

POCIS – Current Applications, On-going Research and Future Needs

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The polar organic chemical integrative sampler (POCIS) has recently seen a dramatic increase in its use for monitoring for pharmaceuticals, polar pesticides, and wastewater-related chemicals. However, there are many fundamental research issues that need to be addressed before it can reach the level of data quality and acceptance that the semipermeable membrane device (SPMD) has. This presentation will include a discussion of: 1) state of the technology and what type of data that can be expected, 2) recent laboratory and field studies, 3) on-going calibration studies to determine sampling rates and uptake kinetics, 4) status of the performance reference compound (PRC) approach, 5) combination of POCIS with bioindicator/toxicity testing, and 6) future needs from the research community.

Keywords: POCIS, calibration, pharmaceuticals, wastewater, PRC

Presentation type: platform

Passive Samplers On Semi-Permanent Moorings At Three Deep-Ocean Sites

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Semipermeable membrane devices (SPMDs), low-density polyethylene (LDPE) strip samplers and polydimethylsiloxane (PDMS) strip samplers were mounted on semi-permanent moorings in Strait Mozambique, the Canary Basin (west of Africa), and the Irminger Sea (near Greenland) at depths between 0.1 and 5 km for 1 to 1.5 years. The samplers were analysed for polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), 4,4-DDE, and polyaromatic hydrocarbons (PAHs). Strong vertical gradients were observed in the Canary basin. By contrast, vertical gradients were minimal in the Irminger Sea. PAH concentrations were highest in the Canary basin. PAH concentrations increased with depth in Strait Mozambique. HCB concentrations were highest in the Irminger Sea, and concentrations of 4,4-DDE did not vary much among sites. Differences in absorbed amounts between the various sampler types were related to sorption capacity. The in-situ sampling rates of the samplers was low, in accordance with the low flow velocities in the open ocean. The results show that passive samplers that are mounted on open-ocean moorings are valuable tools for evaluating the role of ocean circulation in the global distribution of organic contaminants.

Key words: Water, SPMD, LDPE, PDMS, ocean circulation, PAHs, organochlorines

Presentation type: platform

Use of Chemical Analysis and Assays of SPMD Extracts to Assess the Response of Hydrophobic Organic Contaminants in Streams to Urbanization in Six Metropolitan Areas of the U.S.

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As part of an integrated assessment of stream responses to urbanization, semi-permeable membrane devices (SPMDs) were deployed in streams along a gradient of urban land-use in and around Atlanta, Georgia; Raleigh, North Carolina; Denver, Colorado; Dallas, Texas; Milwaukee, Wisconsin; and Portland, Oregon. The goals of this study were: (1) to assess the occurrence and distribution of selected hydrophobic organic contaminants (HOCs) in streams across a range of urban land use conditions and not having the influence of large point source discharges; (2) to determine if the concentrations of HOCs and their potential toxicity to aquatic biota responded in some way along a gradient of urbanization within each metropolitan area; and (3) to compare these responses among the six metropolitan areas studied. Petite SPMDs (6") were deployed in 30 streams in each metropolitan area for 30-45 days during base flow conditions; Denver, Raleigh and Atlanta in 2003, and Milwaukee, Dallas and Portland in 2004. Despite some losses, a total of 167 SPMDs were retrieved successfully. Of the 74 compounds detected and three assays utilized, 29 were strongly related to increases in urban intensity in at least one of the six metropolitan areas investigated. These 29 endpoints included: 16 polycyclic aromatic hydrocarbons (PAHs), a wood preservative (pentachloranisole), 2 insecticides (chlorpyrifos and chlordane), 3 herbicides (benfluralin, trifluralin, and dacthal), a synthetic musk (AHTN), 2 furans (methyl-dibenzofuran and benzo(b)naphtho [2,3-d]furan), and a flame retardant (BDE 47). In addition, the number of compounds detected and results of the Fluoroscan, Microtox®, and P450RGS assays were strongly related to urban intensity. Petrogenic PAHs and dibenzofurans increased with increasing urban intensity in Atlanta, Raleigh, Milwaukee, and Denver while pentachloroanisole, pyrogenic PAHs, and P450RGS increased with increasing urban intensity in all six metropolitan areas. The number of endpoints related to urban intensity ranged from three in Portland to 21 in Raleigh and Denver. In addition to the numbers and types of endpoints related to urban intensity, graphical methods and analysis of covariance were used to investigate differences in the response patterns in the six metropolitan areas. Analytical chemistry and in-vitro assays of petite SPMDs extracts proved to be a powerful tool to assess response of HOCs in streams to urbanization.

