# Determining the Estrogenic Activity of Chemicals Sequestered by SPMDs and POCIS in the Santa Ana River Basin

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The Santa Ana River basin in Southern California is heavily influenced by discharges of tertiarytreated wastewater. Declines in the populations of the federally threatened Santa Ana sucker (Catastomus santaanae) prompted the USGS and USFWS to develop methods to test of the presence of potential endocrine disrupting chemicals. Passive samplers were used as a means of mimicking the exposure of the Santa Ana sucker and other fishes in the watershed. Semipermeable membrane devices (SPMD) and the polar organic chemical integrative sampler (POCIS) were deployed at each of four sites known to be impacted by wastewater and at a reference site free of any wastewater influence. Sequestered chemical residues were recovered from the SPMDs and POCIS using established procedures and were subsequently tested via the yeast estrogen screen (YES) for the potential to produce an estrogenic response. Estrogenic extracts were subjected to a fractionation scheme which was developed to potentially isolate and identify the chemical(s) responsible for the estrogenic response. The most prevalent chemicals identified in active fractions were the nonylphenols (surfactants) and galoxolide (fragrances) which are both known to be estrogenic.

Keywords: POCIS, YES, wastewater

### **Evaluation Of Passive Sampling Devices For Monitoring Non-Polar Organic Pollutants In Surface Waters**

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Passive sampling shows promise as a method for measuring time-weighted average (TWA) concentrations of a wide range of contaminants on the European Water Framework Directive (WFD) list of priority substances. These devices measure the truly dissolved (toxicologically relevant) fraction of contaminants in the water column. Further, the time-integrative nature of the monitoring allows the collection of this information that would be difficult to obtain at a reasonable cost with classical bottle sampling. The performances of several passive sampling devices for measuring non-polar organic pollutants were evaluated in a field study [Chemcatcher, Membrane-Enclosed Sorptive Coating or Copolymer sampler (MESCO & MECOP), low density polyethylene membrane and silicone (PDMS) strips, and Semipermeable Membrane Device (SPMD)]. The samplers were deployed for overlapping exposure times varying from 1 to 4 weeks. Analyte-specific uptake rates, volumes of water cleared of the compound of interest per unit of time, are available for most samplers and were used to calculate TWA concentrations of PAHs and PCBs. Where possible, performance reference compounds were used to adjust uptake rates for variations in temperature and turbulence. In order to assess the utility of this approach for regulatory purposes, frequent spot (bottle) sampling was carried out throughout the trial. Despite differnces in design and sampling rates, the results obtained were broadly consistent, and a wide range of non-polar pollutants was sequestered. Some pollutants were present at concentrations below the detection level grab sampling. However, because samplers accumulate these compounds over extended deployment times the masses extracted enabled their effective quantification. This factor will become more important as levels specified in environmental quality standards are lowered, and particularly where it is important to detect trends due to the withdrawal of harmful substances, and remediation activities. This trial indicates a potential role for this technology in supporting the WFD.

Key words: water, Chemcatcher, LDPE, PDMS, MESCO, SPMD, performance reference compounds

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# Prospectus for compliance sampling of CECs in effluents of POTWs: Lessons from SPMD sampling of California Ocean Plan compounds.

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USEPA regulates the management of the nation's waters for beneficial uses. Most of the sampling and analytical methods developed and/or adopted for compliance monitoring, since the inception of the Clean Water Act (CWA) have been modeled after conventional pollutants whose concentrations are amenable to detection with sampling processes including twenty-four hour composites (C-24) and grab sampling; and whose toxicities may be detected by chronic and/or acute outcomes. However, Compounds of Emerging Concern (CEC) usually present at trace and ultra-trace concentrations in the environment, and are therefore undetectable by EPA approved methodologies when preceded by snapshot sampling technologies. Therefore they remain unregulated though their presence has been documented in various drinking water sources, wastewater effluent-dominated streams, and their effects have been demonstrated among several aquatic and amphibian species. Because of their toxicological significance and their increasing impacts in ecological outcomes in the nation's water environment, it is imperative that CECs be reliably sampled and analyzed. Advances in analytical methods (GC/MS; HPLC) coupled with integrative sampling technologies including SPMD, and POCIS provide a prospectus for this. The City of Santa Cruz applied SPMD and POCIS technologies in effluent sampling to measure trace organics, previously undetectable through C-24 and grabs.

This poster summarizes the:

- 1) Successful uses of SPMD as a reliable alternative for sampling wastewaters for trace compounds in the California Ocean Plan Table, coupled with approved EPA methods for compliance monitoring.
- 2) Comparisons between C-24 sampling methods and SPMD in resolving the detection of some California Ocean Plan (COP) Table B Compounds.
- SPMD and POCIS provide data from a time-weighted average basis providing corresponding basis for evaluating human and environmental health objectives of the COP Table B compounds.
- 4) COP Table B compounds compare with many CECs for concentrations and ecological impacts, which are measured over generations of environmental exposure.

