ABSTRACT

O'NEAL, KELLY LYNNE. Use of Passive Sampling to Measure the Bioavailability of Chemical Contaminants in Surface Waters and Soil. (Under the direction of Dr. Damian Shea).

Bioavailability is key to accurately determining environmental exposure of chemical contaminants. It is the fraction of contaminant available for uptake by organisms and is best represented by the freely dissolved fraction of chemical. This is fundamental to any chemical exposure assessment and it is therefore of the utmost importance to have methods that can accurately measure this fraction. Passives sampling devices (PSDs) can be used to measure the bioavailable fraction of a chemical by passively accumulating and concentrating chemicals over time to give a time weighted average measure of exposure. Uptake into passive sampling devices follows first order kinetics until equilibrium is reached with three unique uptake phases: linear, curvilinear, and equilibrium. PSDs can be used to estimate environmental concentrations by using sampling rates calculated from the linear phase or from equilibrium partition coefficients and/or exchange rate constants.

This research presents important advances in the use of passive samplers to assess both polar and non-polar analytes as well as novel applications that should significantly advance our ability to assess risks associated with chemical exposure in the environment. PSD applications were examined with two different classes of chemicals: polycyclic aromatic hydrocarbons (PAHs) and pesticides. Both have widespread and historic use and can be found in the environment due to use and through unintended release.

This research first evaluated the ability of polyoxymethylene (POM) to act as an equilibrium sampler for PAHs and measured the equilibrium polymer-water partition coefficients for 54 PAHs and related heterocyclic compounds and for 4 oxygenated PAHs (oxy-PAH). My measured partition coefficients (KPOM) are in good agreement with previously published values for the US EPA "PAH-34" list and my data set extends the values to a larger and more useful group of PAH and oxy-PAH degradation products. This research then went on to develop a more universal passive sampling device (uPSD), which is composed of a non-selective porous stainless steel cartridge and a mixed-polymer sequestration sorbent. The uPSD was calibrated in the laboratory for 35 current-use pesticides with log Kow values ranging from 1.49-8.15. This sampler was deployed at numerous field sites and chronic exposure estimates using the uPSDs closely match those using sequential grab sampling. With this laboratory calibration and field verification it is believed that this new uPSD should have very broad application to most organic chemicals. In my final laboratory study, the uPSD was evaluated by using it to sample both a parent pesticide and its degradation product, capitalizing on the ability of the uPSD to accumulate polar chemicals from water. This research included a laboratory study of uptake rates of the fungicide chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile, CHT) and its primary degradation product, 2,5,6-trichloro-4-hydroxyisophthalonitrile (4OH-CHT) into the uPSD under controlled conditions where environmental parameters that could influence uptake rates were varied. I examined the effects that flow rate can have on the sampling rate of CHT and 4OH-CHT and four different scenarios where the sampling rates of both CHT and 4OH-CHT might be impacted through saturation or competition for adsorption sites in the sampler including 1) increasing concentrations of dissolved organic carbon (DOC), 2) increasing pesticide concentration, 3) increasing total suspended solids (TSS) and 4) decreasing particle size of TSS. Finally, a field validation study of PSD performance on multiple contaminants was conducted at an experimental turf grass site in Guangdong Province, China.

Altogether, this research represents a significant advance in our ability to measure chronic exposure to freely dissolved and bioavailable chemicals, has wide application to most non-ionic chemicals, and will provide a cost-effective means of reducing uncertainty in assessing risks to chemical exposure.

Use of Passive Sampling to Measure the Bioavailability of Chemical Contaminants in Surface Waters and Soil

by
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DEDICATION

This dissertation is dedicated to my parents, Dick and Carolyn, without them the completion of this would have never been possible.

BIOGRAPHY

Kelly Lynne O'Neal was born and raised on a farm in Columbus, Indiana. The youngest of three, she grew up with a curiosity about the world and a love of the outdoors. This led to the pursuit of an undergraduate degree in Biology at Purdue University. At Purdue her studies took on a more chemistry focus and she conducted undergraduate research in a lab in the chemistry department. Upon graduating in 2006, she did not feel like she was done learning and sought a Ph.D. with an environmental chemistry emphasis. This led to her enrollment at North Carolina State University in the Department of Environmental and Molecular Toxicology. Eventually transitioning into what is now known as the Department of Biological Sciences she has focused on the bioavailability of chemicals in surface water, sediment and soils. In addition to her studies, she still enjoys outdoor activities such as hiking as well as swimming.

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INTRODUCTION

1. Bioavailability and chronic exposure

Simply because an organism is exposed to a chemical in the environment does not mean that it will be taken up by the organism or that there will be a harmful effect. Uptake and toxicity are dependent upon what the bioavailability of the chemical is to that organism. Bioavailability is the amount or fraction of a chemical that is readily available to be taken up by an organism. Each chemical has its own distinctive bioavailability that is driven by a number of chemical factors including water solubility, vapor pressure, speciation and a number of environmental conditions in water and sediment such as water composition, pH, temperature, and organic carbon content[1, 2]. In soil and sediment, the bioavailable fraction may be much lower than the total measured concentration due to the chemical being sorbed to organic matter of the sediment. Chemicals with very low water solubilities more readily sorb to organic carbon in the water column, such as particulate or dissolved organic carbon. The rate of desorption partially determines what that chemical's bioavailability is. If desorption occurs rapidly then the chemical has more potential to be fully bioavailable. However, if desorption occurs slowly, then the chemical may not be as readily available. This becomes important when considering risk assessments or remediation actions of contaminated sites because not considering the bioavailability of a chemical can lead to overestimations of exposure and thus toxicity/risk that can lead to unnecessary cleanup expenditures. Decrease bioavailability can also lead to prolonged persistence of contaminants in the environment due to a contaminant's inaccessibility to the microorganisms that degrade them. This, combined with acute environmental poisoning events becoming increasingly rare, has led to environmental concern shifting to more long-term, chronic exposures at very low concentrations. This presents the challenge of measuring or estimating chronic low level environmental exposure and assessing human and ecological risks associated with those exposures. Obtaining an estimate of chronic exposure can require extensive sampling and analysis over the exposure period and this often proves too expensive and highly impractical. Obtaining an accurate and low-cost estimate of chronic exposure in water remains a significant challenge.

2. Passive Sampling Devices

With the importance of bioavailability and chronic exposure it is vital to have a tool to accurately measure both of these in the environment. Traditionally, estimates of chemicals in surface water have used grab sampling to estimate exposure. This requires large volumes of water to be collected and extracted in order to have detectable concentrations. This can be cumbersome and only offer a snapshot of the exposure at the moment the sample is collected making this an impractical sampling regime as water concentrations can vary significantly with time. This is particularly true of some contaminants such as current-use pesticides due to the episodic nature of seasonal application and therefore exposure. Thus, in order to gain an estimate of average chronic exposure, many samples would need to be collected sequentially over the exposure time period and in most cases this proves to be expensive and highly impractical. However, without such an exhaustive sampling plan, grab samples cannot accurately demonstrate the potential chronic exposure to contaminants making an effective time-weighted-average (TWA) sampling method integral to estimating chronic exposure to any environmental contaminant. Passive sampling devices or PSDs can be used to estimate chronic exposure to the truly dissolved or bioavailable fraction of a chemical. Originally developed by Huckins and co-workers in the early 1990's, passive sampling devices have greatly improved environmental monitoring efforts providing both qualitative and quantitative data to describe the extent of environmental exposure [3]. Passive sampling devices passively accumulate and concentrate chemicals over time to give a TWA measure of exposure. Uptake into passive sampling devices follows first order kinetics until equilibrium is reached with three unique uptake phases: linear, curvilinear, and equilibrium. PSDs can be used to estimate environmental concentrations by using sampling rates calculated from the linear phase or from equilibrium partition coefficients and/or exchange rate constants.

