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Technical Note

Model stream channel testing of a UV-transparent polymer-based passive sampler for ultra-low-cost water screening applications

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ABSTRACT

Passive samplers are increasingly being considered for analyses of waters for screening applications, to monitor for the presence of unwanted chemical compounds. Passive samplers typically work by accumulating and concentrating chemicals from the surrounding water over time, allowing analyses to identify temporally short concentration surges that might be missed by water grab samples, and potentially reducing analysis and sample handling costs, allowing a greater number of sites to be monitored. The work described here tests a recently-developed passive sampling device which was designed to provide an ultra-low-cost screening method for organic chemicals in waters. The device was originally designed for detection of endocrine disrupting chemicals, but has the advantage that it is capable of simultaneously detecting a wide range of other aqueous organic contaminants as well. The device is based on a UV-transparent polymer which is used both to concentrate dissolved chemicals, and as an optical cell for absorbance detection and full-spectrum deconvolution to identify compounds. This paper describes the results of a test of the device conducted at the US EPA Experimental Stream Facility in Milford, Ohio. The test examined detection of triclosan and 4-nonylphenol in model stream channels using two different deployment methods. Results indicate that deployment method can significantly impact measured results due to differences in mass transfer. Passive samplers deployed in vials with permeable membrane septa showed no detection of either compound, likely due to lack of water motion in the vials. In contrast, passive samplers deployed directly in the flow were able to track concentrations of both compounds, and respond to temporal changes in concentration. The results of the work highlight the importance of using internal spiking standards (performance reference compounds) to avoid false non-detection results in passive sampler applications.

1. Introduction

The use of passive samplers for water sampling has grown in recent years, and a number of different designs have been developed and, in some cases, commercialized. Passive samplers work by concentrating dissolved chemicals into a separate phase, typically a polymer or coated granular material (Booij et al., 2002; Alvarez et al., 2005; Adams et al., 2007; Cornelissen et al., 2008; Harman et al., 2008). After deployment in waters for days or weeks, the samplers are analyzed for the presence of the chemicals of interest. Passive samplers have the potential to provide lower-cost analyses because they simplify the handling requirements for samples (water grab samples typically must be preserved, and often must be collected in large volumes for desired detection limits), and because they eliminate labor intensive pre-concentration steps (water samples often must be concentrated using solid phase microextraction). However, despite the potential cost savings from passive samplers, their analysis nevertheless often still requires a solvent extraction step prior to analysis, and the use of sophisticated and costly laboratory equipment such as GC/MS or LC/MS for identification and quantification of unknown chemicals.

The passive sampler design tested here was developed to provide a method that further reduces costs associated with analyses through the use of low-cost analytical equipment coupled with automated computer deconvolution to identify components. A detailed description of the method and an examination of its performance in a laboratory setting has been provided elsewhere (Kibbey et al., 2009). In short, the method consists of a UV-transparent polymer that acts both as a medium for concentrating chemicals from aqueous solution, and an optical cell for detection using full-spectrum UV absorbance measurements coupled with spectral deconvolution. Although the detection limits of the method are higher than traditional methods for many chemicals, analyses can be completed using low-cost commercial charge-coupled

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device (CCD) spectrophotometer systems. This makes the method applicable to a wide range of applications, including water screening applications in emerging regions of the world where cost is of primary importance, and where affordable water analysis could ultimately reduce health risks. While the method was primarily designed for detection of endocrine disrupting chemicals (EDCs), analysis simultaneously provides information on the presence of other conventional organic water contaminants.

The focus of this paper is on the second of two tests of the method conducted at the US EPA Experimental Stream Facility in Milford, Ohio, a facility designed to study how streams respond to emerging contaminants. The first test, conducted during Summer 2008, involved five model stream channels containing triclosan in concentrations ranging from 0.1 to 10 $\mu g\,L^{-1}$, as well as two control channels with no added triclosan. The primary focus of that test was on studying the impact of the antimicrobial agent triclosan on ecological function in model stream channels. In that test, passive sampler polymers were deployed in vials covered with permeable membranes (described in detail in Section 2). The ultimate result of the test was that no consistent triclosan detection was observed by the sampler, despite weeks of contact time, high concentrations exceeding the calculated detection limits of the method by an order of magnitude, and successful laboratory tests using the same water. At the time it was hypothesized that the reason for the inability of the sampler to detect triclosan during the test might be due to limited water motion in the vials producing a stagnant water region, reducing mass transfer rates. Trial samples tested at the end of the run using alternate deployment methods (polymer in mesh housings or suspended on wires directly in the flow) showed promise, but were not run in sufficient quantities for firm conclusions.