Keywords: SPMD, POCIS, Compounds of Emerging Concern (CEC), California Ocean Plan (COP), Compliance

# WITHDRAWN

# Use Of DGT For Estimation Of The Potentially Bioavailable Fraction Of Copper, Arsenic And Mercury In Polluted Soils

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The existing Italian and European regulation is based on a risk assessment procedure that takes into account only the total concentration of heavy metals in soils. This conflicts with the well-known assumption that the concentration to which organisms and plants are exposed is represented by the 'bioavailable' fraction. The fraction bioavailable to plants is the amount that can be taken up by the roots of a given plant species and strongly depends on its oxidation state on the chemical form, on soil properties and on the root activity. The technique of diffusive gradients in thin films (DGT) is by now recognized as a tool to measure the potentially available concentration in soil solution and as a mime for plant uptake. This work represents a survey of three different investigations, realized separately to study the bioavailability of copper, arsenic and mercury in three different cases-study, all represented by Italian soils, polluted by long-term human activities. In all cases, even if concentration of metals was very high and, according to the law, unacceptable for crop cultivation, the soluble and the bioavailable concentrations were very low, suggesting an unlikely accumulation in crops. Subsequently, for copper and arsenic, we also investigated the mobilization induced in the rhizosphere by a tolerant and a hyperaccumulator plant respectively (Zea mays and Pteris vittata). In the case of mercury, we analyzed the effects of purified root exudates and humic acids on the bioavailability. All the experiments were performed by DGT: each metal was measured with an appropriate binding-phase.

Keywords: DGT, soil, copper, arsenic, mercury

# A Probabilistic Assessment of Virginia Rivers Using Semipermeable Membrane Devices (SPMDs)

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The Virginia Department of Environmental Quality (VDEQ) has been charged with monitoring factors which may be indicators of water quality in free flowing freshwater streams and in estuarine waters. The VDEQ has adopted a strategy which incorporates a probabilistic monitoring program for free flowing freshwater streams, consisting of all non-tidal perennial streams and rivers within the Commonwealth of Virginia. As an integral part of this much larger study, lipid-containing semipermeable membrane devices (SPMDs) were used to sample ultra-trace ( $\leq ng/L$ ) and trace (ng/L to mg/L) levels of hydrophobic organic contaminants in the water column of selected streams. The SPMDs were prepared by US Geological Survey (USGS) scientists and were deployed at 50 study sites by VDEQ personnel; SPMDs were recovered from 46 of the sites. The SPMDs were processed and analyzed by USGS to determine concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and selected current-use pesticides in stream waters. A number of OCPs, PAHs, and current use pesticides were detected in SPMDs at most sites. However, only pentachloroanisole (PCA; a microbial methylation product of the wood-preservative pentachlorophenol) was found at quantifiable levels at every site analyzed. Detectable levels of PCBs were found at only two sites. Phenanthrene, fluoranthene and pyrene were the individual PAHs found at the greatest concentrations. This observation is typical of PAH concentrations in environmental waters where these chemicals originate from pyrogenic sources. Previously developed models were employed to estimate aqueous concentrations of contaminants of concern in the water columns of the rivers studied.

Keywords: SPMDs, Water Concentrations, OCPs, PAHs

### Assessment of Indoor Airborne Organic Contaminants Using Semipermeable Membrane Devices (SPMDs)

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As a focused part of a much larger study of human exposure to chemicals in the Southwest United States, jointly conducted with the U.S. Environmental Protection Agency and the University of Arizona, semipermeable membrane devices (SPMDs) were used to assess airborne bioavailable organic contaminants in 57 indoor areas along the border between Arizona and Mexico. Numerous organic contaminants of historic concern were detected, including organochlorine pesticides (for example, the DDT complex, and chlordanes) polychlorinated biphenyls, and polycyclic aromatic hydrocarbons. In addition, a variety of contaminants of emerging concern, including diazinon, chlorpyrifos, and permethrin, were also determined to be present in these areas. Selected sample extracts (specifically the organochlorine fraction) were analyzed by gas chromatography/mass spectrometry wherein as many as 400 individual chemicals were tentatively identified, some of which may have physiological activity. The effects of exposure to such complex mixtures of toxic chemicals are unknown, but respiration is increasingly being recognized as a significant route of exposure. Research continues to define the identities of airborne organic chemicals and to assess the potential consequences of exposure.