PSDs that are deployed during the linear uptake phase can be used to calculate a quantitative estimation of exposure integrated over time. These integrative samplers typically have a lower surface area to volume ratio so that they act as an almost infinite sink for analytes and remain in the linear uptake phase for the entire exposure time. The PSDs are first calibrated in laboratory uptake experiments to yield integrative sampling rates (R_s). These sampling rates are then used to calculate estimates of exposure concentrations in field samples. The sampling rate is a measure of the volume of water quantitatively sampled per unit time (L/d), and is determined using the following equation,

$R_s = N_t / C_w t$

(1)

where R_s is the sampling rate (L/d), N_t is the amount (ng) of analyte accumulated in the sampler at the end of exposure, time in days, C_w is the average concentration of freely-dissolved analyte in water (ng/L), and t is the duration of the exposure measured in days [4].

In field samples, estimates of environmental concentrations (C_w) can be determined by rearranging equation 1 as follows,

$C_w = N_t / R_s t$

(2)

where N_t is the amount (ng) of analyte in the PSD at the end of the deployment period, t, in days, R_s is the laboratory-derived sampling rate (L/d), and t is the duration of the deployment in days [4].

The second approach to passive sampling devices is to deploy them until they reach equilibrium or steady state with the surrounding environment. This method simplifies the model used to estimate environmental concentrations and can be used to estimate a body burden in organisms [5]. Equilibrium samplers typically have a lower sorptive capacity and higher surface area to volume ratio, and environmental concentrations are estimated using the equation,

$C_W = N_{PSD\text{-}E}/K_{PSD}$

(3)

Where C_W is the concentration in the water, $N_{PSD\text{-}E}$ is the concentration of target analytes in the PSD at equilibrium (ng/g) and K_{PSD} is the water partition coefficient for the PSD. The partition coefficient for the passive sampling device can be determined by,

$K_{PSD} = k_u/k_e$

(4)

where k_u is the uptake rate into the PSD and k_e is the elimination rate from the PSD. Log K_{OW} can be used to estimate K_{PSD}, however for many PSDs, this correlation becomes poor at log K_{OW} values above 6.0 [6].

Either approach to passive sampling however can be plagued by a variety of environmental factors that can alter the uptake rate of analytes into the PSD. These environmental factors can include flow rate, temperature and biofouling. Flow rate can control the uptake of more lipophilic compounds with log K_{OW}s $\geq$ 4-5. This is because flow rate determines the thickness of the aqueous boundary layer (ABL) adjacent to the PSD surface. The aqueous boundary layer is the layer of fluid in the immediate vicinity of a bounding surface where the effects of viscosity are significant and higher flow rates decrease ABL thickness, which results in faster uptake for hydrophobic compounds [7, 8]. These environmental factors can lead to false estimates of environmental concentrations and it would be next to impossible to determine uptake rates for every condition, therefore performance reference compounds or PRCs are used to account for these discrepancies or effects. PRCs are analytically noninterfering compounds that have similar physical chemical properties as the analyte of interest [9]. Through isotropic exchange kinetics, the loss of the PRC is proportional to the uptake of the chemical of interest and this site specific loss can be used to account for any environmental factors affecting the uptake into the PSD [8-10]. Mathematically this can be modeled with the equation,

$$N_t = N_0 * e^{(-ket)} \tag{5}$$

where N_t is the amount (ng) of PRC remaining in the sampler at time t in days, N_0 is the amount (ng) of PRC initially loaded into the sampler, k_e is the elimination or exchange rate constant (d^{-1}), and t is the time in days [8]. Then an environmental adjustment factor (EAF) can be used to compare the field elimination rate with a laboratory derived elimination rate using the following equation,

$$EAF \equiv k_{ePRC\text{-}f} / k_{ePRC\text{-}cal} \tag{6}$$

where $k_{ePRC\text{-}f}$ is the PRC elimination rate constant in the field (d^{-1}) and $k_{ePRC\text{-}cal}$ is the PRC elimination rate constant determined in the laboratory (d^{-1}) [9]. Changes in uptake rate are corrected for by applying the EAF to the PSD-estimated water concentrations.

Since their inception roughly 20 years ago, several types of passive sampling devices (PSDs) have been developed for monitoring chronic chemical exposure in aquatic systems however their use is largely limited to hydrophobic chemicals [11]. Traditional sampling methods have focused on generating qualitative data while attempting to identify the chemical suite of exposure [12]. Passive sampling devices (PSDs), such as the semi-permeable membrane device (SPMD) were developed to quantitatively evaluate chemical loads with greater precision and increased sampling specificity for various classes of compounds [3, 11]. Many of the PSDs were designed to target compounds sharing similar chemical properties and have been shown to work very well with hydrophobic organic compounds such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and various other organochlorines and organophosphates [5, 13]. However, there are still difficulties associated with sampling polar, ionic chemicals, and with few exceptions, current PSD designs do not adequately address this shortcoming.

The organic version of the Chemcatcher and the polar organic chemical integrative sampler (POCIS) were developed for hydrophilic organic contaminants; however neither provide sufficient quantitative exposure estimates [14, 15]. The organic version of the Chemcatcher combines a 47-mm C18 Empore disk as the receiving phase with a polyethersulfone diffusion-limiting membrane [14]. The Chemcatcher has been calibrated and used to look for a limited suite of 10 polar and semi-polar pesticides however it displays a limited linear uptake of 14 days and in the field, displayed high biofouling with no way to account for the resulting changes in sampling rates as it was concluded that the

Chemcatcher did not show elimination of performance reference compounds or PRCs from the receiving phase in a laboratory calibration [16, 17]. The POCIS is made up of a sequestration medium sandwiched between two thin polyethersulfone membranes [15]. The POCIS has been demonstrated to work well for compounds with a log Kow < 3 such as herbicides, pharmaceuticals and personal care products [18, 19]. Nevertheless, the POCIS is faced with its own set of weaknesses. Specifically, there is very little sampling rate data available for the POCIS making quantitative assessments difficult. The thin polyethersulfone membrane can be easily punctured during field deployment or even during laboratory extraction. Also the POCIS is subject to biofouling which can cause a deficit in uptake to occur and most importantly, correcting for the biofouling or sheer flow effects by using performance reference compounds (PRCs) is complicated due to the strong sorptive properties of the sorbent medium used in the POCIS and matrix effects during quantification [20, 21].

Therefore despite all of these advances there is still a need for further development of passive sampling devices and expanding the applications of these PSDs to provide better estimates of chronic environmental exposures and bioavailability. This work presents important advances in the use of passive samplers to look at both polar and non-polar analytes as well as novel applications that will have significant environmental impacts. PSD applications were examined with two different classes of chemicals: polycyclic aromatic hydrocarbons (PAHs) and pesticides. Both have widespread and historic use and can be found in the environment due to use and through unintended release.