Keywords: SPMD, streams, urban, analytical chemistry, assays

Presentation type: platform

Determination Of Uptake Rates For VOCs In Ambient Air By Using Axial Type Thermal Desorption Passive Tubes

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Passive samplers have been widely used as a cost-effective and reliable technique in measuring ambient Volatile Organic Compounds (VOCs) concentrations. The main source of uncertainty in environmental applications of passive sampling is the use of uptake rates determined in the laboratory (Tolnai et al., 2000). With the exception of BTX compounds, information on uptake rates of VOCs present in ambient air is limited. In this paper, uptake rates for more than 50 aromatic, olefinic, paraffinic and halogenated organic compounds that may be present in ambient air were determined for different concentration and meteorological conditions by sampling parallel to an online-GC between, September 2005 and May 2006, at an urban site in the city of Bursa, Turkey.

In this period, hourly VOC concentrations were measured using an HP Gas Chromatograph (GC) with Flame Ionization Detector, equipped with a Deans Switch that was coupled to a Unity Thermal Desorption and Air Server sampling system. The instrument was calibrated to detect 148 VOCs with carbon numbers ranging between C₂ and C₁₂. However, approximately 66 of these were detected during measurements.

Passive sampling tubes are filled with Chromosorb 106 adsorbent. Fifty compounds ranging from C₂ to C₁₂ were detected upon thermal desorption and subsequent GC-FID measurement. Data from seven exposure periods are included in this discussion. For each exposure period more than 3 tubes were co-located with online GC inlet. The meteorological data were obtained from the nearest meteorological station, which is approximately 5 km from the measurement point. Data from a total of 49 passive sampling tubes and 1296 hourly active measurements were used to evaluate the effect of meteorology on uptake rates. The mean uncertainty range and the coefficient of variation for each compound were calculated for active and passive sampling. After obtaining uptake rate for each exposure period, influence of meteorological condition on uptake rates was investigated.

Keywords: tube type passive sampling, air, VOCs, uptake rate

Presentation Type: platform

Reference:

Tolnai, B., Gelencser, A., Gal, C., Hlavay, J., 2000. *Evaluation of the Reliability of Diffusive Sampling in Environmental Monitoring*, Analytica Chimica Acta Vol:408, 117-122

Spatial Distributions Of Organic And Inorganic Pollutants At An Industrial City On The Northwestern Turkey

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Preliminary information on spatial distribution of air quality in Bursa, which is city with population of 600 000, located on the Northwestern Turkey, is being studied using passive sampling. The parameters that are measured by passive monitors include SO₂, NO₂, O₃ and approximately 70 VOCs. Concentrations of these species were measured at 50 locations at a 22 km x 10 km area, which includes residential, traffic impacted and industrial sectors in the city one week at October 2005 and one week in April 2006. An online GC were operated parallel with the passive samplers to determine the uptake rates of the VOC samplers under meteorological conditions that existed during passive sampling interval. The distribution maps prepared by interpolating data allowed us to differentiate hot spots in the city and identified locations where air quality monitoring stations should have been located. The center of the city with congested traffic, and kurtulu district, which is densely populated area in the city have the highest concentrations of VOCs. SO₂ concentrations, on the other hand, were the highest at Osmangazi organized industrial area. Ozone concentrations were low within the city, due to destruction of ozone by high concentration of NO, and high at the peripherals of the city. Sources contributing to observed distributions are determined using positive matrix factorization as multivariate statistical tool.

Keywords: passive sampling, VOC, inorganics, urban, pollution mapping, source apportionment

Presentation type: platform

Using Passive Samplers in Lake Mead National Recreational Area to Assess Sources of Endocrine Disrupting Compounds

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Two types of passive samplers, SPMDs and POCIS, were deployed in March 2006 at seven sites in Lake Mead National Recreational Area (Nevada and Arizona) to help assess sources of endocrine disrupting compounds (EDCs). Extracts were analyzed by GC/MS using two detection methods, electron capture, and negative capture ion. A total of 47 compounds were detected, 19 of which are known or suspected EDCs. The major source of EDCs was Las Vegas Wash, which consists of tertiary treated effluent, surface runoff from the Las Vegas Valley, and groundwater discharge. A commonly used polycyclic musk fragrance, tonalide, was found at considerably higher levels in both SPMDs (260 µg) and POCIS (9.8 µg) deployed in Las Vegas Wash compared to other EDCs, followed by another musk fragrance, gaxolide. Both of these compounds were also detected downstream from Las Vegas Wash in Lake Mead and tonalide was detected further out in Boulder Basin but not below Hoover Dam or at the two major inflows to Lake Mead, Overton Arm and Gregg Basin. Polycyclic musks have been shown to be only weakly estrogenic, however, they are present in Las Vegas Wash and Bay at orders of magnitude higher than levels of other EDCs, including many legacy organochlorine compounds. Another estrogenic EDC commonly present in treated wastewater as a surfactant, octylphenol, was detected in Las Vegas Wash and Bay samples. The presence of these estrogenic EDCs is supported by evidence of endocrine disruption in male fish collected from the Las Vegas Wash and Bay, and below Hoover Dam. Effects include altered sex steroid hormones, reduced gonadal development, and lower sperm quality suggesting exposure to estrogenic EDCs.