Keywords: SPMD, indoor air, organic contaminants

# Determinations of Uptake Rate Constants for Vapor Phase Organic Contaminants using Semipermeable Membrane Devices (SPMDs)

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Most people spend much of their lives inside buildings where they are exposed to complex mixtures of airborne chemicals of unknown toxicity. Chronic exposure to contaminants in indoor air is recognized as having detrimental effects, the so-called "sick building syndrome." Consequently, monitoring the ubiquitous occurrences of airborne contaminants, and assessing their potential biological effects, is becoming ever incresingly important. Passive samplers, such as the semipermeable membrane device (SPMD), can be used to effectively monitor many airborne contaminants. However, to fully utilize SPMDs as passive air samplers, SPMD kinetic uptake data are needed. As an integral part of a multi-year effort, scientists at the USGS's Columbia Environmental Research Center (CERC) have jointly conducted research with EPA scientists to calibrate the semipermeable membrane device (SPMD) as an air sampler in support of a larger effort to monitor both atmospheric and indoor air quality. A vapor phase chemical production and delivery system, capable of generating and maintaining constant concentrations of vapor phase chemical mixtures, was developed at CERC (US Patent # 6,877,724) and has been used to calibrate the SPMD air sampler. SPMD sampling rate data have been obtained for several classes of organic chemicals including; 1) Organochlorine Pesticides (OCPs), 2) Polycyclic Aromatic Hydrocarbons (PAHs), 3) Brominated Diphenyl Ethers (BDEs), 4) Phthalates, 5) Pyrethroids, and 6) Organophosphate / Organosulfur pesticides. The SPMD sampling rates, expressed as linear-uptake rate constants ( $k_{\mu}s$ , units of  $m^3/d \cdot g$ ), were within the range of expected values based on mass transfer theory. These SPMD uptake kinetic data (sampling rates) and graphic representations (as the slopes of the uptake curves) are presented and discussed.

Keywords: SPMD, air sampling, uptake rates

# Application of the Chemcatcher Passive Sampler for the Monitoring of Pharmaceutical Residues in Water

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Problem of residues of pharmaceuticals in the environment is now gaining interest of researches all over the world. Lot of pharmaceuticals are resistant to biodegradation and are also very hard to remove in waste water treatment. Residues of pharmaceuticals cause problems to biocenose of water environment. Application of passive samplers for monitoring pollutans in water is getting more and more popular nowadays. Unfortunately most of the samples, like e.g.:SPMD, MESCO, LDPE strip can be used mainly for enrichment of nonopolar compounds. Only POCIS sampler was constructed for sampling pharmaceuticals so far. Chemcatcher the passive sampler for the measurement of non-polar and polar organic and inorganic priority pollutants has been designed at the University of Portsmouth. The device uses a common design of sampler body with interchangeable receiving phases and diffusion limiting membranes depending on the application (figure 1). The original design of the Chemcatcher (C18 empore disk as a receiving phase and a low-density polyethylene membrane) was successfully used for collecting nonpolar pollutants such as PAH and OCP. Now, the preliminary experiments for collecting pharmaceuticals have been performed. The aim was to check the possibilities of using the Chemcatcher passive sampler for monitoring pharmaceuticals residues in fresh and waste water.

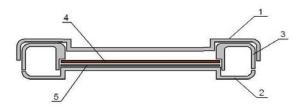


Figure 1. Schematic diagram of the Chemcatcher passive sampling device. Key: (1) a cap seal for transport and storage, (2) and (3) body parts, (4) membrane, (5) support for the receiving phase.

Keywords: Chemcatcher, surface water, pharmaceuticals

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# Estimation of Bioavailable Concentrations of PCBs, PCDDs, and PCDFs in Water Supporting a TMDL Source Assessment of the Bluestone River Watershed, Virginia and West Virginia

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The objectives of this study were to gather information about the concentrations, patterns, and distribution of selected congeners of PCBs, PCDDs, and PCDFs at specific study sites to expand current knowledge about PCB impacts and to identify potential undiscovered sources of contamination. SPMDs were used to integratively accumulate the dissolved fraction of PCBs and PCDDs/PCDFs at each site. PRCs were added to the SPMDs prior to deployment and used to determine site-specific sampling rates of SPMDs, enabling estimations of time-weighted average (TWA) water concentrations of PCBs and PCDDs/PCDFs during the period deployed. Concentrations of total PCBs in water ranged from 130-18,000 pg·L<sup>-1</sup> (VA PCB Water Quality Standard 1,700 pg·L<sup>-1</sup>) and concentrations of 2,3,7,8-TCDD in water ranged from 0.5-41 fg·L<sup>-1</sup> (VA 2,3,7,8-TCDD WQS 1.2 pg·L<sup>-1</sup>). The VADEQ, WVDEP, and USEPA are jointly developing TMDLs for the Bluestone River Watershed and will compare the TWA water concentrations determined in this study with surface water-listing criterion to help identify locations and analytes that may potentially exceed the proposed TMDLs.