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CHAPTER 1. Use of Equilibrium Passive Sampling Devices for Measuring Dissolved PAH and Oxy-PAH

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Use of Equilibrium Passive Sampling Devices for Measuring Dissolved PAH and Oxy-PAH

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ABSTRACT. Passive sampling devices (PSDs) that are allowed to reach equilibrium with water or water-particle slurries have shown promise in estimating the readily desorbable and potentially bioavailable fraction of polycyclic aromatic hydrocarbons (PAHs). To make further progress toward this goal, we measured the equilibrium polymer-water partition coefficients for 54 PAHs and related heterocyclic compounds and for 4 oxygenated PAHs (oxy-PAH) using polyoxymethylene (POM) as a non-depleting sorbent phase. Our measured partition coefficients (K_{POM}) are in good agreement with previously published values for the US EPA "PAH-34" list and our data set extends the values to a larger and more useful group of PAH and oxy-PAH degradation products. We used both a static-renewal water only exposure and a soil-water slurry exposure to measure K_{POM} and found good agreement between the two methods. Our measured log K_{POM} values were linearly correlated to log K_{OW} (r^2 = 0.9857 for static-renewal experiment and r^2 = 0.9655 for soil-water slurry). We then measured dissolved PAH in a soil-water slurry, using PAH-contaminated soil from the field, and compared the POM method to solid-phase microextraction (SPME) for measuring freely dissolved PAH. The POM provided data for 39 PAH and oxy-PAH compared to only 3 PAH

for the SPME owing to the much lower detection limits of the POM method. Furthermore, to provide toxicological relevance to our chemical measurements, we conducted experiments to test the effect of adding activated charcoal to PAH contaminated soil in our soil-water slurry systems. We found the dissolved phase PAH measured with the POM was reduced 97% and was consistent with a decrease in earthworm toxicity from 100% mortality to 0% mortality after the addition of activated charcoal.

INTRODUCTION

Accurate estimation of trace concentrations and the freely dissolved form of chemicals in water is critical to understanding the fate and effects of chemicals in aquatic and sediment/soil systems as it is generally thought that only the freely dissolved form can readily pass through biological membranes (1-4). Complementary approaches are being developed to either model or measure freely dissolved chemicals. Models require laboratory and/or field experiments to quantitatively understand how measurable parameters control the partitioning, surface adsorption, and complexation of chemicals that determine the speciation and phase distribution of the chemical. These models range from simple two-phase partitioning models such as the partitioning of hydrophobic organic compounds (HOCs) between sediment/particulate organic carbon and water (5, 6), to more complex multi-phase partitioning and surface adsorption models such as those designed to incorporate additional sorptive phases like soot carbon and non-aqueous phase liquids (NAPL) (7, 8), to very complex speciation models such as the aqueous and surface complexation models for metal speciation (9). An important value of these models is a better mechanistic understanding of the chemistry that controls the behavior and fate of chemicals. While the predictive capability has generally improved with increasing experimental data and complexity of the models, these speciation models have yet to provide the accuracy desired for risk assessments and management decisions under the broad range of conditions encountered in nature. Even the simple equilibrium partitioning of HOCs between water and sediment/soil organic carbon has failed to explain toxicity (or lack thereof) or measured dissolved concentrations at many sites.

A complementary approach to these models is to measure chemical speciation and particularly the freely dissolved form of the chemical (3, 4, 10-13). These approaches have included use of ion-selective electrodes and other electrochemical measurements for metals and selective and sequential filtration/ultrafiltration for HOCs. More recent work has focused on the use of passive sampling devices (PSDs) that utilize a sorptive phase that sequesters and accumulates only the freely dissolved phase of the chemical (3, 4, 10, 13). These have included ion-exchange gels for metals and various polymers for organic chemicals. The most promising of these PSD methods has been the use of hydrophobic polymers to estimate freely dissolved HOCs, in large part due to the relative simplicity of the equilibrium partitioning process involved. The concept, described in greater detail elsewhere (3, 4, 10, 13-20), is to expose the polymer to water or a soil/sediment-water slurry and estimate the freely dissolved concentration of chemical using either a first-order uptake rate (sampling rate) when the HOC accumulation is in the linear uptake phase or a partition coefficient if the dissolved HOC and polymer are allowed to reach equilibrium. The former has had important application in estimating time-weighted-average concentrations of HOCs in water while the latter has been used mostly for estimating dissolved or bio/chemically available HOCs in soils and sediment. The use of polymers to measure dissolved phase HOCs in sediment slurries dates back at least to the work of Crecelius et al. (14) where they used polyethylene (PE) in sediment-water slurries to measure polychlorinated biphenyls (PCBs). This work was augmented by others, and notably by Jonker et al. (10) who used polyoxymethylene (POM) to measure a small number of PCBs and polycyclic aromatic hydrocarbons (PAHs). Very recently, the use of POM was extended to a broader list of 34 PAHs and alkylated PAHs with estimated detection limits as low as 1 pg/L (13) and with a primary application of providing data on freely dissolved PAH for use with the US Environmental Protection Agency (USEPA) hydrocarbon narcosis model for assessing PAH toxicity in sediment and soil. In addition, this work (12) presented PAH POM/water partition coefficients (K_{POM}) for these 34 PAHs. This has been an important advance, but it does not include other important PAHs: other alkylated PAHs, related petroleum heterocyclic compounds, and degradation products of these chemicals – all of which are important to help understand the sources, fate and effects of PAHs in the environment. For example, alkylated homologues of PAHs and sulfur heterocyclic compounds such as dibenzothiophenes are important for oil source identification and understanding oil weathering and bioremediation (21). The alkylated PAHs also are the most abundant PAHs in both fresh and weathered crude oil and most petroleum products. Oxygenated PAH degradation products (oxy-PAH) can be important to understanding mechanisms of natural attenuation and bioremediation as well as assessing toxicity (22). The objective of this work was to further extend the use of POM for measuring freely dissolved concentrations of 58 PAHs (54 PAHs and related heterocyclic compounds and 4 oxy-PAH) by measuring K_{POM} values for these compounds (Table 1). The method was then applied by running experiments in field-collected oil-contaminated soil along with standard soil toxicity testing.

MATERIALS AND METHODS.

Materials. Alaska North Slope crude oil was a gift from Battelle, Duxbury, MA and coal tar was obtained from Chemservice, Inc., West Chester, PA. Polycyclic aromatic hydrocarbons were obtained from Accustandard, New Haven, CT and deuterated PAHs from Cambridge Isotopes, Andover, MA. All solvents were ultra-resi analyzed or HPLC grade. The POM was obtained in 3 sizes, 25-µm and 50-µm POM (custom fabricated by Shenzhen Xiongyihua Plastic Insulation Ltd., Shenzhen, China), and 76-um POM (CS Hyde Co., Lake Villa, IL, USA)..

Preparation of POM. Strips were cut to approximately 1 cm x 4 cm (ca. 50 mg each) and cleaned by placing in 1:1 acetone:hexane and shaking at 300 - 350 rpm for 30 minutes, replacing the solvent mixture five times during this procedure. The POM was dried at 50°C for 10 minutes after extraction. All 58 PAHs were below the limit of detection after this cleaning procedure.