Keywords; SPMD, POCIS, EDC, Lake Mead, musk fragrance

Presentation type: platform

Measuring HOC Chemical Activity In Sediments Using Polyethylene Passive Samplers

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In order to determine the hazards posed by hydrophobic organic compounds (HOCs) like PAHs and PCBs in sediment beds, we have initiated a study to explore the use of small polyethylene (PE) sheets as passive sampling devices for measuring HOC chemical activities in this complex environmental compartment. Bench scale experiments showed that the chemical activities in PE brought to equilibrium with sediment samples matched porewater chemical activities within a factor of two for six PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, and chrysene) in two sediment samples. Next tracer chemicals, impregnated within the PE, were used to calibrate a mass transfer model for PE inserted in the same sediments for short times (days). Target chemical activities were then deduced using the build up of mass of these HOCs within the PE and knowing their PE-water partitioning coefficients and the aqueous solubilities. These corrected non-equilibrium results compared well with the results of the equilibration experiment, and were within a factor of two of porewater measurements. Chemical activities deduced from analyses of the sediments and normalizations using an EqP model which considers organic carbon and black carbon differed from porewater measurements by a factor of 10. Finally, PE samplers were deployed in-situ at a coal tar-polluted site in the Boston Harbor. Results of this experiment showed the vertical profile of PAH activity increasing over a depth of 20 cm. PE samplers were found to be durable enough to withstanding insertion into several types of sediment beds, including those littered with shells, rocks, and other jagged materials, and provided enough material that several analyses of the same sample were possible. We believe PE passive samplers to be well suited to measuring HOC chemical activities in sediment beds.

Keywords: polyethylene, PE, sediment, PAH

Presentation type: platform

A Holistic Passive Sampling Calibration For Alkylated Phenols

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As part of our ongoing work studying the effects of operational discharges from the oil and gas industry in the North Sea we present results from a study to calibrate passive samplers for alkylated phenols (AP). The uptake characteristics of Semipermeable membrane devices (SPMD) and both types of commercially available polar organic chemical integrative sampler (POCIS) were determined for 30 AP. Samplers were exposed in a flow through system at concentrations of 100ng L^{-1} for a period of up to one month. The most polar AP were not accumulated in SPMDs in quantifiable amounts with significant uptake only occurring for compounds with $\log K_{ow} > 3$. Sampling rates ranged from $0.02 - 4 \text{ L}^{-\text{d}}$, being highest for the most hydrophobic compounds. Sampling rates were $< 1 \text{ L}^{-\text{d}}$ for POCIS with some considerably higher than those reported in the literature for other compounds. These sampling rates allow, for the first time, the calculation of time weighted water concentrations of these compounds. This will hopefully afford a more complete risk assessment of offshore discharges and also aid the study of the degradation products of alkylphenol ethoxylates from land based effluents. Results are discussed in terms of, physico-chemical properties of analytes, differences between sampler types, limitations of the experimental and analytical methods and the relevance to offshore monitoring.

Keywords: SPMD, POCIS, seawater, alkylated phenols, produced water

Presentation type: platform

Environmental Investigations Using Versatile, Vapor-Permeable, Adsorbent-based Passive Samplers

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Environmental professionals agree that a conceptual site model (CSM) derived from accurate and comprehensive site assessment data will provide the foundation for implementing an efficient and cost-effective site remedy. A well-developed CSM can accelerate the site clean-up and closure process, and minimize the associated sampling and monitoring costs substantially. Vapor-permeable passive samplers provide a unique method for site assessment. Their simplicity, sensitivity and overall cost effectiveness allows one to collect a robust dataset that can be used to focus subsequent more complex and expensive sampling techniques. These versatile samplers can also be used to monitor remedial progress, in vapor intrusion investigations, and in long-term groundwater monitoring.

Passive samplers are capable of sampling soil gas, sub-slab soil gas, air, and water; however, use and performance are a function of sampler design. Typically, passive samplers are easy-to deploy and have minimal operating requirements. The patented GORE™ Module is a versatile, diffusion-based passive sampler. The sampler is constructed of a vapor-permeable, waterproof GORE-TEX® membrane, which houses hydrophobic adsorbents. The unique design of the GORE™ Module allows it to be deployed directly in unsaturated and saturated soils and sediment, in surface and groundwater, and in indoor, outdoor, and crawlspace air. The GORE-TEX® membrane facilitates vapor transfer to the adsorbent, while protecting the adsorbent from soil, liquid water or other potential interferences, maintaining sample integrity.

Case studies demonstrating its utility in a variety of sampling applications will be presented, along with a discussion of the passive sampler.

