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Use of Semipermeable Membrane Devices (SPMDs) in Petroleum Polluted Waters

Passive samplers, in particular semipermeable membrane devices (SPMDs), can be used in monitoring petroleum spills. This document is intended to provide a brief discussion of issues surrounding the use and capabilities of the SPMD.

Background

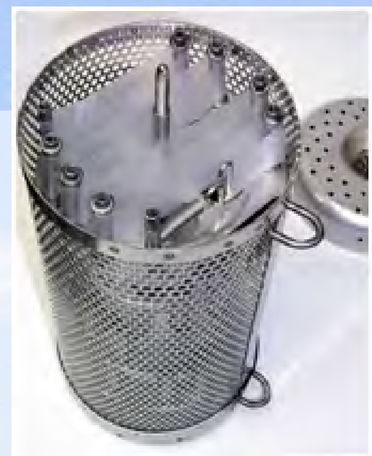
SPMDs are constructed of a layflat low density polyethylene membrane containing triolein, a high purity neutral lipid. They are designed to mimic the potential bioaccumulation of neutral hydrophobic organic chemicals by aquatic, terrestrial, and marine organisms. Chemicals with a log octanol-water partition coefficient (log K_{ow}) greater than three and a cross-sectional diameter less than 10 Å (1 nanometer) are preferentially sampled from air and water by SPMDs. Sampled chemicals include petroleum constituents, such as polycyclic aromatic hydrocarbons (PAHs), and aliphatic hydrocarbons, as well as other nonionic hydrophobic chemicals, such as polychlorinated biphenyls (PCBs), chlorinated pesticides, dioxins, and furans. SPMDs only sample chemicals dissolved in the water column. Chemicals bound to suspended sediment, particulates, or colloidal matter are not sampled by the SPMD.

Deep Ocean Sampling

SPMDs have been successfully used at extreme depths to assess the contaminant loading of deep ocean currents. Dr. Kees Booij, Royal Netherlands Institute for Sea Research (NIOZ), has conducted year long studies measuring PAHs and other organic contaminants at depths ranging between 0.1 and 5 kilometers.

Dispersants

There has been considerable discussion recently on whether or not SPMDs would sample dispersants used in conjunction with an oil spill. Although there has been considerable research using SPMDs to determine the bioavailable fraction of PAHs near off-shore oil platforms and in produce waters, little is known about the sampling of dispersants. It is expected that many of the components of the dispersants will be too large in molecular size or be too polar to be sampled by the SPMD. A potential option may be to use the polar organic chemical integrative sampler (POCIS) designed to sample chemicals with greater water solubility and has been demonstrated to effectively sample alkylphenolic compounds.



SPMDs in a protective deployment canister.

Impacts of Oil and Dispersants on SPMD Performance

Use of SPMD data to estimate PAH concentrations in water is confounded when SPMDs come in contact with oil sheen, oil layers, or tar mats which may coat the surface of the SPMD. It also is unknown how a coating of dispersants on the SPMD surface may affect the uptake of dissolved chemicals into the SPMD. If the surface of the water has visible contamination, it is recommended to disperse the surface contamination before placing the SPMDs in the water.

Photodegradation of PAHs in Sunlight

PAHs can rapidly undergo photolysis with exposure to sunlight. The polyethylene membrane of the SPMD is transparent to UV radiation, and the protective deployment canisters offer little protection against photolysis, especially in clear ocean waters. It has been shown that PAHs can rapidly photolyze inside SPMDs in clear waters or when directly exposed to sunlight in the air. The use of a photolysis marker, such as a high log K_{ow} deuterated PAH (chrysene-d_{12} and dibenz[*a,h*]anthracene-d_{14} are often used), in conjunction with the performance reference compounds (PRCs) is important when working with photosensitive chemicals including PAHs. A significant loss of this photolysis marker provides an indication that other PAHs sampled from the environment may have undergone photolysis.

Considerations for Designing a Field Study Using SPMDs

Laboratory Selection

Before obtaining the SPMDs, it is important to decide on the list of chemicals to be sampled. Selection of the laboratories to conduct the analyses and requirements of the methods will help determine the number of SPMDs deployed at each site.

Performance Reference Compounds (PRCs)

Site-specific environmental variables including water movement, temperature, and the buildup of a film on the membrane surface can affect the rate at which chemicals are sampled. The effects of such variables can be accounted for through incorporation of PRCs, such as deuterated PAHs, into the SPMD during construction. By determining the amount of the PRCs lost during field deployment, results can be adjusted to account for site-specific environmental variations.

Quality Control

The use of blanks, both field and laboratory, are extremely important. SPMDs are efficient air samplers; therefore, potential accumulation of target chemicals from the air during deployment and retrieval operations needs to be accounted for. This is especially true for field work conducted from small boats and ocean vessels where engine exhausts, fuels, oils and vapors from equipment and decking may be potential sources of contamination.

Analytical Considerations

Care should be taken with regards to the processing methods used. Size exclusion chromatography (or gel permeation chromatography) is a common cleanup step in the processing of SPMD samples. This results in an enriched sample containing molecules within a specific size range. Molecules falling outside of this range are excluded from the sample. Using a typical fractionation for PAHs, many of the high molecular weight surfactants and long-chain hydrocarbons may not be collected in the final sample. The chemical laboratories should be contacted to determine specific method requirements before processing of the SPMDs.

Selected References

Bartkow, M.E., Kennedy, K.E., Huckins, J.N., Holling, N., Komarova, T., Müller, J.F., 2006, Photodegradation of polyaromatic hydrocarbons in passive air samplers—Field testing different deployment chambers: Environmental Pollution, v. 144, p. 371–376.

Booij, Kees, van Bommel, Ronald, van Aken, H.M., van Haren, Hans, Brummer, Geert-Jan, Ridderinkhof, Herman, 2007, Passive samplers on moorings at three deep-ocean sites: 7th Passive Sampling Workshop and Symposium, Reston, Va., accessed June 28, 2010, at *http://www.clu-in.org/studio/passsamp_042407/day2/ppframe2.cfm?s=225&p=23&res=1280x1024&simul=1*.

Harman, C., Thomas, K.V., Tollefsen, K.E., Meier, S., Bøyum, O., Grung, M., 2009, Monitoring the freely dissolved concentrations of polycyclic aromatic hydrocarbons (PAH) and alkylphenols (AP) around a Norwegian oil platform by holistic passive sampling: Marine Pollution Bulletin, v. 58, p. 1,671–1,679.

Huckins, J.N., Petty, J.D., and Booij, Kees, 2006, Monitors of organic chemicals in the environment—Semipermeable membrane devices: New York, Springer, 223 p.

U.S. Geological Survey, 2010 Passive sampling: U.S. Geological Survey, Columbia Environmental Research Center, accessed June 28, 2010, at *http://www.cerc.usgs.gov/Branches.aspx?BranchId=8*.

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