



# Characterization of performance reference compound kinetics and analyte sampling rate corrections under three flow regimes using nylon organic chemical integrative samplers



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## ABSTRACT

Performance reference compounds (PRCs) can be spiked into passive samplers prior to deployment. If the dissipation kinetics of PRCs from the sampler corresponds to analyte accumulation kinetics, then PRCs can be used to estimate *in-situ* sampling rates, which may vary depending on environmental conditions. Under controlled laboratory conditions, the effectiveness of PRC corrections on prediction accuracy of water concentrations were evaluated using nylon organic chemical integrative samplers (NOCIS). Results from PRC calibrations suggest that PRC elimination occurs faster under higher flow conditions; however, minimal differences were observed for PRC elimination between fast flow (9.3 cm/s) and slow flow (5.0 cm/s) conditions. Moreover, minimal differences were observed for PRC elimination from Dowex Optipore L-493; therefore, PRC corrections did not improve results for NOCIS configurations containing Dowex Optipore L-493. Regardless, results suggest that PRC corrections were beneficial for NOCIS configurations containing Oasis HLB; however, due to differences in flow dependencies of analyte sampling rates and PRC elimination rates across the investigated flow regimes, the use of multiple PRC corrections was necessary. As such, a “Best-Fit PRC” approach was utilized for Oasis HLB corrections using caffeine-<sup>13</sup>C<sub>3</sub>, DIA-d<sub>5</sub>, or no correction based on the relative flow dependencies of analytes and these PRCs. Although PRC corrections reduced the variability when *in-situ* conditions differed from laboratory calibrations (e.g. static versus moderate flow), applying PRC corrections under similar flow conditions increases variability in estimated values.

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## 1. Introduction

Passive sampling devices are promising environmental monitoring tools for the aquatic environment, capable of measuring trace and fluctuating contaminant concentrations under numerous environmental conditions. Analytes accumulate following first-order, one-compartmental models consisting of an initial linear (or kinetic) integrative phase followed by a curvilinear phase indicative of chemical equilibrium [1,2]. During the initial linear phase, accumulation is integrative and time-weighted average concentrations can be obtained [3,4]. Contaminant sampling rates (*R*<sub>s</sub>) can be empirically determined under controlled laboratory calibrations [5]; however, environmental exposures rarely occur under stable conditions due to intermittent inputs, contaminant dissipation, and flow variations [6–9]. Fluctuating contaminant concentrations can

be compensated for using integrative samplers such as Chemcatchers [10] or the Polar Organic Chemical Integrative Sampler (POCIS) [3,11]; however, these samplers may accumulate target analytes at different rates when there is variation in flow across the sampler membrane [2,5,12–17]. Theoretically, changes in flow across the sampler causes variations in the thickness of aqueous boundary layer (ABL); therefore, contaminant diffusion across this boundary layer is highly influenced by flow. This is especially true when the rate-limiting step of accumulation is diffusion across the ABL rather than diffusion/permeation through the sampler membrane [2,5,18].

Performance reference compounds (PRCs) have been suggested as a viable method to improve calibration for POCIS-style samplers by providing *in-situ* flow calibrations [5,18–20]. Equilibrium-based passive samplers have benefitted from PRCs as stable isotope compounds can be spiked into samplers prior to deployment and dissipation occurs proportional with uptake [21]. However, the integrative nature of POCIS-style samplers presents a challenge for PRCs due to minimal fugacity out of labelled analytes [5,20]. Regardless, several PRCs have been suggested to have suffi-

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cient fugacity out of classical POCIS devices including desisopropyl atrazine- $d_5$  [18–20,22] and caffeine- $C_{13}$  [3,18]. These PRCs are especially important for adjusting  $R_s$  when analyte accumulation is controlled by the ABL rather than diffusion through the membrane [18,19].

Previous investigations have evaluated modified configurations of POCIS-style passive samplers, in attempt to increase analyte  $R_s$ , reduce lag-phase accumulation, and ultimately provide integrative sampling of hydrophobic contaminants [18,23]. Samplers were constructed similarly to classical POCIS specifications; however, polyethersulfone (PES) membranes (0.1  $\mu\text{m}$  pore size) were replaced with high porosity nylon mesh screening (30–35  $\mu\text{m}$  pore sizes). These POCIS-Nylon configurations are hereafter referred to as Nylon Organic Chemical Integrative Samplers (NOCIS) [23]. Although this modification successfully increased  $R_s$  and the ability to measure hydrophobic contaminants, analyte accumulation was governed by diffusion through the ABL resulting in increased flow dependence as compared to classical POCIS configurations [23]. Specifically, NOCIS configurations were shown to be highly flow dependent with five- to ten-fold differences in median  $R_s$  between static and flow (9.3 cm/s) treatments [23]. In contrast, accumulation in classical POCIS configurations is generally limited by permeation through the diffusion membrane where POCIS only have a two- to three-fold differences in  $R_s$  under different flow conditions [12,13]. Differences in flow dependence suggest that PRC dissipation should also be evaluated over a range of flow conditions to ensure satisfactory flow corrections. Moreover, these data suggest that finding a PRC approach that adequately corrects for *in-situ* flow differences may be more important for NOCIS configurations that experience greater flow sensitivities as compared to classical POCIS configurations.