Keywords: SPMD, TMDL, PCBs, dioxins

# The Bluestone River Watershed RARE Study: Patterns of PCBs, PCDDs, and PCDFs Accumulated by SPMDs and their Estimated Concentrations in Water Using an Empirical Uptake Rate Model

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Normalized SPMDs accumulation profiles and the corresponding estimated water concentration profiles of PCBs, PCDDs, and PCDFs were compared for the Fall-2005 deployment in the Bluestone River watershed. Profiles were investigated with simple charting and by principal components analysis using SIMCA®. Patterns at the most highly contaminated sites: Beacon Cave, Beaver Pond Branch at the resurgence, and Brush Fork were closely related to Aroclor®1242, while less contaminated sites showed increasing Aroclor® 1248 and 1254-like character, the Wrights Valley Creek site showed much greater Aroclor® 1260-like character. PCA results indicated very high precision between field replicates. Comparisons between SPMD-accumulated amounts of PCBs and PCDDs/DFs and resulting water concentrations demonstrated the significance of the compound-specific sampling rate  $(R_s)$ , which is directly related to their SPMD-Water partition coefficients ( $K_{sw}$ ). Estimates of sampling rate varied from 0.14  $L \cdot d^{-1} \cdot SPMD^{-1}$  for hepta- and octachlorodibenzo-*p*-dioxins, to 9.6  $L \cdot d^{-1} \cdot SPMD^{-1}$  for tri- and tetrachlorobiphenyls. PCDD and PCDF congener patterns were not significantly composed of 2,3,7,8substituted congeners, but were composed instead of complex mixtures of many non-2,3,7,8-congeners. The exceptions to these patterns of complex mixtures were the patterns for the tetrachlorodibenzo-pdioxin congeners, which were predominately composed of one congener, tentatively identified as either 1,2,3,7- or 1,2,3,8-TCDD.

Keywords: SPMD, PCBs, dioxins, congener patterns

# Quality Control Measures for Semipermeable Membrane Device Studies: Application to the Determination of PCBs, PCDDs, and PCDFs in the Bluestone River Watershed RARE Study

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A Quality Control (QC) plan for the Bluestone River watershed SPMD passive sampling study is outlined, including: estimates of the number of standard SPMDs needed to achieve target MDLs for PCBs and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). While the MDL for TCDD was predominately sample-size limited, MDLs for PCBs were much more dependent on laboratory background than simply sample size. Steps leading to the minimization of PCB background and checkpoints for monitoring PCB background during field handling and sample preparation are presented. As anticipated, PCB background increased with each additional level of sample preparation and was especially prevalent at HPLC steps where PCB carryover was scrupulously monitored and controlled. Several unanticipated points for PCB and PCDF contamination and for interference with instrumental analysis by dual-column gas chromatography-electron capture detection were found. First, a commercially prepared internal standard had low level background of PCB-209 and a significantly high level background of a non-2,3,7,8-tetrachlorodibenzofuran. Second, anticipation of low levels of PCBs biased sample preparation methods toward a minimum number of steps, leading to the inadvertent inclusion of high levels of interfering organochlorine pesticides, polybrominated diphenyl ethers, and several unknown interfering compounds. Third, the PCB congeners selected as performance reference compounds (PRCs) because of their reportedly negligible environmental concentrations were found to accumulate to significant levels in SPMDs. Quality Control of these interferences relied on a series of solutions ranging from: exhaustive preliminary checks of materials; maintenance and restricted [low level] use of preparation equipment; to confirmation by SIR GC-qMS; to final censoring of data.

Keywords: SPMD, PCBs, dioxins, furans, quality control

# Using an Empirical Uptake Rate SPMD Model to Estimate Bioavailable Concentrations of PCBs, PCDDs, and PCDFs in Water from the Bluestone River Watershed RARE Study

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Many different methods have been used to estimate bioavailable concentrations of analytes in water from passive sampling information. Here, an empirical uptake rate model is applied to SPMDs containing several performance reference compounds to estimate parts per quadrillion (ppq,  $10^{-15} \text{ g} \cdot \text{L}^{-1}$ ) to parts per quintillion (ppqt,  $10^{-18} \text{ g} \cdot \text{L}^{-1}$ ) concentrations of 128 PCB congeners, and seventeen 2,3,7,8-substituted congeners and homologs of PCDDs and PCDFs. The various terms in the model are discussed, showing the behavior of the sampling rate ( $R_s$ ) as a function of analyte partition coefficient ( $K_{ow}$ ). The relative contributions of the various terms to the overall uptake rate are likewise discussed. Sampling rate intercepts ( $a_{OPRC}$ ), used to estimate average sampling rates, are compared with the range of PRC released (or the percent PRC remaining). The working range of PRC release for reliably estimating uptake is determined for the analytical methods used. Comparisons of three PCB congeners and five PAH-d compounds used as PRCs are presented, indicating the high precision of the PRC approach.