Keywords: GORE™ Module, soil gas, air, water

Presentation type: platform

TMDL Development Based Upon Passive Sampling Results; From Monitoring Plan to Loading Calculations

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For the first time, a Total Maximum Daily Load, TMDL, of persistent bioaccumulative toxins, PBTs, is being developed primarily using passive sampling. This Regional Applied Research Effort, RARE, project is a collaborative effort of USEPA NRMRL, USEPA Region III, USEPA ORD, USGS, WVDEP, and VADEQ. The project has expanded the historical use of SPMDs allowing accurate assessment of PCB and dioxin loadings in an area with complex surface, karst, and pseudokarst hydrogeology. The Commonwealth of Virginia has been evaluating our reliance upon sediment, fish, grab and high volume water sampling, and other biomarkers for source and risk assessment, watershed characterization, impairment listing, and seasonal loading potential. Validation of the benefits of SPMD technology are the upcoming Virginia Bluestone PCB TMDL and a West Virginia Bluestone TMDL being developed in the near future.

SPMD deployment for TMDL development requires an appropriate plan, in this case a detailed Quality Assurance Project Plan, QAPP. Plans should account for impairment basis; accurate flow monitoring and hydrology; seasonal effects; soil type; monitoring location selection; interstate, interagency, and stakeholder communication; site security (including vandalism and extreme weather events); ingress and egress; bioaccumulation; pollutant transport vectors; quality assurance; and quality control. Choosing the correct sampling and deployment devices require an understanding of the limitations and advantages of various technologies.

The project results suggest that most effects of temperature, facial velocity-turbulence, biofouling, and perhaps other environmental variables on the PBT analyte uptake rates with a range of SPMD-water partition coefficients can be determined from several different Performance Reference Compounds, PRCs. This study demonstrates that various types of PRCs yield similar results. Additionally, the complexities of the hydrology of the watershed, including the groundwater transport issues may be largely accounted for using monitoring site selection, accurate frequent/continual flow monitoring, and continual rainfall measurements.

Key Words: SPMD, PRC, TMDL, Total Maximum Daily Load, PBT, Persistent Bioaccumulative Toxin, PCB, Polychlorinated Biphenyl, Dioxin, Passive Sampling, hydrology, geohydrology, Bluestone River, RARE, Regional Applied Research Effort, Virginia Department of Environmental Quality, VADEQ.

Presentation Type: platform

Laboratory Calibration and Field Deployment of the Polar Organic Chemical Integrative Sampler (POCIS) for Pharmaceuticals and Personal Care Products

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Sampling rates for 25 different pharmaceuticals and personal care products (PPCPs) were determined on the passive commercially available Polar Organic Chemical Integrative Sampler (POCIS). Passive sampling devices such as the POCIS can capture time-weighted average (TWA) water concentrations of water-soluble organic pollutants. To date, calibration of POCIS sampling rates has only been carried out for a limited list of compounds, mainly pesticides. In this work, laboratory calibration experiments were conducted under flowing and quiescent water conditions. Uptake rates were 0.040 L/d to 2.462 L/d under flowing conditions while quiescent conditions resulted in uptake rates between 0.016 L/d and 0.223 L/d. The uptake of many PPCPs appears to be controlled by the effective thickness of the stagnant aqueous boundary layer at the sampler surface. This is indicated by sampling rates that are higher in flowing conditions. The controlling factor for some PPCPs still remains unclear. Sampling rates correlated with physical-chemical properties such as octanol-water partition coefficients. Field deployments of several weeks, accompanied by regular grab-samples, were carried out in wastewater and surface water. The field study demonstrated that the POCIS, when coupled with laboratory derived uptake rates herein, can be used to generate accurate TWA concentrations of PPCPs in the aquatic environment.

Keywords: POCIS, surface water, wastewater, PPCPs, calibration

Presentation Type: platform

Application of Passive Samplers for Drinking Water Monitoring

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Passive sampling has been widely used for controlling chemicals in natural waters and has been an area of growing concern in recent years. The possibilities of this technique as a complementary method for monitoring drinking water are under study at *Aigües de Barcelona* (Barcelona's Water Laboratory) as health regulations are mainly addressing average intake in humans rather than the usual but also compulsory spot sampling.

A patent pending passive sampler (developed by H. de Jonge and G. Rothenberg (1) for water quality measurements), that functions as a water-permeable, semi-infinite sink for passing solutes of interest was applied among other passive sampling devices to monitoring of drinking water. It consists of a small plastic cartridge filled with an adsorbent designed to detain certain predefined chemicals (organics and/or inorganics), and a tracer-salt that dissolves proportionally and stores information on the volume of water passing through the sampler during the installation period, thus enabling the calculation of average concentrations of chemicals per litre of water. Analysis of the samples is made by standard laboratory methods providing comparable results with historical data. The aim of this study is to demonstrate the applicability and usefulness of these emerging and low cost tools to obtain a more representative measure of priority pollutants in drinking water monitoring in support of the Water Framework Directive.