Exposure Methods. The POM were exposed to PAHs using two methods: 1) a static-renewal water only exposure and 2) equilibrating with a slurry of water and PAH-contaminated soil (8). For the water only exposure, approximately 64-L deionized water was spiked with a mixture of 70-µL Alaska North Slope crude, and 22-µL coal tar, and individual PAH and oxy-PAH standards in 8-mL 1:1:1 acetone:ether:reagent alcohol and stored at 23 ±

1 °C and containing 150 mg/L sodium azide to prevent biological growth. The reservoir was equilibrated for 48 hours. Water was filtered through a 1.5-µm glass fiber filter and 1-L water was transferred to a clean silanized 1-L beaker with renewal every 12 hours (±1 hour). Renewal rates were approximated so that PAH concentrations in water did not change by more than 10%. One POM strip was placed in a beaker attached to a wire suspended from the top of the beaker/aquarium and the beaker was covered with foil to prevent photodegradation. The POM were collected in triplicate (three separate beakers) on days 2, 4, 7, 15, and 30. Preliminary experiments over a 61-day period indicated that equilibrium should be reached within 2 weeks (i.e., see Figure 1) and K_{POM} values were independent of PAH concentration from ~10-800 ng/L for individual PAHs (higher concentrations were not tested). Analyte concentrations in water were measured after exposure (every two days) and directly from the reservoir (once/week). Composite samples were also collected by taking 100 mL from each liter after each exposure. Analyte concentrations in water were less than the water solubility in all exposures. This exposure was conducted at 23 ± 1 °C. For the soil-water slurry exposures, two soil types were used: 1) a clean loam to which was added a known amount of crude oil, coal tar, and individual PAH to allow all 58 PAHs to be present and 2) a soil containing naturally weathered crude oil. For each exposure, 10 g (dry weight) of soil, one strip of POM (~50 mg), and 50-mL deionized water containing 150 mg/L sodium azide were added to a 60-mL centrifuge tube with PTFE cap. Tubes were placed on an orbital shaker at 150 rpm for 14 days and the POM was removed, rinsed with deionized water, air-dried for 1 hr, and extracted as described below. Uptake experiments to determine the time

reach equilibrium were conducted over a 30 day period with POM sampled in triplicate on days 2, 4, 7, 15, and 30.

Sample Processing. All glassware was solvent rinsed and baked at 400 °C for 24 hrs prior to use. Water was extracted by shaking three times in dichloromethane (DCM) (60-mL DCM to 0.5-L water) in a separatory funnel. Dichloromethane was eluted and dried with anhydrous sodium sulfate. The extract was then concentrated using a rotovap and a gentle stream of nitrogen, filtered [Whatman Uniprep filter vial, 0.45 µm, poly(tetrafluoroethylene)], and further concentrated to 1 mL. The POM were extracted by shaking in 1:1 acetone:hexane for 3 hrs at 300 - 350 rpm. Earthworm tissue and soil samples were extracted as described previously (2, 8). Samples were lyophilized and shaker-extracted (200 rpm) for 24 h with methylene chloride:acetone (1:1) (v:v). Tissue lipid content was determined by passing extracts through a gel permeation chromatography (GPC) column, collecting the lipid fraction, evaporating, and weighing. Any samples not extracted immediately were stored at -20°C.

Instrument Analysis and Quality Control. Extracts were analyzed using an Agilent 6890 gas chromatograph equipped with electronic pressure control and an Agilent 5973 mass selective detector (MS-electron ionization) in selected ion monitoring mode. The column was a Restek 30 m x 0.25 mm ID with 0.25 µm film thickness with a 5-m guard column (Rtx 5MS with Integra guard). The initial temperature was 40°C ramped at 25°C/minute to 100°C, then at 5°C/minute to 300°C, and held for 15 minutes. This method is similar to that described previously (2, 3). Quantitation of the PAHs and oxy-PAHs was based on four or five point calibration curves (0.02 to 1 µg/mL with relative standard deviations of less than

25% and benzo[a]pyrene-d12 and phenanthrene-d10 recovery internal standards. The solid phase microextraction analyses were conducted using the same instrumentation according to ASTM Standard Test Method D 7363-07 (23). Alkyl homologues were quantified as described previously (2, 3, 8). The molecular ion of the alkyl homologue was extracted and the areas of the individual isomers summed by a straight line, baseline integration. The response factor used to quantify a specific homologous series was the response factor of an isomer of that homologue or when no isomer of the homologous series existed in the analytical standard, the response factor of the parent compound was used.

The method limit of quantitation (MQL) was calculated as the mean response plus 10x the standard deviation of the blanks. Average MQLs were approximately 0.005 ng/POM and 0.06 ng/L for water. Procedural blanks and matrix spikes were completed for both POM samplers and water samples. The POM blanks did not contain any signal for the PAHs. Water blanks did contain some low levels of naphthalene and C1-naphthalene, but all background was less than 0.5% (with an average of 0.05%) of the amount measured in samples and generally less than the lowest calibration standard. Recoveries of matrix spikes for POM ranged from 77% to 100% with coefficients of variation (CV) less than 5%. Surrogate internal standards (naphthalene-d8, acenaphthene-d10, chrysene-d12, and perylene-d12) were spiked into all tissue, soil, and water samples (and into the POM extraction solvent just prior to adding the POM), prior to extraction, to monitor recoveries in samples. Average surrogate internal standard recoveries in samplers ranged from 88% - 96%. Matrix spike recoveries for water ranged from 71 - 98% with the lowest recoveries occurring for naphthalene and all CVs were 20% or less. Average surrogate internal standard recoveries for water ranged from 74% - 94%. All water samples were corrected for recovery based on the surrogate internal standard occurring closest to the compound in the chromatogram. The POM concentrations were not recovery corrected because all recoveries were near 100%.

Earthworm Exposures. Earthworm exposures followed standard procedures (24). Ten adult (visible clitellum) earthworms (*Eisenia foetida*, from Carolina Biological Supply, Greensboro, NC, USA) ranging from 300 to 600 mg each, were added to 200 g soil (60-70% maximum water holding capacity) in a pre-cleaned canning jar with holes in the lid. Earthworms were kept under constant light to encourage burrowing. Mortality and PAH concentrations were measured after a 14 day exposure. Soil was collected using a small stainless steel hand shovel from a crude oil contaminated site, placed in pre-cleaned amber glass jars, and stored at 4°C. Soil samples included untreated soil and soil from a test where activated charcoal (AC) was added to the soil in a attempt to irreversibly bind the PAH and decrease desorption to water or biota. These soils also were mixed with water and POM as described above to determine the concentration of freely dissolved PAHs that desorb from the soil at equilibrium.

RESULTS AND DISCUSSION.

Uptake Kinetics of PAH into POM. Exploratory experiments were conducted over 61 days with a small subset of PAH that spanned the range of log K_{OW} from 3.37 (naphthalene) to 7.24 (coronene) indicating that even the most hydrophobic PAH reached steady state and apparent equilibrium in 2 weeks or less. Based on these data, 30-day uptake experiments were conducted for a broader suite of PAH and oxy-PAH and representative data are shown in Figure 1. Within 7 days, all chemicals reached 90% or greater of their final 30-day concentration and at 15 days all chemicals were within 97-105% of the 30-day concentration. This is consistent with previous work, though perhaps slightly faster than some studies that contained particulate material (e.g., sediment or soot carbon) that might have slower rates of PAH desorption to water (8). We noted during preliminary experiments that steady state was reached more rapidly when the source of PAH was a dissolved standard or a water accommodated fraction of oil compared to slighter longer equilibrations times when the PAH source was an oil-contaminated sediment (Table 2). Using the time to reach 95% of the equilibrium value as a guide, there was essentially no difference between the dissolved standards and the crude oil (water accommodated fraction) as the PAH source. A few of the sediment samples did take slightly longer to reach equilibrium, but even the most hydrophobic PAH reached 95% of final value in 11 days or less. It is possible for sediment or soil to contain phases that have slower desorption rates. For example, we previously found that soot carbon can, but does not always, have slower PAH desorption rates than sediment organic carbon (8). However, we did not test different sediment samples for this work.

