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Uptake rate constants and partition coefficients for vapor phase organic chemicals using semipermeable membrane devices (SPMDs)

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ABSTRACT

To fully utilize semipermeable membrane devices (SPMDs) as passive samplers in air monitoring, data are required to accurately estimate airborne concentrations of environmental contaminants. Limited uptake rate constants (k_{ua}) and no SPMD air partitioning coefficient (K_{sa}) existed for vapor-phase contaminants. This research was conducted to expand the existing body of kinetic data for SPMD air sampling by determining k_{ua} and K_{sa} for a number of airborne contaminants including the chemical classes: polycyclic aromatic hydrocarbons, organochlorine pesticides, brominated diphenyl ethers, phthalate esters, synthetic pyrethroids, and organophosphate/organosulfur pesticides. The k_{ua}s were obtained for 48 of 50 chemicals investigated and ranged from 0.03 to 3.07 $m^3\ g^{-1}\ d^{-1}$. In cases where uptake was approaching equilibrium, K_{sa}s were approximated. K_{sa} values (no units) were determined or estimated for 48 of the chemicals investigated and ranging from 3.84E+5 to 7.34E+7. This research utilized a test system (United States Patent 6,877,724 B1) which afforded the capability to generate and maintain constant concentrations of vapor-phase chemical mixtures. The test system and experimental design employed gave reproducible results during experimental runs spanning more than two years. This reproducibility was shown by obtaining mean k_{ua} values ($n = 3$) of anthracene and p,p'-DDE at 0.96 and 1.57 $m^3\ g^{-1}\ d^{-1}$ with relative standard deviations of 8.4% and 8.6% respectively.

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1. Introduction

Atmospheric contaminants from domestic and industrial activity, energy production, and agriculture are often transported great distances before removal from the atmosphere by particulate fallout, vapor-phase solution, rainout and snowfall of particulate matter, and vapor-phase sorption processes. Consequently, airborne contaminants have the potential to adversely affect ecosystems and human populations far removed from their initial sources. Indoor air is expected to contain all the contaminants found in outdoor air as well as many additional chemicals originating from building materials, furnishings, cooking, and other human indoor activities. These complex mixtures of airborne organic chemicals often have detrimental health effects, e.g., the so-called "sick building syndrome," and assessing the consequences of exposure to these chemicals is of great concern. Monitoring efforts, mandated under the provisions of the Clean Air Act, have historically been related to gaseous pollutants (SO_X, NO_X, etc.), toxic metals, and particulate matter. More recently, the atmospheric transport and deposition of toxic organic compounds including polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), brominated diphenyl ethers (BDEs), phthalate esters (PEs), synthetic pyrethroids (SPs), and organophosphate/organosulfur pesticides (OPPs/OSPs) has received attention.

Several passive sampling techniques have been employed to measure airborne contaminants utilizing reactive materials/sorbents (Fowler, 1982; Shoeib and Harner, 2002; Wania et al., 2003), the waxy outer surfaces of plants (Böhme et al., 1999), and polymer-coated plates (Harner et al., 2003). Even more widely employed are active or forced-air sampling systems incorporating polyurethane foam (PUF) plugs, Tenax, and XAD-2 resin (Ockenden et al., 1998). While progress has been made in improving active air-sampling technology, these devices suffer the disadvantages of complexity associated with mechanical operation and are generally limited to comparatively short sampling intervals. Passive air samplers of either the air-diffusion or membrane-permeation design are attractive because of their long-term integrative capacity.

The semipermeable membrane device (SPMD) was developed as a sampler for hydrophobic organic chemicals in water (Huckins et al., 1993; Lebo et al., 1995), but its utility as a passive air sampler was recognized (Petty et al., 1993; Huckins et al., 1995; Ockenden et al., 1998, 2001; Shoeib and Harner, 2002; Huckins et al., 2006). It

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consists of layflat polyethylene tubing containing a thin film of triolein. The polyethylene membrane functions by allowing airborne contaminant molecules to pass through transient membrane cavities, which is phenomenologically similar to the size limiting transport of hydrophobic contaminants through biomembranes *via* respiration (Oppenhuizen et al., 1985). Although complex, the respiration/passive sampling process *via* air exposure can be simplified by considering three elements which include diffusion through a thin air boundary layer, the biomembrane, and finally, the key element, partitioning of the chemical into the organism's lipid pool (Barron, 1990). Thus, SPMDs appear to simulate key portions of respiratory uptake of chemicals by many species, including humans where the three critical parameters in the kinetic uptake phase are surface area, face velocity, and temperature (Bartkow et al., 2004a,b).