Keywords: SPMD, PCBs, dioxins, furans, empirical uptake rate model

# Are Persistent Organic Pollutants Contributing To The Restricted Occurrence Of *Margaritifera Margaritifera* In The Haukås River? – Assessment By SPMDs.

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Based on previous observations a survey of persistent organic pollutants was conducted in the Haukås River, near Bergen, Norway. The main aims of this study were to determine which parts of the river receive contaminants and whether levels are of concern for the remaining local population of the red listed, freshwater pearl mussel, *Margaritifera margaritifera*. Of primary interest was the previous detection of DDT derivatives in sediments. The survey was carried out using semipermeable membrane devices (SPMDs), with additional water and limited mussel samples. Results indicated that chloroorganic substances, including DDT and its derivatives, are unlikely to be contributing to the decline of the mussel population being below the limit of detection in almost all samples. Polycyclic aromatic hydrocarbons (PAH) were, however, found in most samples with levels of up to 20ng L<sup>-1</sup> (EPA16) estimated from SPMD accumulations. Differences were found in the pattern of PAH within biota and earlier sediment samples when compared to that taken up by SPMDs. It is suggested that these differences show that the main pathway by which the mussels are accumulating PAH is from ingestion and filtering of particles and not directly from the 'freely dissolved' fraction. Remedies aimed at preventing particles from run off reaching the river should, therefore, correspondingly reduce the exposure of mussels to PAH.

Keywords: SPMD, river water, freshwater pearl mussel, PAH, DDT

# Advanced Monitoring Method for Air Environment by Ogawa Passive Sampler

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The Ogawa Passive Sampler is one of the only known methods of passive simultaneous monitoring of more than two components in the air. The first advantage of Ogawa Sampler is to have two chambers with the same configuration where one can place two different kinds of collection filter pads.

In the case of simultaneous collection of NO and NO<sub>2</sub>, The NO<sub>2</sub> collection filter coated with triethanolamine and the NOx collection filter coated with both triethenolamine and PTIO, which is specially prepared oxidation reagent of NO to NO<sub>2</sub>, are set in each of two chambers respectively. NO<sub>2</sub> can be collected on the NO<sub>2</sub> filters. NO is oxidized to NO<sub>2</sub> by PTIO and then collected on the NOx filter together with NO<sub>2</sub>. On the other hand, SO<sub>2</sub> is also collected on the NO<sub>2</sub> collection filter at the same time. Today, The Ogawa Sampler can collect and measure NO, NO<sub>2</sub>, NOx, SO<sub>2</sub>, NH<sub>3</sub> and O<sub>3</sub> in the air.

The second advantage of Ogawa Sampler is to be reusable countless times, only the pre-coated collection filter pad is expendable. The same sampler can be used for all above shown gasses. Consequently, Ogawa Sampler can be represented as one of the lowest cost effective device for accurate measurements of large scale or local pollution, as well as indoor pollution and personal exposure.

The analytical procedures, after collecting, have been developed by spectrophotometric method and ion chromatographic method for each analysis. In order to carry out an advanced monitoring, an analytical procedure should be simple and high through-put, because the number of sampler used in a research program will be extremely large. Analytical method coupled with flow injection analysis (FIA) has been proved to be useful and versatile in many practical analyses, moreover, FIA technique is easy to apply to an automatic procedure. By coupling Ogawa passive sampling method with FIA technique, the performance of the monitoring for air environment could be extremely enhanced.

Today Ogawa Sampler is being used world-wide for the collection of NO, NO<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub> and O<sub>3</sub>. In Japan, this proposed monitoring method has been performed to carry out special programs for the research of the air environment. The results obtained have been successful and have been continued for a long time.

Keywords: air, Ogawa sampler, NOx

# **Evaluating the Efficiency of Diffusion Samplers for Collection of VOCs and Aldehydes Based on Sampling Rates**

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There are many kinds of diffusion samplers, which are commercial available, for collecting volatile organic compounds (VOC) and aldehydes now. The diffusion samplers are actually used for the public field research of indoor and outdoor environments as well as active sampling. However, all samplers do not have sufficient accuracy for the proper measurement of VOC and aldehydes. The sampling rates, which are usually compared to results from an active sampling method, are not recognized as possibly being not correct because of the samplers. In this work, we tried to evaluate the efficiency of diffusion samplers for VOC and aldehydes collection in terms of sampling rate. The diffusion sampler has been developed, of course, based on the diffusion theory. A sampling rate has been well known to be one of important factors in the diffusion sampler.

