



Calibration of nylon organic chemical integrative samplers and sentinel samplers for quantitative measurement of pulsed aquatic exposures



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ABSTRACT

Environmental exposures often occur through short, pulsed events; therefore, the ability to accurately measure these toxicologically-relevant concentrations is important. Three different integrative passive sampler configurations were evaluated under different flow and pulsed exposure conditions for the measurement of current-use pesticides ($n = 19$), polyaromatic hydrocarbons ($n = 10$), and personal care products ($n = 5$) spanning a broad range of hydrophobicities ($\log K_{ow}$ 1.5–7.6). Two modified POCIS-style samplers were investigated using macroporous nylon mesh membranes (35 μm pores) and two different sorbent materials (i.e. Oasis HLB and Dowex Optipore L-493). A recently developed design, the Sentinel Sampler (ABS Materials), utilizing Osorb media enclosed within stainless steel mesh (145 μm pores), was also investigated. Relatively high sampling rates (R_s) were achieved for all sampler configurations during the short eight-day exposure (4300–27 mL/d). Under flow conditions, median R_s were approximately 5–10 times higher for POCIS-style samplers and 27 times higher for Sentinel Samplers, as compared to static conditions. The ability of samplers to rapidly measure hydrophobic contaminants may be a trade off with increased flow dependence. Analyte accumulation was integrative under pulsed and continuous exposures for POCIS-style samplers with mean difference between treatments of 11% and 33%; however, accumulation into Sentinel Samplers was more variable. Collectively, results show that reducing membrane limitations allows for rapid, integrative accumulation of a broad range of analytes even under pulsed exposures. As such, these sampler designs may be suitable for monitoring environmental substances that have short aquatic half-lives.

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1. Introduction

Toxicological responses are driven by the magnitude and frequency of exposure to the bioavailable fraction of contaminants (i.e. freely dissolved in water). This basic principle becomes complicated in aquatic systems because contaminant concentrations are continuously in flux due to intermittent inputs, contaminant dissipation, and flow variations [1–3]. Anthropogenic substances such as current-pesticides, polyaromatic hydrocarbons (PAHs), and personal care products (PCPs) that enter aquatic systems have short aquatic half-lives due to sorption to sediments [4,5] and other organic matter [6,7]. Regardless of short exposure periods, intermittent exposures can elicit significant toxicological responses

[1,5]. Therefore, developing effective sampling technologies capable of measuring short-term exposures (eight days or less) is important for providing toxicologically-relevant exposure concentrations for contaminants that rapidly pulse through aquatic systems.

Current integrative passive samplers, such as polar organic chemical integrative samplers (POCIS), continuously accumulate freely dissolved contaminants throughout their deployment and have been a reliable technique for providing time-weighted average (TWA) concentrations of some organic contaminants [8,9]. Continuous sampling allows for better detection and identification of contaminants while providing TWA concentrations, which is particularly important for contaminants that rapidly dissipate or degrade following release into the environment [8,10]. Typically, exchange kinetics follow a first-order, one-compartmental model consisting of an initial linear (or kinetic) integrative phase followed by a curvilinear phase indicative of chemical equilibrium [8,9]. Assuming an infinite sink, two processes primarily regulate

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uptake of an integrative sampler: 1) Diffusion through the aqueous boundary layer (ABL) and 2) Permeation through the sampler membrane. The thickness of the ABL changes with flow across the sampler thus sampling rates can be highly influenced by variations in flow [9,11]. Ultimately, whichever process has the slowest kinetics determines the sampling rate [12].

The classical POCIS configuration utilizes microporous polyethersulfone (PES) membranes (0.1 μm pore size) which Alvarez et al. [8] selected over several other membranes based on high sampling rates of polar substances, minimal biofouling, and durability. This membrane has helped establish POCIS as a valuable tool for providing TWA concentrations of polar contaminants; however, diffusion limitations cause inherent problems for accumulation of hydrophobic contaminants. First, the properties of the PES membrane generally restricts accumulation to hydrophilic chemicals with octanol-water partitioning coefficients ($\log K_{ow}$) less than four [8,13–15]. Although some hydrophobic chemicals accumulate in POCIS, the diffusion limiting membrane generally causes a lag-effect in the initial accumulation kinetics [15]. As such, the classical POCIS configuration may under predict actual exposure concentrations for more hydrophobic contaminants due to limited or delayed accumulation of hydrophobic substances as they pulse through the system, binding to sediment and biota. Second, POCIS are typically deployed for 30 (or more) days and have long integration times with linear accumulation of many polar contaminants greater than 28 days [8,16]. For contaminants that are acutely toxic and quickly pulse through aquatic systems, 4–8 day TWA concentrations would likely be more comparable to toxicological endpoints. Collectively, the lag-effect phenomenon and long deployment times present major challenges for predicting water concentrations of hydrophobic substances using the classical POCIS configuration.

