light-sensitive chemicals. When possible, avoid deployments in the extremely turbulent flow to prevent damage. The biggest danger to the sampler is vandalism. Keeping the samplers securely tethered, hidden, and out of areas frequented by people can help prevent vandalism.

#### **Decontamination Requirements**

Prior to initial SPMD construction, the lipid, membrane, and deployment hardware undergo a thorough cleaning to remove any potential interferences. Only minimal surficial cleaning to remove sediments, biofouling, etc., which may adhere to the membrane surface, is necessary following use and during sampler processing. This cleaning generally involves gentle scrubbing of the SPMD surface with a soft brush.

#### **Sample Shipping**

SPMDs should be shipped between the laboratory and sampling site in air-tight containers to prevent potential contamination from airborne chemicals. Shipping the SPMDs frozen, or at least cold, helps to prevent loss of chemical or additional sampling from the surrounding air.

# **Future Considerations**

- 1. Determination of additional sampling rate data. Sampling rates are necessary to estimate the ambient concentration of targeted chemicals. Sampling rate data is available for many of the classical environmental contaminants in water. To date, a limited number of chemical sampling rates have been determined in air.
- 2. How to reduce or eliminate the potential for biofouling of the membrane surface.

# **Selected References**

Huckins, J.N., Petty, J.D., Prest, H.F., Clark, R.C., Alvarez, D.A., Orazio, C.E., Lebo, J.A., Cranor, W.L., Johnson, B.T. A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants; Report for the American Petroleum Institute (API); API publication number 4690; API: Washington, DC, 2002.

Huckins, J.N., Petty, J.D., Lebo, J.A., Almeida, F.V., Booij, K., Alvarez, D.A., Cranor, W.L., Clark, R.C., Mogensen, B.B. Development of the Permeability/Performance Reference Compound Approach for *In Situ* Calibration of Semipermeable Membrane Devices. Environ. Sci. Technol. 2002, 26, 85-91.

Huckins, J.N., Prest, H.F., Petty, J.D., Lebo, J.A., Hodgins, M.M., Clark, R.C., Alvarez, D.A., Gala, W.R., Steen, A., Gale, R., Ingersoll, C.G. Overview and Comparison of Lipid-Containing Semipermeable Membrane Devices and Oysters (*Crassostrea gigas*) for Assessing Organic Chemical Exposure. Environ. Tox. Chem. 2004, 23, 1617-1628.

# **Information and Contacts**

http://wwwaux.cerc.cr.usgs.gov/SPMD/

U.S. Patent #5,098,573 - Huckins, J.N.; Lebo, J.A.; Tubergen, M.W.; Manuweera, G.K.; Gibson, V.L.; Petty, J.D. March 24, 1992.

**U.S. Patent #5,395,426** - Huckins, J.N.; Petty, J.D.; Zajicek, J.A.; Gibson, V.L. March 7, 1995.

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# **Locating Vendors**:

Information on vendors can be obtained from the USGS Technology Transfer office. http://www.usgs.gov/tech-transfer/patent.html



**Columbia Environmental Research Center** 

# Semipermeable Membrane Device (SPMD)

# **Description and Application**

#### **Brief Background**

The Semipermeable Membrane Device or SPMD is designed to sample lipid or fat-soluble (nonpolar or hydrophobic) semivolatile organic chemicals from water and air. The SPMD is an integrative sampler which provides a time-weighted average concentration of sampled chemicals over a deployment period ranging from days to months. This device is a passive sampler meaning that it has no mechanical or moving parts, requires no power nor supervision during use. SPMDs sample chemicals from the dissolved phase, mimicking the bioconcentration of organic contaminants into the fatty tissues of organisms. SPMDs provide a highly reproducible means for monitoring contaminant levels, and are largely unaffected by many environmental stressors that affect biomonitoring organisms. The SPMD also enables in situ concentration of trace organic contaminant mixtures for toxicity assessments and toxicity identification evaluation (TIE) approaches.

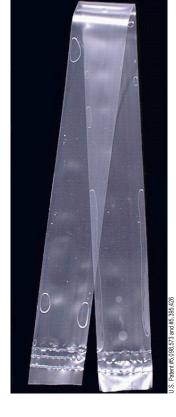
## **Physical Characteristics**

The SPMD consists of a neutral, high molecular weight lipid (> 600 Da) such as triolein which is encased in a thin-walled (50-100  $\mu$ m) layflat polyethylene membrane tube. The nonporous membrane allows the nonpolar chemicals to pass through to the lipid where the chemicals are concentrated. Larger molecules > 600 Da and materials such as particulate matter and microorganisms are excluded. A standard SPMD is 2.5 cm wide by 91.4 cm long containing 1 mL

A standard lipid-containing SPMD with three molecular welds near each end. NOTE: The low interfacial tension causes intimate contact (i.e., the presence of a lipid film on the membrane interior surface) between the triolein and the membrane even where air bubbles exist.

of triolein. SPMDs of different sizes can be made by maintaining the  $\approx 100 \text{ cm}^2/\text{g}$  SPMD ratio.

Deployment of SPMDs



typically are for 1 month, however, depending on the study design, deployment times can range from days to months. SPMDs are transported to and from the sampling site in gas-tight metal cans. Following receipt of a field deployed SPMD, the device is stored frozen until processing. Chemical residues in the SPMD are recovered using a dialytic extraction step into an organic solvent such as hexane. Following dialysis, all sequestered chemicals are in the organic solvent; the used SPMD can then be discarded. At this point, the sample is ready for further processing (cleanup and/or fractionation), analysis, toxicity

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screening, etc.