At first, a calculating method of sampling rate was developed theoretically, by using both the geometries of samplers and the physical properties of VOC and aldehydes. The geometries of samplers have various features in diffusion area and diffusion length, which are measured accurately using an electron microscope. The physical property could influence the diffusion coefficient, which was obtained by calculating, using Fujita's equation, based on molecular structure of compounds.

At the second step, in order to inspect the agreement between theoretical sampling rate and experimental one, the exposure tests were carried out for each diffusion sampler by introducing the VOC and aldehydes gases into 350 L chamber. As a result, it was found that almost sampling rates for diffusion samplers tested in this work were agreeable between theoretical and experimental. Therefore, we can accurately estimate the sampling rates by theoretical calculation for any kinds of diffusion samplers. By increasing the complexity in the structure of sampler, it becomes gradually more difficult to estimate the sampling rate.

From this study, it is clear that Ogawa Passive Sampler is an ideal diffusion sampler for VOC and aldehydes collection. The Ogawa Sampler is a simple structure consisting of a solid Duracon cylinder with two chambers, into which small trays are placed containing active carbon for VOC and DNPH silica for aldehydes in each chamber. The adsorbent is held in a stainless steel screen covered stainless steel cup, situated behind a diffusion barrier and end-cap with 25 holes. The diffusion areas were 0.152 cm<sup>2</sup> and 0.785 cm<sup>2</sup>, respectively. The diffusion length of the stainless steel screen and end-cap were 0.02 cm and 0.6 cm, respectively. The sampling rate of the Ogawa Sampler can be calculated easily, by combining the sampling rates of the stainless steel screen and end-cap.

Keywords: diffusion sampler, Ogawa Passive Sampler, air, VOC, aldehydes.

# **Modified Peat Bags As Passive Samplers Of Airborne Contaminants**

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Among approaches for air quality observation and monitoring, the so called passive samplers are of certain interest due to several reasons: They can provide adequate and sensitive information about differing impacts of airborne pollutants; They are cheap and do not require expensive analytical technique; Passive samplers provide integrated information about environmental quality and presence of airborne contaminants; Passive samplers can be applied in remote areas and can significantly reduce constraints due to sampling process. Many studies have clearly demonstrated the importance of passive samplers and a need to continue studies aimed in their development. Several approaches has been suggested and many passive samplers are nowadays produced to cover growing needs in this simple and reliable technique. Mostly the most important elements in the passive sampling devices are synthetic sorbents providing sensitivity and efficiency in the airborne pollutant trapping. In the same time just the selectivity of sorbents often is factor determining their costs which sometimes can be quite high. Of a definite interest thus can be cheap, but similarly efficient sorbents. Another aspect of the development of passive contaminant samplers is in their source. Considering the results of the previous works, within this study possibility to develop passive samplers based on peat and modified peat as sorbents has been studied. The peat contains functional groups which may significantly influence their ability to bind many airborne pollutants. Modification can allow to increase rigidity of obtained materials as well as increase their sorption capacity and selectivity towards substances of interest. Peat is cheap and natural material, so its treatment after usage does not provide significant problem. In the same time there are possibilities to apply modification methods to change basic properties of peat to increase their sorptive capacities in respect to chemicals of concern.

Key words: peat, modification, passive samplers

Presentation choice: poster

# Passive Sampling of Persistent Organic Pollutants in an Urbanized Estuary: Contributions from Different Reservoirs

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As part of a larger study to identify the sources of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) to demersal fish in an urbanized estuary, passive sampling devices (PSDs) were deployed from May to November of 2006 in Narragansett Bay, RI. The PSDs consisted of strips of commercial polyethylene sheeting, pre-cleaned and spiked with performance reference compounds (PRCs). The application of PRCs provided *in situ* mass transfer coefficients for deriving air and water column concentrations for PSDs not yet at equilibrium at the time of retrieval. The PSDs were deployed in a vertical array consisting of three samplers: one just above the sediment bed, one at 1m depth and a PSD sampling diffuse air ~1m above the surface in a protective casing. Derived activities could then be assessed in terms of their respective reservoirs (sediment, water, or air). Sondes deployed at the same site yielded a range of environmental parameters (salinity, temperature, pH, dissolved oxygen, etc) which facilitated the interpretation of the derived concentrations by stimulating insight into the extent of stratification, primary productivity and local hydrography.