Previous research has suggested that adjustment of sampler designs to reduce diffusion membrane limitations is possible [15]. Specifically, replacing the microporous-PES membrane with nylon mesh screens with 30 μm pores reduces diffusion membrane limitations [15]. Belles et al. [15] called this sampler configuration the “Nylon POCIS”; however, we will refer to this design as the Nylon Organic Chemical Integrative Sampler (NOCIS) to emphasize the obvious advantage of this modification for increased sampling rates for hydrophobic contaminants. As opposed to the classical POCIS configuration, nylon configurations could be used for integrative measurement of hydrophobic contaminants pulsing through the water column; ultimately expanding the utility of the sampler by providing toxicologically-relevant exposure data and better risk assessments for more hydrophobic substances.

However, there are some notable issues with the nylon configuration that should be addressed. First, the increased pore size increases membrane permeation; resulting in increased sampling rates and may reduce linear accumulation phases to weeks or days as compared to the long integration times of the classical POCIS configuration for most compounds. This potential weakness may not be problematic for most applications as shorter-term exposures (8 days or less) are typically a more useful measure of toxicity as it relates better to exposure scenarios used in standard 96-h acute toxicity tests. Regardless, linear accumulation should be confirmed for short-term exposures. Second, replacement of the diffusion-limiting PES membranes may increase flow sensitivity of these samplers, thus affecting contaminant-sampling rates. As such, accumulation in NOCIS designs may be more flow dependent and require more calibrations under different flow conditions or use of other flow correction mechanisms.

Investigating new sampler configurations, whether it be modifications of previously described samplers or designs entirely new to literature, is important for expanding our knowledge base and utility of passive samplers for environmental monitoring. For instance,

Oasis HLB is well established as the classical POCIS receiving phase; however, other sorbents (e.g. Dowex Optipore L-493) have been incorporated in ceramic passive samplers and could provide a comparable performance within POCIS-style samplers [17]. An added advantage of Oasis HLB and Dowex Optipore L-493 is that both sorbents are water wettable and require no pretreatment prior to deployment. Moreover, a new sampler design was recently developed called the Sentinel Sampler (ABSMaterials, Inc., Wooster, OH) which encapsulates Osorb media (ABSMaterials, Inc.) within stainless steel mesh. Osorb media (ABSMaterials, Inc.) consists of swellable organically modified silica particles with a strong affinity for a wide range of organic contaminants; however, sorbent pretreatment with ethanol is required prior to deployment. The combination of high capacity Osorb media and 145 μm stainless steel mesh openings suggests that this sampler configuration could be conducive for rapid sampling of a broad range of contaminants and warrants investigation.

The overall objective of this research was to evaluate options for optimization of integrative passive samplers with the goal of maintaining integrative accumulation over toxicologically-relevant periods (i.e. 8 days) while obtaining high sampling rates for organic contaminants with a broad range of hydrophobicities ($\log K_{ow}$ range: 1.5–7.6). Throughout all of our investigations, we used two NOCIS configurations incorporating either Oasis HLB (Waters Corp., Milford, MA) or Dowex Optipore L-493 (The Dow Chemical Co., Midland, MI) and Sentinel Samplers (ABSMaterials, Inc., Wooster, OH). The first step in evaluating the performance of these sampler configurations was to perform a controlled laboratory calibration using an eight-day deployment period and two flow conditions. The second investigation evaluated the integrative nature of these samplers by comparing accumulation under different exposure scenarios. Specifically, we evaluated eight-day sampling rates of sampler configurations continuously exposed compared to samplers that experienced a four-day pulse immediately followed by four days in clean water.

2. Experimental

2.1. Chemicals and reagents

Selected analytes included current-use pesticides (i.e. fungicides, herbicides, and insecticides), polyaromatic hydrocarbons (PAHs), and personal care products (PCPs). Relevant chemical properties of all analytes of interest ($n=34$) are listed in Table 1. Analytical-grade standards of current-use pesticides and PCPs were of the highest available purity (>98%) from Sigma-Aldrich (St. Louis, MO, USA). An expanded PAH mixture was purchased from Accustandard (New Haven, CT) and was used for analytical standards and spiking solutions. Atrazine- d_5 and benzo(a)anthracene- d_{16} were used as surrogate standards and a semi-volatile internal standard mixture, containing deuterated PAHs, was purchased from Accustandard. All solvents (acetone, dichloromethane, ethyl acetate, and methanol) were analytical grade or better. The tap water source at Oklahoma State University is Lake Carl Blackwell (Stillwater, OK) and was used for all experiments. Hardness ranged from 180 to 200 mg/L as calcium carbonate, pH ranged from 6.9–7.3, and experimental unit temperature was maintained at 20 $^{\circ}\text{C}$ (± 1 $^{\circ}\text{C}$).

2.2. Sampler design and assembly

Three passive sampler configurations were investigated and each configuration contained a different sorbent media. The nylon organic chemical integrative sampler (NOCIS) configurations were homemade containing 200 mg (± 5 mg) of either Oasis HLB or Dowex Optipore L-493 sorbents, held between porous nylon mesh

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