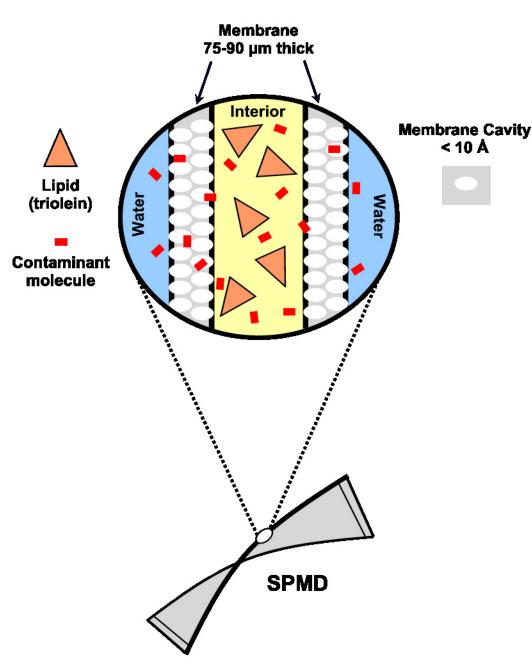




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U.S. Department of the Interior U.S. Geological Survey

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Exploded view showing the nonporous membrane size-exclusion phenomenon in the uptake and loss of organic compounds.

SPMDs use the Performance Reference Compound (PRC) approach to account for site-specific environmental factors (flow/turbulence, temperature, biofouling, etc.). A PRC is a compound which is added to the SPMD during construction with a percentage lost to the surrounding water or air during deployment. Determination of the amount of PRC lost provides an environmental adjustment factor to adjust laboratory-derived sampling rates.

### Target Media

SPMDs can sample hydrophobic organic contaminants from water or air under nearly any environmental conditions.

# Potential Target Analytes

Chemicals sampled by SPMDs include hydrophobic, bioavailable organic chemicals such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, dioxins and furans, selected organophosphate and pyrethroid pesticides, and other nonpolar organic chemicals.

#### Sample Volume

The volume of water sampled during a SPMD deployment is a function of the sampling rate for a particular chemical and the sampling duration. For example, a SPMD deployed for 30 days, sampling a

chemical with a sampling rate of 5 L per day, will result in an equivalent of 150 L of water sampled. These sampling rates can vary with changes in the water flow/turbulence, temperature, and buildup of a biofilm on the sampler's surface. To satisfy certain detection limit requirements, the extracts from multiple devices can be combined thereby increasing the total volume of water sampled.

# "State of the Art"

#### **Stage of Development**

Lab Testing

Characterization of the SPMD for the sampling of various classes of nonpolar organic chemicals in water and air has been performed in the laboratory. Calibration of the SPMD to determine sampling rates for select chemicals under different flow/turbulence and temperature regimes has allowed for the development of theoretical models to describe sampler performance. Optimization of processing techniques, instrumental analysis methods, and application of bioassay/toxicity testing have been performed for the SPMD matrix.

Following processing of SPMDs in the laboratory, the sample is an enriched extract in an organic solvent such as hexane. Depending on the desired use of the sample, additional processing (i.e., cleanup and/or fractionation) may be necessary.



A commercially available stainless steel deployment apparatus, which has a capacity of five standard SPMDs. Each SPMD is placed on individual racks which maximize the overall sampling surface area. The racks are secured in place by a threaded center pin and protective cover, as shown in the picture.

#### Field Testing

SPMDs have been used in numerous field deployments across the United States and internationally since the early 1990s. These deployments have ranged from stagnant pools to major river systems, clear natural springs to biologically-active wastewater streams, and freshwater to marine systems. SPMDs have been used for sampling indoor and outdoor air contamination as part of human health assessments. Comparison of water and air concentrations of select targeted chemicals derived from SPMD data to that from traditional sampling methods (grab samples, HiVol samplers, biomonitoring organisms) validate the SPMD's ability to concentrate nonpolar organic contaminants.

#### Acceptance of Technology

SPMDs have been used by many US federal agencies (e.g., USGS, US EPA, National Park Service and the US Fish and Wildlife Service) and internationally for the monitoring of water-soluble organic contaminants in numerous studies across the globe. The Virginia Department of Environmental Quality is currently using SPMDs in a statewide probabilistic study and is examining the use of SPMDs for their Total Maximum Daily Limit (TMDL) determinations of PCBs. The US EPA has been instrumental in developing the SPMD as an airborne contamination monitor. The Environment Agency of England and Wales has adopted the SPMD as part of their monitoring programs. The UK Environment Agency has nearly completed an accreditation process for the SPMD. The Institute of Public Health in the Czech Republic is also performing an accreditation of the SPMD as a standard method and currently the SPMD is being considered by the European Union as a standard method for dissolved phase chemicals.

# **Features and Limitations**

#### **Deployment Considerations**

Careful selection of the study site is important for a successful deployment. When sampling water, it is critical that the samplers be deployed where they will remain submerged, but not buried in the sediment, during the exposure period. Keeping the samplers shaded may prevent degradation of some