Previously, Belles et al. [18] investigated PRC elimination from classical POCIS configurations and NOCIS configurations and suggested the approach was promising with three PRCs including desisopropyl atrazine- $d_5$ , caffeine- $C_{13}$ , and salbutamol- $d_3$ . All three PRCs demonstrated similar dissipation rates from samplers, thus illustrating the potential of relating PRC elimination to analyte accumulation. However, dissipation was only investigated under a single flow regime, thus the full capacity of the PRC approach was not evaluated.

The overall objective of this research was to build upon previous work to improve the utility of NOCIS configurations by evaluating PRC dissipation under several hydrodynamic conditions to provide  $R_s$  flow corrections for organic contaminants with a broad range of hydrophobicities (log  $K_{ow}$  range: 1.5–7.6). First, to calibrate PRC elimination rates under several flow conditions, PRC dissipation was evaluated as a function of time using fast (9.3 cm/s), slow (5.0 cm/s), and static (0 cm/s) flow treatments. Second, analyte  $R_s$  and PRC dissipation were concurrently measured to quantitatively evaluate the prediction accuracy of known water concentrations based on PRC corrections and previously described analyte calibration studies [23].

## 2. Experimental

### 2.1. Chemicals and reagents

The selected analyte list ( $n = 34$ ) matched previously published work and included current-use pesticides (*i.e.* fungicides, herbicides, and insecticides), polyaromatic hydrocarbons (PAHs), and personal care products (PCPs) [23]. Relevant chemical properties of all analytes of interest are listed in Table S1. Analytical-grade standards of current-use pesticides and PCPs were of the highest available purity 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. Performance reference compounds included atrazine- $d_5$ , caffeine- $^{13}C_3$ , cotinine- $d_3$ , desisopropyl atrazine- $d_5$  (DIA- $d_5$ ; Santa Cruz Biotechnology, Dallas, TX), fluoranthene- $d_{10}$ , and lindane. Benzo(a)anthracene- $d_{16}$ , dibutyl chlorendate, and tetrachloro-*m*-xylene 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 6.9–7.6, and experimental unit temperature was maintained at 20 °C ( $\pm 1$  °C).

### 2.2. Sorbent fortification

Oasis HLB sorbent was removed from Oasis solid phase extraction (SPE) cartridges and the DOWEX sorbent was graciously provided by Dow Water and Process Solutions (The Dow Chemical Company, Midland, MI). Prior to use, sorbents were cleaned with methanol, dried under a vacuum, and held at 40 °C overnight. Sorbents were fortified with PRCs using modified methods proposed by Mazzella et al. [22]. Aliquots (10 g) of both sorbents were weighed out in 200 mL French Square glass bottles, covered with 30 mL of methanol, and fortified with PRC stock solutions. Fortified bottles were placed on a rotating table and shaken at 125 rpm for 4 h to evenly distribute PRCs across the sorbents. Solvent was allowed to evaporate by removing the lids and rotating overnight ( $\sim 12$  h) at 125 rpm and 30 °C. This method provided constant agitation throughout the solvent evaporation process while drying the fortified sorbents to a uniform consistency. Four 200 mg aliquots were immediately analyzed to determine PRC fortification levels and homogeneity. The remaining fortified sorbents were used to construct samplers for PRC dissipation studies ( $n = 27$  per sorbent), *in-situ* analyte uptake and PRC loss studies ( $n = 9$  per sorbent), and additional quality control samples ( $n = 6$  per sorbent). Quality control samples were weighed into glass vials, stored frozen at  $-80$  °C, and analyzed with passive samplers to determine PRC stability.

### 2.3. Sampler design and experimental units

The nylon organic chemical integrative sampler (NOCIS) configurations were homemade containing 200 mg ( $\pm 3$  mg) of either Oasis HLB or Dowex Optipore L-493 that were fortified with PRC as previously described. Similar to the classical POCIS configuration, stainless steel washers contained circular openings with 5.5 cm internal diameter, resulting in approximately 48 cm<sup>2</sup> of exposed surface area per sampler; however, the standard polyethersulfone (PES) membranes (0.1  $\mu\text{m}$  pore size) were replaced with nylon mesh screening (35  $\mu\text{m}$  openings; Pentair Aquatic Ecosystems). Constructed samplers were individually wrapped in aluminum foil, stored in plastic bags, and exposed directly in experimental units without freezing. Physical properties of sorbents and NOCIS configurations were previously described [23].

### 2.4. General design/layout of experimental unit

Experimental units were constructed as described in a previous investigation [23]; however, additional flows were investigated to provide a more robust evaluation of the PRC approach. Passive samplers were exposed to analytes of interest using experimental units consisting of stainless steel pots (inner diameter: 40 cm, height: 30.5 cm) containing 30 L of tap water (Fig. S1). To achieve laminar flow, smaller stainless steel pots (inner diameter: 15 cm, height 17.7 cm) were secured to an aluminum crossbar and sus-

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