Like previous published work (9), we have used different thicknesses of POM depending on the POM source and our desire to reach equilibrium more rapidly. The thickness of the POM should not affect the K_{POM} values but thinner POM should reach equilibrium more quickly unless desorption from a solid source phase (e.g., sediment) is the rate limiting step. We repeated the uptake experiment using custom made 25-µm and 50-µm strips, and the more readily commercially available 76-µm POM strips and found the expected decrease in equilibration time with increasing surface area-to-volume ratio (ie., decreasing thickness) as shown in Table 2. Although we did not test different methods of POM exposure, it is possible that small differences of up to several days to reach equilibrium could exist between orbital shaking, sonication, rotating box, and other methods that might be a source of difference in equilibration times reported in the literature (8). Based on these data, all subsequent experiments used a 14-day equilibration time and used the 76-µm POM strips.

POM/Water Partition Coefficients. As described in detail by others (8, 10, 13), the key to measuring freely dissolved chemicals with an equilibrium non-depletive PSD is to have accurate and standardized polymer/water partition coefficients or K_{PSD}. Although the standardization of K_{POM} measurements is still under development, Hawthorne et al. (13) have proposed and reported on a procedure utilizing contaminated sediments to buffer the freely dissolved concentrations during the uptake experiments and to use the same commercially available 76-µm POM strips that we used. They also reported data from a different laboratory using pure compounds added to water and found very good agreement between the two methods. For our work, we were seeking a broader suite of PAH and related compounds so rather than using just natively contaminated sediment, or a sediment fortified with a PAH source (such as oil or NAPL), or the addition of standards to water or sediment, we used a method we previously reported where crude oil is mixed with coal tar and then fortified as needed with authentic standards to create a secondary standard mix of PAHs that covers the much broader range of PAH listed in Table 1 (2, 3, 8). This also allows for better control over the PAH concentrations helping to ensure detection of all compounds and a smaller range of concentrations across the different PAHs. This mixture was then used in both static renewal and fortified sediment exposure to determine K_{POM} values for the PAH.

We obtained K_{POM} values for all 54 PAH and related heterocyclic compounds and the four oxy-PAH (Table 1). Data reported by Hawthorne et al. (13) also are listed for comparison. There was excellent agreement between the water-only static renewal and sediment exposure methods with a slight negative bias and higher variability for the sediment exposure method. Hawthorne also found higher variability using the sediment phase compared to pure standards in water, but in both cases the variance is still rather low.

The values we obtained for parent (non-alkylated) PAH are in excellent agreement with those of Hawthorne et al. (13), except for some of the most hydrophobic PAH where our K_{POM} values become consistently higher at log K_{POM} values above 6.5 with the greatest difference being benzo[g,h,i] perylene. We also found substantial differences in K_{POM} values for the alkylated PAH, again with our values being higher. The differences were only a few tenths of a log unit for most of the alkyl PAH (C1-C2 naphthalenes, C1-C3 fluorenes, C1-C3 phenanthrenes, C1 fluoranthenes, and C1-C3 chrysenes), but for the higher alkyl substituted PAH (C3-C4 naphthalenes, C4-phenanthrenes, and C4-chrysenes) the difference was between 0.5 and 1.04 log units and these differences were statistically significant ($p > 0.05$ using a paired t-test). Hawthorne et al. (13) reported that unlike the parent PAH, the alkylated PAH K_{POM} values did not increase linearly with log K_{OW} with values falling increasingly below the regression line with increasing alkyl substitution. We found much smaller negative deviations that were slightly more pronounced with the sediment exposure compared to the water-only exposure, but overall there was an excellent linear fit between log K_{POM} and log K_{OW} (Figure 2). Note that our data includes 9 authentic alkylated standards all of which are in excellent agreement with the aggregated alkylated PAH isomers indicating these differences are not likely a result of analytical artifacts but more likely a result of experimental system differences, perhaps due to differences in the sediment. Although we cannot explain this discrepancy, it only is apparent with a few of the most highly alkylated PAH and with these few exceptions there is remarkable agreement among the data sets. With respect to the use of POM to measure freely dissolved PAH for the USEPA narcosis model risk assessment, further work is probably needed on the K_{POM} values for C3- and C4-naphthalenes and C4-phenanthrenes because these PAH can make up a significant percentage of PAH in oil contaminated soils and sediments. For these few individual PAHs the differences in exposure estimates could exceed an order of magnitude, but for the complex mixtures of PAH typically observed the additivity of the PAH narcosis model would likely make these differences insignificant when all PAH concentrations are summed. Until this discrepancy is resolved, we recommend that an average of the values we obtained and those reported by Hawthorne (12) be used to estimate freely dissolved PAH from residues in POM.

PAH Measurements in Soil-Water Slurry. To test the performance of this POM method for measuring dissolved PAH in a field collected (not artificially fortified) soil sample we repeated the POM desorption experiment with soil collected from a site contaminated with various petroleum products. We also performed this desorption experiment using SPME to determine how well the two methods compare. The results are shown in Table 1 (last four columns). Using the POM, we detected most of the PAH in the dissolved phase with the lowest concentration being 0.018 ng/L for C3-chrysene. The PAH that were not detected in the dissolved phase with POM were all very hydrophobic and their concentrations in the source soil were all below 1 ng/g. Hawthorne et al. (13) estimated detection limits for these

PAHs near 1 pg/L using the POM method. The precision of these dissolved PAH measurements was generally very good and improved with higher PAH concentrations. One of the oxy-PAH degradation products (1,4-naphthoquinone) also was detected using the POM indicating the potential for dissolved phase measurements of both parent PAH and transformation products with the POM. In contrast to the POM dissolved PAH measurements, the SPME method was able to detect only three PAH, all naphthalenes that had concentrations above 100 ng/L. The SPME method yielded higher values and much higher variability. This is a dramatic illustration of the improvement of using POM versus SPME for measuring a more comprehensive suite of dissolved phase PAH at lower concentrations.

Potential Application for Measuring Bioavailability of PAH in Soil. One ultimate goal of this POM method is to measure the bioavailable PAH in soil, with the assumption that PAH must dissolve in water to become bioavailable. We conducted a preliminary test of this by measuring PAH in 1) soil, 2) POM exposed to soil-water slurry, and 3) earthworms (i.e., tissues) exposed to the soil, before and after the addition of activated charcoal (AC) designed to reduce PAH bioavailability (Table 3). We also measured mortality of the worms. As expected, the addition of AC to the soil did not affect the total PAH concentration in the soil, but it did reduce PAH accumulation in the worms and in the POM exposed to the soil-water slurry. Worm mortality was 100% after 14 days in the soil and dropped to 0% following amendment with AC. These data are insufficient to establish a quantitative relationship between dissolved PAH measured using POM and either PAH bioaccumulation in or toxicity to earthworms. However, along with the other data presented here the POM method appears to be a potentially very good method for measuring dissolved PAH in water and bioavailable PAH in soil and sediment. Further testing in the laboratory and field will be needed to determine if this method could replace the use of bioaccumulation and toxicity testing for PAH contaminated soils and sediment.

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Table 1. Measured partition coefficients and dissolved concentrations for PAHs and related heterocyclic compounds.