Keywords: drinking water, regulations, public health, passive samplers

Presentation type: platform

(1) De Jonge, H., and Rothenberg, G. (2005). New Device and Method for Flux-Proportional Sampling of Mobile Solutes in Soil and Ground Water. *Environ. Sci. Technol.* 39:274-282.

Dissipation Of Polar Xenobiotics From Pharmaceutical POCIS And Suggestion Of A Performance Reference Compound

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This work set out the calibration of pharmaceutical POCIS with 20 herbicides. The calibration revealed linear and integrative uptakes of several herbicides for 21 days but some compounds like sulcotrione, mesotrione, atrazine-desisopropyl (DIA) and atrazine-desethyl (DEA) exhibited curvilinear uptakes. We assumed first-order isotropic exchanges for these polar compounds and we estimated the elimination rate constant of the DIA. For this purpose, we spiked the sorbent contained within pharmaceutical POCIS with DIA, simazine and isoproturon and we studied their dissipations for 10 days. For DIA, the exchanges appeared to be isotropic and the dissipation was correctly described by a first-order monophasic kinetic law.

Further microcosm experiments were performed with river freshwater and strong turbulences (from 10 to 20 times more elevated than calibration flow velocities). The POCIS containing sorbents fortified with DIA were exposed during 9 days. The waters were spiked with terbuthylazine-desethyl (DET), terbuthylazine, isoproturon and acetochlor at either moderate and constant concentrations or 3-day peak concentrations. The real concentrations determined with repetitive grab sampling and time-weighted average concentrations estimated from POCIS were compared. The results showed that a peak of pollution is correctly integrated by the POCIS but the TWA concentrations can be overestimated. However, the use of DIA as a performance reference compound (PRC) provided a good correction of the turbulence and biofouling effects. In fact, the TWA concentrations estimated with the PRC dissipation were closer to the real values. As for SPMDs [1], multiple PRCs are probably needed to cover the wide range of environmental exposure conditions and further works will concern the dissipation of other polar organic chemicals from pharmaceutical POCIS.

Keywords: POCIS, PRC, DIA

Presentation type: platform

[1] J.N. Huckins, J.D. Petty, J.A. Lebo, F.V. Almeida, K. Booij, D.A. Alvarez, W.L. Cranor, R.C. Clark, B.B. Mogensen, *Environ. Sci. Technol.* 36 (2002) 85.

Comparison SPMDs and selected abiotic samplers using Gnostic data analysis

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The semipermeable membrane device (SPMDs) together with some selected biotic organisms has been applied for monitoring of rivers in the Czech Republic. Some criteria were used for evaluation of the quality of results, mainly: sensitivity and measuring range, homogeneity of results, internal and external consistency and precision. Data were used from monitoring of 19 sampling sites of 15 rivers, realized in 2003-2006. Monitoring data of selected POPs, like polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs) were used for the comparison. Robust algorithms maximizing the information of results based on this theory have been developed for many applications, as well as for passive sampling and environmental monitoring.

Keywords: SPMDs, biota, Gnostic analysis, PCA

Presentation type: platform

Rigid Porous Polyethylene Passive Diffusion Samplers

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For several years now Passive Diffusion Sampler (PDS) technology has been applied to many sites to improve the information gained during groundwater monitoring and to reduce the cost of sampling. Wide acceptance of these samplers has been gained for hydrophobic Volatile Organic Compounds (VOCs) using the polyethylene bag technique with hundreds of studies demonstrating their effectiveness since 1998. While this material is extremely useful for these specific target analytes, there is a need to identify additional materials that would enable similar performance for hydrophilic organics, semivolatile organics and inorganic target analytes as well. Additional studies using new materials have been underway and progress can be reported on a new type of passive diffusion sampler: the Rigid Porous Polyethylene Sampler (RPPs).

These efforts to develop passive diffusion samplers for common long term monitoring inorganic and organic parameters include both laboratory and field demonstration studies. Recent data will be presented to demonstrate the performance and feasibility of these materials. Data will include that from recent ERDC CRREL studies as well as data from the passive diffusion sampler comparison study performed at McClelland Air Force Base and others. There will also be a short discussion of the laboratory considerations that must be addressed with use of these samplers.

Key Words: RPP, Rigid Porous Polyethylene Sampler, Passive Sampling, Passive Sampling for water-soluble analytes.

Presentation Type: platform

New Approach in Calibration of Passive Permeation Samplers used for Sampling of VOCs from Air

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Passive sampling is a very attractive alternative to active sampling due to its simplicity and low cost. Among the passive samplers used in air analysis, permeation passive samplers offer unique advantages, including elimination of problems related to moisture, low sensitivity to air currents and to temperature changes. The biggest drawback of permeation passive samplers is the need to calibrate them experimentally for each individual target analyte. This limited the applicability of permeation passive samplers exclusively to target compound analysis. The approach proposed to estimate the values of the calibration constants based on physico-chemical properties of the analytes and/or their retention parameters eliminate this fundamental limitation of permeation passive sampling.