2. Experimental section

2.1. Materials

All laboratory chemicals were ACS Reagent grade and all organic solvents were Optima grade from Fisher Scientific. Two batches of 99% purity triolein (1,2,3-tri-[*cis*-9-octadecenoyl]glycerol) were obtained, one from Sigma Chemical Co., St. Louis, MO and the second from Nu-Chek Prep, Inc. of Elysian, MN. Each batch was purified (Lebo et al., 2004) to reduce the levels of impurities remaining following synthesis. Virgin low-density polyethylene layflat tubing (2.54 cm wide with a wall thickness of 84–89 μm) was purchased from Environmental Sampling Technologies, St. Joseph, MO. The tubing was cleaned by batch extraction using hexane (Rastall et al., 2004). PUF plugs, 21 mm diameter by 26 mm long, were obtained from VWR Scientific Products, St. Louis, MO. The PUF plugs were purified by repeated extraction with dichloromethane (DCM) until no additional reduction in analytical background was observed. Coconut charcoal, PCB Carbon G was obtained from Calgon Carbon Corporation, Pittsburgh, PA. The method of Alvarez (1999) was used to pre-clean the charcoal. Charcoal impregnated polyurethane foam (PUF-C) plugs were prepared from the purified PUF plugs using modifications to the method of Stalling et al. (1978) where the polyurethane to charcoal ratio was approximately 20:1 (w:w). The BDE congeners were not commercially available as pure compounds in the quantities needed. A technical mixture of BDEs at approximately 35 and 48% respectively of BDE-47 (2,2′,4,4′-tetrabromodiphenyl ether) and BDE-99 (2,2′,4,4′,5-pentabromediphenyl ether), Great Lakes Chemical Corporation DE-71TM, West Lafayette, IN, served as the source of BDE-47 and BDE-99. Following fractionation with hexane on silica gel (SG-60, 70–230 mesh, Thomas Scientific, Swedesboro, NJ), 409 mg of material was obtained containing $>$ 99.8% of BDE-47 & BDE-99 in the ratio of 53:47 respectively.

2.2. Test system

A system to produce constant vapor-phase concentrations of test chemicals in a moving airstream to which SPMDs would be exposed, was developed and patented (Fig. 1) (Petty et al., 2005). The multicomponent system has a core element enclosing a series of generator SPMDs (G-SPMDs) (i.e. nonporous polyethylene tubes containing triolein with mixtures of various masses of chemicals) and a fan to circulate air within the core element. Other components include a pump to draw ambient air into the core unit and to deliver, via high precision flow valves, constant concentrations of a mixture of vapor-phase chemicals to the exposure chambers containing uptake SPMDs (U-SPMDs) at a controlled flow rate. To determine the vapor-phase concentrations of chemicals in the airstream, the airstream was actively sampled using stacked PUF plugs and PUF-C plugs in a flow through parallel test system which did not contain U-SPMDs.

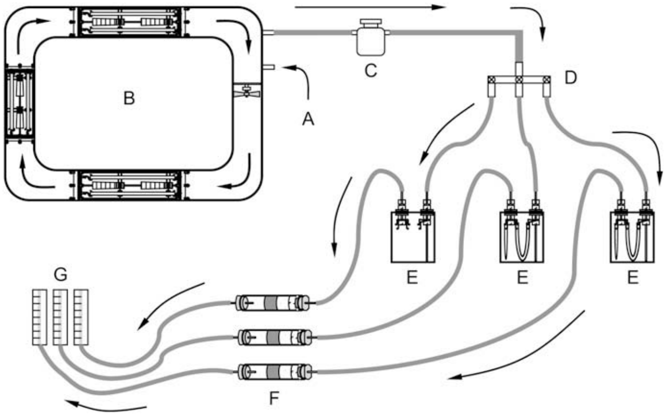

Fig. 1. Test system used in determination of SPMD sampling rate constants ($k_{ua}s$) and equilibrium air partition coefficients ($K_{sa}s$). Arrows indicate direction of air flow. A) Filtered and scrubbed ambient air inlet; B) Core element containing generator SPMDs and internal booster fan; C) Air pump; D) Air distribution manifold with high precision flow valves; E) Exposure chambers for both uptake SPMDs and controls; F) Active air sampling tubes containing PUF and PUF-C plugs; and G) Flow meters.

Three experiments were conducted during which temperature was ambient and airflow was maintained at 4.2 L min^{-1}. Stacked PUF and PUF-C plugs were placed at the output ends of each SPMD exposure chamber and control system and renewed at either 3 or 7 day intervals. The PUF and PUF-C plugs from the control system were subsequently analyzed to determine the time weighted average (TWA) vapor-phase concentrations of the chemicals. At 4.2 L per minute per uptake chamber, the test system simultaneously supported only one control chamber and two SPMD exposure chambers, each containing 3 U-SPMDs. U-SPMDs were collected at each sampling point and subsequently analyzed for sampled chemicals (Table 1).

2.3. Preparation of SPMDs

Two types of SPMDs were used: U-SPMDs to sample chemicals from the airstream and G-SPMDs to generate vapor-phase chemicals. Both had weight to surface area ratios which were consistent with a "standard" SPMD as specified by Huckins et al. (2006). U-SPMDs contained acenaphthylene-d_8, acenaphthene-d_{10}, fluorene-d_{10}, phenanthrene-d_{10}, and pyrene-d_{10} as performance reference compounds (PRCs). The PRCs were included in the study to expand the database for such compounds in air sampling. The mean weight of a U-SPMDs was 0.735 g ± 0.002 g, membrane weight was 0.612 g ± 0.001 g, triolein weight was 0.123 g (by difference) and the containment seal-to-seal length ranged from 12.4 to 13.0 cm. Two sizes of G-SPMDs were required to fit the support racks of the test system. These two lengths of cleaned tubing, at 102.9 cm and 164.5 cm, were approximately 1.2 and 1.8 times longer than an 88.9 cm SPMD (Huckins et al., 2006). These G-SPMDs contained 1.2 or 1.8 mL of triolein containing 1 mg mL^{-1} of each chemical in the mixture being investigated. The ends of the G-SPMDs were heat sealed and connected with a half twist giving a Mobious configured loop. This configuration prevents the membrane from adhering to itself and reducing the effective surface area in contact with the airstream.

2.4. Study design

Kinetic data are required to fully utilize SPMDs to estimate ambient airborne concentrations of contaminants. The sampling