samples measured by the ELISA method, 38% contained microcystin. In the smaller subset of SPATT samples analyzed by LC-MSMS, 21% contained lyngbyatoxin, 5% contained saxitoxin, and 3% contained anatoxin.

- Microcystins were analyzed by ELISA using the Envirologix QuantiPlate™ kit (Envirologix, Portland, ME, Cat. No. EP 022). The BIOO Scientific MaxSignal™ Saxitoxin test kit (BIOO Scientific Corp., Austin, TX, Cat. No. 1034) was used for saxitoxin analysis.
- For the SPATT samples analyzed by LC-MS, electrospray ionization with selected ion monitoring on an Agilent 6130 Phenomenex Kinetix™ C18 column was employed.

The application of SPATT successfully determined the prevalence of microcystins, and the findings recommended that this device should be incorporated in ambient monitoring and assessment programs. SPATT was particularly useful in capturing ephemeral events that traditional grab samples do not capture.

OIMA

OIMA/SWAMP freshwater harmful algal bloom staff worked with the University of California, Santa Cruz to synthesize research to characterize the adsorption and potential desorption kinetics of cyanobacteria toxins to resins employed by SPATT. The cyanobacteria toxins of different polarities include: microcystin congeners (LA, LF, LR, LW, LY, RR, WR, YR, desmethyl RR and LR), anatoxin-a, homoanatoxin, cylindrospermopsin, and saxitoxins. As part of the project, costs of the PSD (including consumables) were also considered during research of the following resins/adsorbents:

- SPATT with different resins including, at a minimum, DIAION HP20, SEPABEADS® SP700, and additional resins based on research by Lane et al., 2010. The SPATT is the preferred passive sampler system considering the low cost of device assembly and consumables, however, numerous resins compatible with SPATT are available on the market that will be researched under this project.
- Chemcatcher resin/disks for polar and non-polar chemical adsorption. The following disks are recommended based on research conducted by SWAMP for other classes of compounds: Empore's SDB-RPS, SDB-XC, C18, and Oasis® HLB.

The following deliverables were produced as part of this project:

- A research synthesis report that includes expert recommendations on the feasibility of surface water monitoring of cyanobacteria toxins (listed above) using PSDs for streams, lakes, wetlands, and estuaries. The report includes relative ranking of PSD performance for listed cyanobacteria toxins.
- An SOP for "SPATT Assemblage and Extraction for Freshwater and Brackish Harmful Algal Toxins."

Summary

For surveillance projects with the objective of determining the presence or absence of pollutants, PSDs provide better data than grab sampling. PSDs have also been successfully used for determining the occurrence of cyanobacteria toxins in a relatively extensive manner, and the reports produced from these projects suggest their application needs to expand. To help implementation, an SOP for “Solid Phase Adsorption Toxin Testing (SPATT) Assemblage and Extraction for Freshwater and Brackish Harmful Algal Toxins” has been developed. The same study recommended additional PSDs for sampling toxicants as well.

The sampling medium for PSDs are manufactured sorbents capable of accumulating compounds, whereas grab samples are simple collections of environmental matrices such as water, sediment, and tissue. The subsequent laboratory analyses used to identify PSD-collected compounds and determine their concentrations, however, are similar to that of grab samples. The difference between the two methods is the way compounds accumulate in the sample, and the extraction procedures for analysis. In addition, the analytical methods measure different properties of the compounds: passive samplers measure the freely dissolved concentration of pollutants, while (water column) grab samples measure the “total” or “dissolved” concentrations (freely dissolved and colloidal with carbon).

PSD and grab sample analyses also differ in their procedures for estimating compound concentrations. Grab samples measure the mass of the compound per volume of water, or gram of sediment, while PSDs measure the mass of the compound accumulated on the device. To accomplish this, the R_s value, which is estimated by kinetic uptake and equilibrium models (first-order, one compartment mathematical model), must be applied. When R_s is known, the TWA concentration of compounds in the water phase can be calculated from exposure time and the mass of analytes accumulated by the PSD. The results are reported as the mass of the compounds sampled by the individual PSD. Therefore, having the R_s values for each of the compounds is of paramount importance to the successful use of PSDs.

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Appendix

Need for an Rs Values Study

Before a passive sampling device (PSD) can be effectively used to monitor one or more target compounds, it is necessary to determine the sampling rate. This is represented by pollutant-specific, waterbody-specific Rs values. This is a key parameter used to deduce the concentration of a target pollutant in the water column from the amount of pollutants accumulated by the PSD. The Rs values can be developed either in the lab or in the field.

Trade-Offs Between Known Rs Value Method Development Approaches

- **Lab Calibration Method:** Significantly controls environmental variables but resulting Rs values must be corrected to infer field conditions.
- **Field Calibration Method:** Requires extensive data collection for each environmental condition but produces more accurate, environment-specific Rs values to calculate concentration.

Potential Scope of a Future Rs Values Study

Over two decades of field water quality data have been accumulated by the Water Boards and the regulated community to characterize a wide range of geographic conditions across California. This large dataset is available in the SWAMP and CEDEN databases. The Water Boards propose to leverage these existing data to generate Rs values that can be used statewide, and act as the basis for further regional refinement.

Study of the available dataset will provide a greater understanding of the average values of the stream parameters required for calibration procedures, as well as characterizing long-term average stream conditions. By combining these existing datasets with new data collected in strategic locations, it may be possible to generate a more complete field-calibrated list of statewide Rs values for a wide range of pollutants. Passive sampling projects initiated by the Water Boards and any other monitoring entity could then use these Rs values to calculate the concentrations of chemicals for waterbody, avoiding the need to calibrate for each location. The Rs values should periodically be updated to account for climate change and temporal variability.

Recommended Project Tasks

1. Set up science panel and stakeholder group (State Board/Regional Boards)
2. Develop study design / reach consensus on the draft study design
 - a. Identify target pollutants (e.g., metals, pesticides, organics, etc)
 - b. Identify target PSDs
 - c. Identify target waters (e.g., marine, brackish, fresh, etc.) or watersheds
 - d. Identify conditions to be evaluated (e.g., ambient, storm, etc.)

- e. Review literature and select appropriate models to produce R_s values
3. Compile and evaluate statewide water quality field data to be used in the final R_s Value model (desktop analysis and data quality; method quality review)
4. Field reconnaissance and pilot study site selection
5. Finalize study design (based on Tasks 2-4)
6. Obtain, calibrate, and deploy passive samplers at selected sites
 - a. Collect field data
 - b. Collect maintenance data (information on fouling)
7. Conduct modeling and develop statewide R_s values for target chemicals
8. Write report on the findings

References

Wang, L., et. al., 2020. Sampling Rate of Polar Organic Chemical Integrative Sampler (POCIS): Influence Factors and Calibration Methods. *Appl. Sci.* 2020, 10, 5548; doi:10.3390/app10165548.

Device Images

Figure 2. Chemcatcher™ Passive Sampler in preparation for Deployment at Hood Experimental Station



Figure 3. Semi-permeable membrane



Figure 4. Silicone rubber



Figure 5. Micro-extraction devices



Figure 6. Organic Diffusion Gradients in thin films (o-DGT) device piston and cap



Figure 7. CLAM passive sampler