				This work				Hawthorne 2011		Dissolved Concenration (ng/L)			
				Water Exposure		Sediment							
Compound	Symbol	MW	log K_{ow}	log K_{POM}	SD	log K_{POM}	SD	log K_{POM}	SD	POM	SD	SPME	SD
napthalene	N	128	3.37	3.06	0.02	3.02	0.11	3.05	0.09	332	17	480	119
biphenyl	BIP	154	4.01	3.94	0.01	3.87	0.05	nm		17	0.33	nd	
dibenzofuran	DBF	168	4.12	4.03	0.03	4.50	0.05	nm		2.1	0.05	nd	
C1-naphthalenes	N1	142	3.86	3.58	0.02	3.51	0.06	nm		264	19	288	229
C2-naphthalenes	N2	156	4.37	3.84	0.03	3.70	0.05	3.59	0.04	95	11	186	78
C3-naphthalenes	N3	170	4.83	4.32	0.03	4.17	0.07	3.64	0.11	20	0.19	nd	
C4-naphthalenes	N4	184	5.31	4.77	0.03	4.45	0.05	3.73	0.07	3.2	0.27	nd	
1-methylnaphthalene	1MN	142	3.86	3.54	0.03	3.48	0.04	3.32	0.07	101	3.5	nd	
2-methylnaphthalene	2MN	142	3.86	3.57	0.02	3.50	0.04	3.36	0.06	139	4.7	nd	
2,6-dimethylnaphthalene	DMN	156	4.37	3.88	0.02	3.73	0.05	nm		19.5	0.8	nd	
2,3,5-trimethylnaphthalene	TMN	170	4.83	4.37	0.02	4.21	0.07	nm		2.31	0.09	nd	
acenaphthylene	Acy	152	3.94	3.76	0.03	3.71	0.07	3.78	0.06	0.96	0.08	nd	
acenaphthene	Ace	154	3.92	3.71	0.03	3.62	0.05	3.50	0.04	1.40	0.17	nd	
fluorene	F	166	4.18	3.87	0.02	3.79	0.05	3.83	0.12	9.2	0.65	nd	
C1-fluorenes	F1	180	4.97	4.28	0.03	4.21	0.07	4.09	0.10	3.2	0.28	nd	
C2-fluorenes	F2	194	5.21	4.54	0.03	4.60	0.09	4.50	0.12	2.50	0.25	nd	
C3-fluorenes	F3	208	5.50	4.97	0.03	4.89	0.07	4.74		0.94	0.11	nd	
1-methylfluorene	1MF	180	4.97	4.33	0.02	4.25	0.03	nm		2.11	0.08	nd	
dibenzothiophene	D	184	4.38	3.95	0.02	3.87	0.05	nm		2.3	0.09	nd	
C1-dibenzothiophenes	D1	198	4.84	4.49	0.02	4.44	0.04	nm		2.4	0.17	nd	
C2-dibenzothiophenes	D2	212	5.49	5.17	0.03	5.05	0.08	nm		0.71	0.091	nd	
C3-dibenzothiophenes	D3	226	5.76	5.38	0.03	5.40	0.13	nm		0.27	0.035	nd	
C4-dibenzothiophenes	D4	240	6.32	5.85	0.03	5.76	0.12	nm		0.043	0.007	nd	
phenanthrene	P	178	4.46	4.22	0.01	4.17	0.04	4.20	0.07	9.30	0.73	nd	
C1-phenanthrenes/anthracenes	P1	192	5.09	4.66	0.02	4.56	0.08	4.48	0.10	5.1	0.47	nd	
C2-phenanthrenes/anthracenes	P2	206	5.55	5.05	0.03	4.97	0.08	4.90	0.08	1.8	0.12	nd	
C3-phenanthrenes/anthracenes	P3	220	6.06	5.48	0.03	5.40	0.06	5.31	0.07	0.34	0.041	nd	
C4-phenanthrenes/anthracenes	P4	234	6.50	6.09	0.03	5.85	0.08	5.41	0.07	0.08	0.016	nd	
1-methylphenanthrene	1MP	192	5.09	4.69	0.02	4.59	0.05	nm		1.01	0.04	nd	
2-methylphenanthrene	2MP	206	5.09	4.59	0.01	4.55	0.04	nm		nm		nm	
3-methylphenanthrene	3MP	220	5.09	4.64	0.02	4.52	0.04	nm		nm		nm	
anthracene	AN	178	4.54	4.35	0.01	4.28	0.07	4.31	0.09	0.25	0.042	nd	
2-methylanthracene	2MAN	192	4.99	4.70	0.02	4.50	0.05	nm		nm		nm	
fluoranthene	FL	202	5.16	4.71	0.02	4.66	0.06	4.54	0.09	0.03	0.008	nd	
pyrene	PY	202	5.00	4.74	0.02	4.59	0.08	4.55	0.09	0.15	0.009	nd	
C1-fluoranthenes/pyrenes	FP1	216	5.55	5.15	0.03	5.04	0.11	4.90	0.11	0.22	0.014	nd	
C2-fluoranthenes/pyrenes	FP2	230	6.01	5.60	0.04	5.52	0.12	nm		0.14	0.021	nd	
C3-fluoranthenes/pyrenes	FP3	244	6.50	5.89	0.05	5.85	0.14	nm		0.05	0.008	nd	
benz[a]anthracene	BaA	228	5.76	5.42	0.04	5.38	0.08	5.47	0.10	nd		nd	
retene	Re	234	6.35	5.77	0.02	5.71	0.09	nm		nm		nm	
chrysene	C	228	5.73	5.49	0.02	5.41	0.08	5.44	0.12	0.087	0.012	nd	
C1-chrysenes	C1	242	6.20	5.83	0.03	5.75	0.14	5.60		0.066	0.011	nd	
C2-chrysenes	C2	256	6.62	6.09	0.03	6.01	0.11	5.89		0.031	0.006	nd	
C3-chrysenes	C3	270	6.95	6.41	0.04	6.35	0.09	6.18		0.018	0.004	nd	
C4-chrysenes	C4	284	8.00	7.28	0.04	7.09	0.12	6.47		nd		nd	
benzo[b]fluoranthene	BbF	252	6.11	5.84	0.03	5.79	0.04	5.80	0.03	nd		nd	
benzo[k]fluoranthene	BkF	252	6.11	5.87	0.04	5.82	0.09	5.99	0.31	nd		nd	
benzo[a]pyrene	BaP	252	6.19	5.92	0.03	5.86	0.04	5.96	0.03	nd		nd	
benzo[e]pyrene	BeP	252	6.19	5.90	0.03	5.89	0.03	5.67	0.03	nd		nd	
perylene	PER	252	6.50	6.21	0.03	6.13	0.04	6.04	0.05	nd		nd	
indeno[1,2,3-c,d]pyrene	IDP	267	6.85	6.50	0.03	6.38	0.04	6.16	0.03	nd		nd	
dibenz[a,h]anthracene	DBA	278	6.91	6.55	0.04	6.47	0.05	6.30	0.12	nd		nd	
benzo[g,h,i]perylene	BgP	276	7.13	6.72	0.04	6.67	0.06	6.05	0.16	nd		nd	
coronene	COR	300	7.24	6.82	0.04	6.71	0.08	nm		nd		nd	
1,4-naphthoquinone	NQO	158	1.66	1.58	0.05	1.58	0.05	nm		7.20	3.40	nd	
9-fluorenone	FO	180	3.58	3.40	0.04	3.40	0.04	nm		nd	nd	nd	
9,10-anthraquinone	AQO	208	3.39	3.17	0.05	3.17	0.05	nm		nd	nd	nd	
benzofluorenone	BFO	230	4.70	4.44	0.05	4.44	0.05	nm		nd	nd	nd	

SD: Standard deviation; nd: not detected; nm: not measured

Table 2. Time to reach 95% of equilibrium value between water and POM (days) for POM of thickness 20 µm, 50 µm, and 76 µm, and for three different exposure methods. See Table 1 for abbreviations.