The second test, conducted January 2009, was specifically designed to test that hypothesis by including two different deployment methods. The test also was expanded to include 4-nonylphenol (4NP) as well as triclosan, to evaluate simultaneous detection of the two compounds. This paper describes the test, and discusses implications for application of the UV-transparent polymer passive sampler system to detection in natural waters.

2. Experimental

2.1. Chemicals

Chemicals selected for this study were triclosan, an antibacterial agent, and 4-nonylphenol, a degradation product of ethoxylated alkylphenol surfactants. Both compounds are suspected EDCs, and are widely found in treated wastewaters. Model stream flow experiments were conducted with a technical grade 4NP purchased from Acros Organics (Geel, Belgium) with a reported purity of 99%. Triclosan was purchased from Sigma–Aldrich (St. Louis, MO) with a reported purity of >97%. Both chemicals were used as received.

2.2. The experimental stream facility

The US EPA Experimental Stream Facility, located in Milford, Ohio, houses eight 12 m long model stream channels, which can receive continuous flow from the East Fork of the Little Miami River at rates ranging from 27 to 270 $m^3\,d^{-1}$. Recirculation loops are available to allow residence time to be changed while maintaining flow velocity. Each stream channel includes head and tail tanks, and a long gravel section containing removable gravel baskets which can be sampled and replaced during experiments. Contaminants are introduced to stream head tanks through metered pumping from 570 L dosing tanks.

2.3. UV-transparent polymer passive sampler method

The passive sampler method used for this work is based on a UV-transparent polymer which is used both to concentrate chemicals from water, and as an optical cell for concentration analyses. A detailed description of the method has been provided elsewhere (Kibbey et al., 2009). For this work, the polymer Sylgard-184 (Dow Corning, Midland, MI) was used. Sylgard-184 is a functional polydimethylsiloxane, frequently referred to in the scientific literature as PDMS. Very few polymers have the required combination of transparency in the UV region (a very rare feature in polymers) and high partition coefficients for hydrophobic compounds. Previous work found that PDMS combines both of these features with good handling characteristics, including an optical surface that was not easily damaged by handling (Kibbey et al., 2009). Preparation of PDMS for the work involved combining the two-part liquid mixture, pouring into glass-sided molds, and curing. The resulting cured sheets had a thickness of 1.61 mm, and were cut into 1/2 in. diameter discs using an arch punch. An additional 1/8 in. diameter hole was punched near the edge of the discs for deployment. Full details of PDMS preparation for the passive sampler application has been described elsewhere (Kibbey et al., 2009).

Application of the UV-transparent polymer passive sampler method involves submersing the polymer in the water of interest for a known period of time to allow dissolved chemicals to partition into the polymer from the water, and then removing the polymer and scanning it using a low-cost (e.g., <$ 5 k including light source) fiber-optic CCD spectrophotometer capable of conducting full-spectrum UV absorbance scans. The scans are analyzed for chemical concentration in the polymer using a modified version of the classical least squares algorithm (Workman and Springsteen, 1998). Classical least squares is based on Beer's law, and the recognition that at low concentrations, the absorbance at a given wavelength is equal to the sum of absorbances at that wavelength of all chemicals present. Because different chemicals have different spectra (i.e., absorbance varies differently with wavelength), it is possible to deconvolute the spectra of highly complex mixtures to determine the concentrations in the polymer (Kibbey et al., 2009). Application of classical least squares for detection requires a spectrum of each chemical of interest in the same environment as the mixed spectrum (i.e., PDMS). These spectra, known as basis spectra, are summed together to create a trial mixed spectrum. Because the basis spectra contain the spectrum of PDMS itself, PDMS basis spectra must also be included (Kibbey et al., 2009). Deconvolution is done using a nonlinear optimization routine which creates linear combinations of basis spectra to achieve the best fit with the measured mixed spectrum. For this application, concentrations of chemicals are constrained to be positive as the least squares optimization is conducted. A weakness of the classical least squares method is the fact that missing basis spectra can produce false positive detections; however, constraining concentrations to be positive can reduce the severity of that effect (Jochum and Schrott, 1984). It should be noted that the emphasis of the work described here was not on identification of the presence of unknown compounds, but rather on quantifying two specific chemicals (4NP and triclosan) known to be present.

Estimation of aqueous concentrations from concentrations in PDMS requires information about the affinity of the chemical of interest for the PDMS (the partition coefficient, K_{PW}), and rate information, including a mass transfer coefficient (k_f). For the work reported here, values of K_{PW} and k_f were used without modification from the previous work (Kibbey et al., 2009). In addition, the basis spectra for both triclosan and 4NP were used from the previous work. One important implication of this was that while the triclosan used to determine K_{PW}, k_f, and the basis spectrum had the same source and purity as the triclosan used here, the 4NP did not. The