The approach proposed to estimate the values of the calibration constants based on physico-chemical properties of the analytes (carbon atoms among families of compounds, the molecular weights of the compounds, their boiling points) and/or their retention parameters eliminate this fundamental limitation of permeation passive sampling. The PDMS membrane used in permeation passive sampler assured high sampling rates of analytes. This makes it possible to deploy permeation passive samplers in the same way in which active sampling is deployed. The samplers can be exposed to an unknown sample without the need to calibrate their response towards all analytes.

Keywords: permeation sampler, active charcoal, air monitoring

Presentation type: platform

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Pesticide Sequestration In Passive Samplers (SPMDs): The Effect Of Biofouling And Deployment Time In A Tropical Watershed

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Field deployed passive samplers including semi-permeable membrane devices (SPMDs) provide an informative and cost-effective approach in the monitoring of contaminants over time. However, sequestration of contaminants in passive samplers can vary based on a number of environmental factors including water chemistry and flow, biofouling and deployment time. In three one-month long trials, SPMDs were concurrently deployed for 4, 15 and 28 days in three different stream sites in an extensive agricultural area in south-eastern Costa Rica. Water, bottom sediment and suspended sediment grab samples were also collected at corresponding time intervals over each month and several environmental variables were monitored daily. In all three sites, SPMD concentration of the widely-used insecticide chlorpyrifos increased with deployment time, with no significant relationship between membrane biofouling and pesticide uptake. Higher suspended solids concentrations combined with lower water flow conditions were positively correlated to increased chlorpyrifos concentration among replicate sites. The longer exposure period of passive samplers also allowed for the detection of lower concentrations of chlorpyrifos, terbufos and difenoconazole compared to grab samples. In addition to flow and deployment time, several other environmental variables including stream turbidity and morphology may also be important for optimum SPMD deployment and data interpretation.

Keywords: SPMDs, surface water, suspended sediments, Costa Rica

Presentation Preference: platform

In-situ Nutrient Analyzers: The State of the Art After a Decade of Development

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Field deployable and submersible nutrient analyzers have been available since the early 90's, but have never been widely adopted within significant monitoring programs. After over a decade of development are these instruments now useful and reliable monitoring tools? A series of fieldwork case studies will be used to outline the true capability of this technology. Recent and emerging developments, such as high frequency phosphate, ammonia, urea monitoring will be described. A highly novel, sensor-like analyzer developed specifically to provide an easy to use, low-cost tool for monitoring applications will also be presented.

Keywords: nutrient analyzer, in-situ analysis, nitrate, phosphate, ammonia

Presentation type: platform

Using Semi-Permeable Membrane Device (SPMD) Samplers in Cave Environments to Detect PCBs

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The town of Bluefield West Virginia/Virginia is situated along the Greenbrier Limestone and portions of the drainage flow underground into and through a cave system. The community has a long history of coal mining and mining related industry. Historically, numerous business operations in the area were engaged in the maintenance, repair and salvage of electrical mining equipment. From 1930 to 1978 poly chlorinated bi-phenyls (PCBs) were extensively used as a dielectric fluid in mining equipment as well as electrical transformers and capacitors.

As a result of these historic activities, migration of PCBs to surface water has been occurring from an unknown source or sources. The West Virginia Department of Environmental Protection and the Virginia Department of Environmental Quality set out to monitor the presence of PCBs in surface water using semi-permeable membrane device (SPMD) samplers. Along the suspected contaminant flow path, much of the surface water drainage flow is diverted through a cave system within the Greenbrier Limestone. More information was needed to narrow the location of the potential source or sources that are contributing to the PCB contamination. However, the inaccessibility of the underground flow component was an obstacle. Several non-traditional resources were used to assist in the installation of SPMD samplers into flow within the cave system. With only minor modifications of above ground installation techniques, the SPMD samplers have been successfully used to detect PCB movement through the cave system in Bluefield West Virginia/Virginia. This strategy could be repeated in other similar hydrogeologic situations.

Keywords: SPMD, underground, cave

Presentation Type: platform

The Effect of Temperature on the Uptake Rates of a New PDMS-Based Permeation Passive Sampler for VOCs in Air

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Polydimethylsiloxane (PDMS) has interesting sorption and diffusion properties towards many organic compounds and is highly hydrophobic. Due to these features, various analytical techniques utilizing PDMS have been successfully employed in the field of analytical sample preparation (e.g. SPME, stir bar sorptive extraction, membrane extraction with a sorbent interface, etc.,) and separation (e.g. as a stationary phase in capillary gas chromatography). A simple and cost effective permeation passive sampler utilizing these excellent properties of PDMS has been developed in our laboratory to further simplify sample handling and reduce sample contamination during the sample preparation step.