PAH	log K_{OW}	Dissolved Standard			Crude Oil			Sediment		
		20µm	55µm	76µm	20µm	55µm	76µm	20µm	55µm	76µm
N	3.37	2	3	4	2	3	4	2-3	2-4	3-5
C	5.73	3	4	5	3	4	5	3-4	4-6	5-7
C3	6.95	NA	NA	NA	3	4	6	4	4-6	5-8
DBA	6.91	3	4	6	3	4	7	5-6	5-8	7-11

Table 3. PAH concentrations and worm mortality before and after addition of activated charcoal (AC).

	Soil (ug/g)	SD	Worm (ug/g lipid)	SD	Worm % mortality	SD	POM (ng/L)	SD
Soil	640	22	174	31	100	0	7600	370
Soil w/ AC	629	28	20	4	0	0	273	41

SD: Standard deviation

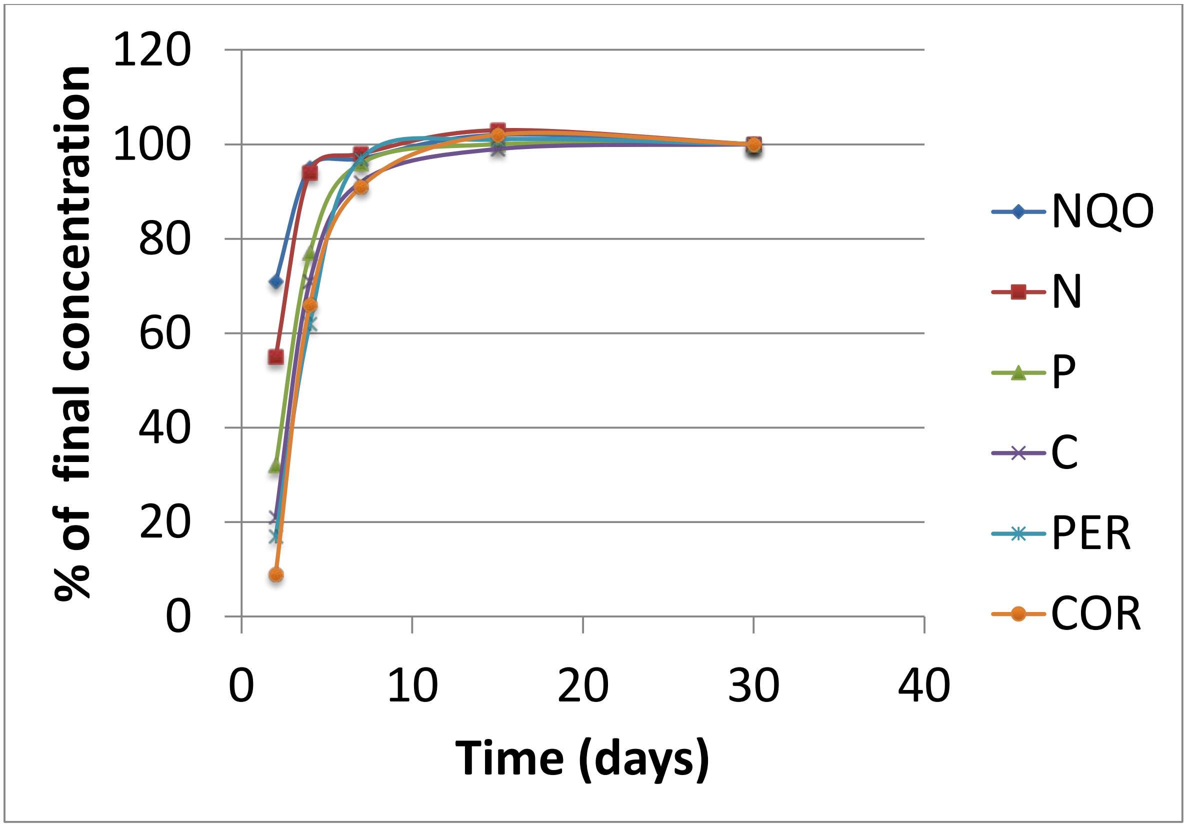

Figure 1. Uptake of PAH to POM in soil-water slurry reached steady state in less than 2 weeks. Abbreviations for PAH are listed in Table 1.

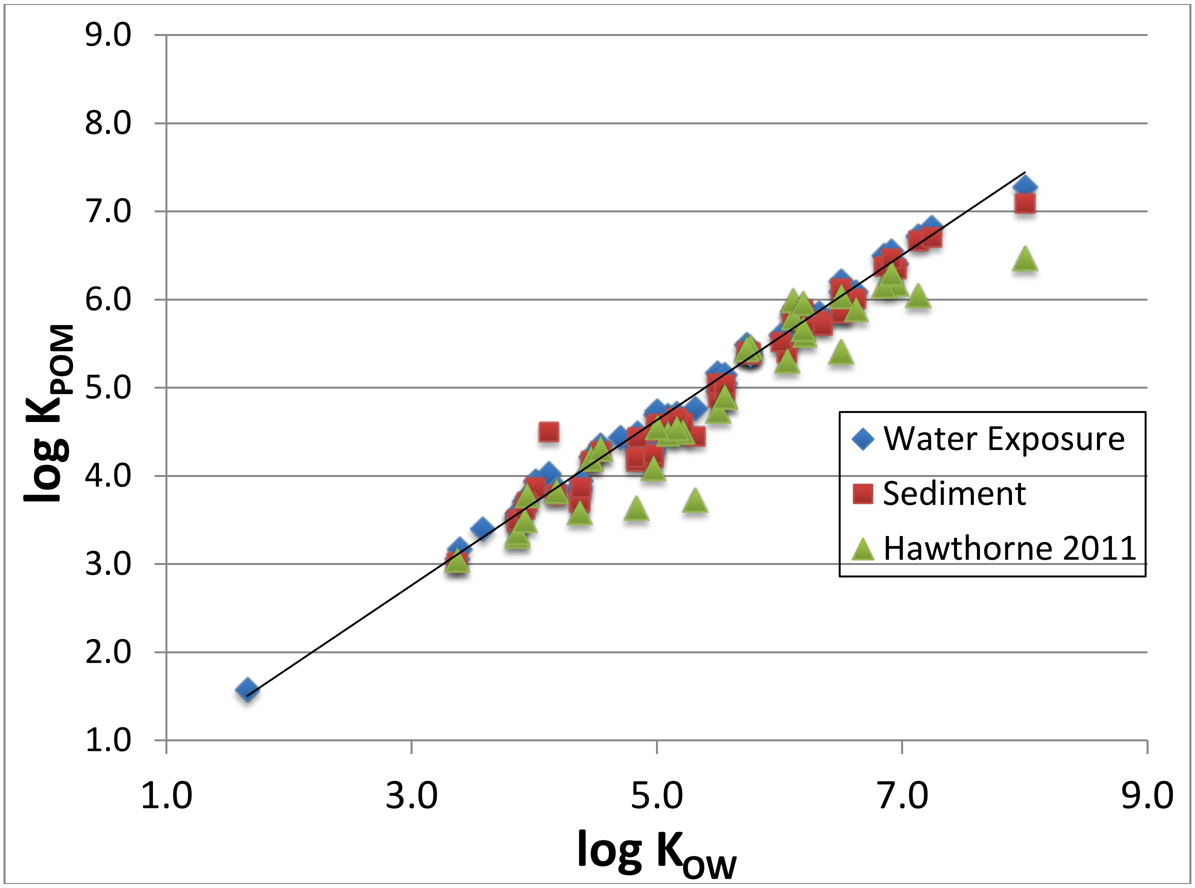

Figure 2. Relationship between log K_{POM} and log K_{OW} for data from this work (Static renewal and Sediment) and data from Hawthorne (2011). The linear regressions for our data were as follows: static renewal (y=0.9367x-0.0487, R^2=0.9857) and sediment exposure (y=0.9309x-0.1007, R^2=0.9655).