Keywords: Polyethylene device (PED), Polychlorinated biphenyls, polycyclic aromatic hydrocarbons

### Levels of selected POPs in Czech rivers

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The semipermeable membrane device (SPMDs) is presented for monitoring priority persistent organic compounds (POPs) in rivers in the Czech Republic, from 2003-2006. Totally 19 sampling sites of 15 rivers have been monitored. Deployment time for SPMDs was about 30 days. From POPs, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDE) were assessed. Data were evaluated using PRCs. Toxicity tests for SPMDs samples were applied as complementary information of total contamination within this range: *Desmodesmus subspicatus, Daphnia magna, and Vibrio fischeri*. Both statistical and Gnostic approaches were used for interpretation of data.

#### Keywords: SPMDs, POPs, PCDD/Fs, PCBs, PAHs, OCPs, MVDA, Gnostic analysis, PCA

### **Studies of Indoor Air Quality with use of Permeation Passive Samplers**

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Organic compounds present in indoor air were given the most attention in research on assessment of indoor air quality and its effects on human organisms. By reason of this accurate and representative indoor air quality (IAQ) measurements are very important when we compare indoor air with guidelines and standards. The short-term measurements typically used for IAQ control may reflect temporary conditions that are not representative for longer periods of time, and in consequence may lead to incorrect decisions aiming at improving the quality of air. Consequently, techniques allowing the measurement of the concentration of indoor air pollutants over extended periods of time become increasingly important.

Passive sampling is generally as accurate as active sampling, while it obviates the need for expensive and sometimes cumbersome active sampling equipment (pumps, flow meters, etc.). It is because of this reason that passive sampling techniques are generally much more acceptable to dwellers of indoor spaces examined.

The main purpose of this paper is to present our study – mainly focused on the development of the method of passive sampling and analysing VOC in indoor air (adsorptive permeation passive sampling/ gas chromatographic separation/mass spectrometric identification) as well as the application of this method in studies of the occurrence and behaviour of VOC in different type of buildings.

Keywords: permeation sampler, active charcoal, indoor air quality control

Presentation type: poster

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### **Monitoring Compounds Produced by Hay Infusion Using Passive Samplers**

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Certain species of mosquitoes, including those that transmit West Nile Virus, are attracted to natural areas where upland grasses are submerged where they desire to lay eggs. Traditional sampling methods yielded many compounds from hay infusions that defined a small scope of the organic chemicals present. Passive samplers were used in a 14-day study to define the compounds exuded by Bermuda grass hay infusions. Three 10-gallon aquariums were filled with 30 L of well water and 200 g of Bermuda grass hay was added to each. The SPMD apparatus was added to one aquarium, a POCIS apparatus was added to another, and the third had nothing more added for use as a positive control. Samples from each tank of the hay-infused water were taken over the course of 2 weeks and bioassayed using gravid *Culex quinquefasciatus* mosquitoes to determine if either passive sampler absorbed the compounds responsible as oviposition attractants. After 14 days, the samplers were removed from the water matrix and shipped to the USGS facility in Columbia, MO for extraction, and the extracts were shipped back the USDA laboratories in Gainesville, FL for chemical analysis.

Keywords: SPMD, POCIS, Hay Infusion

# Using Passive Samplers to Evaluate and Manage Risks Posed by Persistent Environmental Contaminates: New Tools and Applications

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Huckins and others developed a novel technique using Semi-Permeable Membrane Devices (SPMDs) that is now widely used to monitor contaminants in the environment. We are currently developing and testing some new passive sampling devices incorporating Semi-Permeable Membrane Devices (SPMDs) and Solid Phase Extraction Matrices (SPMEs) and other passive samplers to assess environmental contamination and evaluate risk management strategies for persistent pollutants. Our research is focused on developing novel samplers that enhance our ability to effectively evaluate remediation strategies and evaluating the advantages and disadvantages of using surrogate samplers as compared with other biotic sampling methods. In this paper we describe the new samplers we have developed that allow us to examine exchange of contaminants at the sediment water interface and examine contaminant movement in the environment. We present an overview of results from our studies throughout the U.S. that include different capping approaches and dredging and describe how we are using these samplers to examine the mechanisms affecting the success of risk management approaches. Finally we will present some of our plans for future work using passive samplers.

Keywords: SPMD, SPME, PCB, Passive Samplers, Sediments, Water, Contamination

### The Occurrence And Geospatial Distribution In A Statewide Stratum From A Generalized Random Tessellation Stratified Survey Of Toxic Organic Contaminants

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To be protective of human health and the aquatic ecosystem the U.S. Environmental Protection Agency has established water quality criteria for numerous toxic organic compounds. These criteria are expressed as four day water column concentrations averages not to be exceeded more than once on average in a three year period. These maximum concentrations are further classified into three categories of protection: 1) public water supplies, 2) aquatic organisms (both acute and chronic effects), and 3) human health by way of consumption of fish tissue. Typically detection of these toxic compounds is from the analysis of sediment and fish tissue and not by direct measurement of water column concentrations. The difficulty to government agencies in making direct measurements of these toxic chemicals is the high cost of analytical methods needed to reach low concentrations and the representativeness as compared to four day averages.