The PDMS-based sampler is expected to be insensitive to humidity variations as the membrane is highly hydrophobic. Further, theoretical considerations of the mechanism of analyte transport across PDMS membranes indicate that the calibration constant (reciprocal of the sampling rate) should be only slightly affected by temperature variations. This is because the permeability of the polymer towards a particular analyte (the product of the analytes diffusivity in the polymer and its partition coefficient between PDMS and air) defines the uptake rates. While the diffusivity of a particular analyte increases with increasing temperature, the partition coefficient decreases. This trade-off between the two parameters defining the permeability of the polymer results in the uptake rate being only slightly affected by temperature.

Experiments were performed with various model compounds with a wide polarity range to test the hypothesis. The calibration constants were determined at different temperatures, and the energy of activation of permeation (which defines the variation of permeability with variation in temperature) was deduced from the experimental results. In the seminar, the new sampling device, sample preparation methodology, the theory and experimental results obtained will be discussed.

Keywords: Permeation passive sampling, volatile organic compounds, temperature effects, polydimethylsiloxane, air sampling.

Presentation type: platform

Using Integrative Passive Samplers To Monitor Current-Use And Legacy Pesticides In San Francisco Bay, California

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Current-use and legacy pesticides have been detected throughout the San Francisco Bay in surface water and sediment. However, it is difficult and expensive to use traditional sampling techniques in the estuary due to complex hydrodynamics and episodic pulses of pesticides. Passive samplers are important tools used to monitor bioavailable pesticides by collecting an integrative sample over time resulting in fewer samples and eliminating the need to catch definitive “pulses” of pesticides. Measuring various classes of pesticides can be difficult due to the range in their hydrophobicities ($\log K_{ow} < 2$ to >6). SPMDs ($\log K_{ow} > 4$) and POCIS ($\log K_{ow} < 4$) were deployed in tandem at several marsh sites in upper San Francisco Bay to monitor pesticides. Surface water samples were also collected to compare pesticides detected in a typical 1-L point sample to those detected in passive samplers deployed for a month. The more hydrophilic current-use pesticides fipronil, metolachlor, pendimethalin, simazine and trifluralin, were detected in both the POCIS samplers and the 1-L water sample collected at time of deployment and retrieval. The more hydrophobic legacy organochlorine insecticides were detected only in the SPMDs and included DDTs, dieldrin and several chlordanes. Concentrations of these pesticides measured in the SPMDs were below the detection limit for the 1-L water sample. Pyrethroids are a class of current-use pesticides that are increasing in use and are of concern due to their high aquatic toxicity. Pyrethroids are relatively hydrophobic ($\log K_{ow} = 4-6$) and should be sampled by SPMDs. However, preliminary results suggest that the size and steric hindrance of the pyrethroids may limit their ability to pass through the SPMD membrane. Future work will include laboratory uptake studies to validate the effectiveness of SPMDs and POCIS for measuring current-use pesticides, including pyrethroids, in surface waters.

Keywords: SPMD, POCIS, surface water, pesticides, pyrethroids

Presentation type: platform

Semipermeable Membrane Devices Link Site-Specific Contaminants To Effects: Part 1 - Induction Of CYP1A In Rainbow Trout From Contaminants In Prince William Sound, Alaska

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We deployed semi-permeable membrane devices (SPMDs) on beaches in Prince William Sound (PWS), Alaska, to evaluate whether bioavailable contaminants from different pollution sources can induce cytochrome P450 1A (CYP1A) in biota. Deployment sites included canneries, salmon hatcheries, and beaches where lingering oil remains from discharges during the 1964 earthquake or the 1989 Exxon Valdez oil spill. Other sites were selected at random to evaluate region-wide contaminant inputs or were located in salmon streams to evaluate contaminants introduced into PWS by migrating salmon. Following ~28 d deployments, an aliquot of the accumulated contaminants was injected into juvenile rainbow trout (*Oncorhynchus mykiss*), and CYP1A activity measured by the ethoxyresorufin-o-deethylase (EROD) assay after 2 and 7 d. The oiled sites and one hatchery site with numerous creosote pilings elicited strong EROD responses, and the salmon streams elicited significant but weak responses during late summer compared to late spring. Responses from the other sites were not significant, indicating contaminants from these sources are unlikely to cause CYP1A induction in resident biota.

Keywords: SPMD, CYP1A induction, oil spill

Presentation type: platform

Semipermeable Membrane Devices Link Site-Specific Contaminants To Effects: Part II – A Comparison Of Lingering Exxon Valdez Oil With Other Potential Sources Of Cytochrome P450 1A Inducers In Prince William Sound, Alaska

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We deployed semi-permeable membrane devices (SPMDs) on beaches for 28 days at 53 sites in Prince William Sound (PWS), Alaska, to evaluate the induction potential from suspected sources of cytochrome P450 1A (CYP1A)-inducing contaminants. Sites were selected to assess known point sources (23 sites in total), or were chosen randomly to evaluate the region-wide sources (30 sites). After deployment, SPMD extracts were analyzed chemically for suites of persistent organic pollutants (POP) and polycyclic aromatic hydrocarbons (PAH). Results of chemical analyses were compared with hepatic CYP1A enzyme activity (ethoxyresorufin-O-deethylase; EROD) of juvenile rainbow trout injected with the same extracts. Increased CYP1A activity (induction) was associated most strongly with concentrations of PAH in extracts, especially chrysene homologues. There were no correlations between induction and concentrations of persistent organic pollutants such as PCBs. EROD activity levels followed a simple power curve of the form $y = ax^b$, where x is the amount of total PAH or of chrysene homologues injected. The only apparent sources of chrysene homologues were lingering oil from Exxon Valdez, bunker fuels released from storage tanks during the 1964 Alaska earthquake, creosote leaching from numerous pilings at one site, and PAH-contaminated sediments at Cordova Harbor. Our results indicate that PWS is remarkably free of pollution from PAH, as well as from pesticides and PCBs, when an obvious nearby source is absent.

Keywords: SPMD, P450 1A induction, oil spill

Presentation type: platform

Investigating Chemicals from Wastewater Discharges in Tinkers Creek

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The U.S. Geological Survey investigated the presence of pharmaceuticals, health-care products, and other organic-wastewater compounds—often referred to as “emerging contaminants”—entering Tinkers Creek, the largest tributary to the Cuyahoga River, which is the second largest tributary to Lake Erie in Ohio. The Tinkers Creek study evaluated the potential for these compounds to enter from obvious sources; specifically wastewater-treatment plants.

Tinkers Creek was chosen as a study site after biological surveys by the Ohio Environmental Protection Agency indicated that the numbers of fish in the population did not match the available habitat. When fish are not abundant enough to use the habitat available, it is normally a sign of impaired chemical quality of the water. However, chemical surveys done in conjunction with the biological surveys did not identify the usual chemical suspects. The Ohio Environmental Protection Agency then asked the USGS for help investigating whether emerging contaminants were having an effect on the fish population.

Polar organic chemical integrative sampler (POCIS) devices were used to mimic the exposure to chemicals aquatic organisms, such as fish, would experience while living in the stream. A POCIS device can accumulate trace to ultratrace concentrations of chemicals over a long-term exposure. The POCIS approach is proving to be more effective for these kinds of studies than traditional monitoring methods such as grab sampling.

In the Tinkers Creek study, the POCIS devices were set at 18 sites, including positions above and below the seven wastewater-treatment plants discharging to Tinkers Creek and its tributaries. Two streams without wastewater-treatment plants were selected as reference stations. Each reference stream is a tributary of the Cuyahoga River and in a more remote area than Tinkers Creek. The period of sampling lasted 28 days and began May 8, 2006. Analyses of the data are ongoing.

Keywords: POCIS, surface water, pharmaceuticals, emerging contaminants

Presentation type: platform

A Simple Diffusion Sampler for Pore-Water Hydrogen as a Tool for Understanding Redox Conditions in Saturated Sediment

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Dissolved hydrogen gas (H_2) is an important and diagnostically useful intermediate for microbial metabolism. Traditional H_2 -sampling procedures involving monitoring wells, however, are not practical for shallow sediment, such as stream bottoms or swamps. In addition, H_2 analysis by incubating microcosms of sediment and monitoring the headspace H_2 concentration over time to equilibrium is time consuming. Laboratory and field tests demonstrate that a simple, syringe-based diffusion sampler can be used to collect representative samples for analyzing H_2 concentrations in saturated sediments. The simple H_2 diffusion sampler presented here consists of a syringe and attached closed stopcock, with no plunger, sealed in an inert-gas headspace in two layers of low-density polyethylene (LDPE) membrane that function as the diffusive surface. After an equilibration period, the sampler is recovered, the outer LDPE layer is taken off to remove dirt, and the syringe plunger is inserted into the syringe far enough to break through the inner LDPE bag. A needle is attached to the stopcock, and the contents of the vial are injected into serum vials, where the H_2 remains stable until analysis. The H_2 concentrations can be used as indicators of the predominant electron accepting activity, or redox conditions, in the saturated sediment. The samplers equilibrate within about 30 hours; however, they should be allowed to equilibrate in place for at least two weeks to allow equilibration recovery from deployment disturbances. Upon recovery of the samplers, the enclosed gas can be transferred to stable serum vials and shipped to a lab for analysis. The samplers are useful for depths up to about 18 feet below water and can be modified for use at greater depths and in wells.

Keywords: hydrogen, syringe sampler, pore water, redox, terminal electron accepting process

Presentation type: platform