The Virginia Department of Environmental Quality is required by the Federal Clean Water Act and the Virginia Water Quality Monitoring, Information, and Restoration Act to monitor all state waters for all compounds with water quality standards. In order to meet these requirements the Department, for a subclass of these compounds, combined a modified integrative passive sampling device with a probabilistic sampling design. This is the first time that concentrations of trace toxic anthropogenic compounds have been measured on a statewide geospatial scale in free flowing 1<sup>st</sup> through 5<sup>th</sup> order and higher streams (n=41). Because of the nature of the stratified random sample design the Department was able to determine the occurrence and distribution of 67 compounds of which 28 have water quality criteria in approximately 50,000 linear stream miles. The results of the study will be discussed.

Keywords: SPMD, geospatial distribution, water quality criteria

# Passive Dosimetry - An Useful Tool For Monitoring And Mapping Of Atmospheric Pollutants

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Due to human activities an increasing number of harmful substances are emitted into the atmosphere. They are recognized as potentially dangerous to living organisms, mainly because of their toxicity. Among others, compounds from the BTEX group, i.e. benzene, toluene, ethylbenzene and xylenes are considered as such. Because of the aforementioned reason, monitoring of air quality and the analysis of air pollutants, including assessment of the BTEX concentrations in ambient air, has been gaining increased importance. Over the last years the use of passive dosimetry for ambient air quality monitoring, particularly in urbanized areas, has been increased notably. Due to unquestionable advantages a range of passive samplers are used to measure pollutant concentration in urban area. The main goal of this study is to determine BTEX concentrations in ambient air in the Tricity area with use of passive samplers at the stage of sampling of analytes from the atmosphere. Sampling is carried out by mounting inside container, which was especially designed to protect, two type of passive samplers: home-made permeation - type passive samplers; diffusive - type passive samplers : ORSA 5 - National Dräger and Radiello (FS Maugeri). Samplers are collected at selected sites in the Triacity area in monitoring stations belong to Foundation: Agency of Regional Air Quality Monitoring (ARMAAG). At the end of each period of exposure, samplers are taken to the laboratory and stored in a freezer until processed. The catched analytes are extracted by using carbon disulfide as an extraction and thermal desorption. The BTEX concentrations are determined using gas chromatography with flame ionization detector (FID) and mass spectrometry detector (MS). The obtained environmental data will be processed further in order to model pollution transport in the atmosphere and prepare the isoconcentration maps of BTEX in the ambient air in the Tricity area.

Keywords: ORSA 5, Radiello, air, BTEX, monitoring

### **POGS (POlymer-coated Glass Samplers) for Water and Air Sampling**

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POGS are passive samplers comprising a thin polymer film (ethylene vinyl acetate, EVA) coated onto a glass surface. Previously, these have been applied to sampling persistent organic pollutants (POPs) in the atmosphere over relatively short time periods. The high surface area to volume ratio of the films allow chemicals that partition to POGS to approach equilibrium with the atmosphere or water relatively quickly, over hours to days for most POPs, avoiding problems of variable/unknown air or water flow rates, and limiting surface fouling due to the shorter exposure times. In this study, POGS are being developed for application as water samplers and for sampling POPs at the air/water interface. Concurrent deployment of POGs in these compartments will allow chemical fugacities to be assessed and flux directions can be calculated to evaluate air-water exchange. Preliminary method development of the coating procedure shows that film thicknesses of 1-50 µm are achievable and reproducible for POGS comprised of EVA coated onto 47 mm glass fiber filters (GFFs). Mass transfer to POGS is water-side controlled and equilibration times are proportional to the film thickness and related to the K<sub>OW</sub> of the chemical. Laboratory uptake study results indicate equilibration occurs in a matter of days. EVA-water equilibrium partition coefficients (K<sub>EVA-W</sub>) have been measured for a number of compounds of varying K<sub>OW</sub> using a generator column, and the log K<sub>EVA-W</sub> displays a linear relationship to log K<sub>OW</sub>. This relationship can also be used to predict partitioning for other compounds, and will allow quantitative back-calculation of concentrations in water samples from those found in the sampler. The EVA polymer has both polar and non-polar groups, hence we hope to be able to use this or other polymers to sample for current-use pesticides (CUPs) as well as more commonly measured POPs (PCBs, OC pesticides), in rivers and lakes.

Keywords: POGS, surface water, air, EVA, log KOW