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ABBREVIATIONS

PAH, polycyclic aromatic hydrocarbon; oxy-PAH, oxygenated PAH; POM, polyoxymethylene; SPME, solid-phase microextraction; PE, polyethylene; HOCs, hydrophobic organic compounds; NAPL, non-aqueous phase liquids; PSDs, passive sampling devices; PCBs, polychlorinated biphenyls; USEPA, US Environmental Protection Agency; K_{POM}, POM water partition coeffiecient; DOC, dissolved organic carbon; MeOH, methanol; CV, coefficient of variation.

CHAPTER 2. A Univerisal Passive Sampling Device for Simultanenous Measurement of Polar and Non-Polar Pesticides in Water

A Universal Passive Sampling Device for Simultaneous Measurement of Polar and Non-Polar Pesticides in Water

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Abstract

Current-use pesticides are generally less persistent and more polar/hydrophilic chemicals than their chlorinated predecessors. Additionally, acute pesticide poisoning events are very rare and pesticide application rates are very low, so the predominant environmental concern is long-term chronic exposure at very low concentrations of pesticides. This presents new challenges in estimating environmental exposure and assessing human and ecological risks associated with pesticides in aquatic systems. Several types of passive sampling devices (PSDs) have been developed for monitoring chronic chemical exposure in aquatic systems however their use is largely limited to hydrophobic chemicals. There remains a need for a simple, robust method to measure chronic exposure to more polar compounds. A polar organic chemical integrative sampler (POCIS) was developed for hydrophilic organic contaminants, however the POCIS does not provide sufficient quantitative exposure estimates. We have developed a more universal passive sampling device (uPSD), which is composed of a non-selective porous stainless steel cartridge and a mixed-polymer sequestration sorbent. The uPSD has been calibrated in the laboratory for 35 current-use pesticides with log K_{ow} values ranging from 1.49-8.15. We have deployed these samplers at

numerous field sites and chronic exposure estimates using the uPSDs closely match those using sequential grab sampling. We report here on the laboratory calibration and field verification of this new uPSD. We believe this new uPSD should have very broad application to most organic chemicals and has the potential to offer a significant advance in decreasing the uncertainty in risk assessment by increasing our capability to estimate chronic exposure of chemicals in water.

Introduction

The risk of a pesticide eliciting toxicity in a non-target species is a function of the hazard associated with the chemical and the exposure to that chemical (Hodgson book). Traditionally, risk assessments of chemicals in surface water have used grab sampling to estimate exposure. This requires large volumes of water to be collected and extracted in order to have detectable concentrations. This can be cumbersome and only offer a snapshot of the exposure at the moment the sample is collected making this an impractical sampling regime as water concentrations can vary significantly with time. This is particularly true of current-use pesticides due to the episodic nature of seasonal application. Thus, in order to gain an estimate of average chronic exposure, many samples would need to be collected sequentially over the exposure time period and in most cases this proves to be expensive and highly impractical. However, without such an exhaustive sampling plan, grab samples cannot accurately demonstrate the potential chronic exposure to contaminants making an effective time weighted average sampling method integral to estimating chronic exposure to any environmental contaminant. Determining an accurate exposure point concentration is a universal challenge in risk assessment. Use of passive sampling devices or PSDs can reduce the uncertainty associated with exposure assessment, thereby reducing the uncertainty of the overall risk assessment.

Since their development roughly 20 years ago, passive sampling devices have greatly improved environmental monitoring efforts providing both qualitative and quantitative data to describe the extent of environmental exposure. Several types of passive sampling devices (PSDs) have been developed for monitoring chronic chemical exposure in aquatic systems however, their use is largely limited to hydrophobic chemicals [1]. Traditional sampling methods have focused on generating qualitative data while attempting to identify the chemical suite of exposure [2]. Passive sampling devices (PSDs), such as the semi-permeable membrane device (SPMD) were developed to quantitatively evaluate chemical loads with greater precision and increased sampling specificity for various classes of compounds [1, 3]. Many of the PSDs were designed to target compounds sharing similar chemical properties and have been shown to work very well with hydrophobic organic compounds such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and various other organochlorines and organophosphates [4, 5]. However, there are still difficulties associated with sampling polar, ionic chemicals and current PSD designs do not adequately address this shortcoming.

The organic version of the Chemcatcher and the polar organic chemical integrative sampler (POCIS) were developed for hydrophilic organic contaminants; however neither provide sufficient quantitative exposure estimates [6, 7]. The organic version of the

Chemcatcher combines a 47-mm C18 Empore disk as the receiving phase with a polyethersulphone diffusion-limiting membrane [6]. The Chemcatcher has been calibrated and used to look for a limited suite of 10 polar and semi-polar pesticides however it displays a limited linear uptake of 14 days and in the field, displayed high biofouling with no way to account for the resulting changes in sampling rates as it was concluded that the Chemcatcher did not show elimination of performance reference compounds or PRCs from the receiving phase in a laboratory calibration [8, 9]. The POCIS is comprised of a sequestration medium sandwiched between two thin polyethersulfone membranes [7]. The POCIS has been demonstrated to work well for compounds with a log K_{ow} less than 3 such as herbicides, pharmaceuticals and personal care products [10, 11]. Nevertheless, the POCIS is faced with its own set of weaknesses. Specifically, there is very little sampling rate data available for the POCIS making quantitative assessments difficult. The thin polyethersulfone membrane can be easily punctured during field deployment or even during laboratory extraction. Also the POCIS is subject to biofouling which can cause a deficit in uptake to occur [12] and most importantly, correcting for the biofouling or sheer flow effects by using performance reference compounds (PRCs) is complicated due to the strong sorptive properties of the sorbent medium used in the POCIS and matrix effects during quantification [13].

Our lab has developed a novel universal passive sampling device (uPSD) that offers a solution to many of these problems. The uPSD concentrates very low levels of chemicals to detectable levels while providing a time weighted average sample, and this work has demonstrated these uPSDs to have linear uptake rates with similar, consistent sampling rates. They have a relatively simple extraction procedure and their stainless steel casing offers a more durable alternative to what is currently available. In this paper, we report on the laboratory calibration and field verification of this new uPSD for 35 current-use pesticides with log K_{ow} values spanning a range from 1.49-8.15.

Experimental Section

Materials. The uPSDs were assembled using 10µm inlet filters (Alltech Associates, Deerfield, IL, USA), packed with 200 mg Oasis® HLB sorbent with a particle size of 60 µm and specific surface area of 810 m^2/g (Waters Corporation, Milford, MA, USA), which was equivalent to approximately half of the total volume of the stainless steel cartridge (Figure 1). They were then enclosed with a stainless steel screw. The uPSDs used in the laboratory and field studies had an external diameter of 1.25 cm and were 2.8 cm in length, resulting in an internal surface area of approximately 6.19 cm^2. Prior to calibration experiments, uPSDs were washed using a total of 60 mL Ultra Resi-Analyzed® Dichloromethane (DCM) (J. T. Baker, Deventer, The Netherlands) in 20 mL vials and shaken on a digital orbital shaker (IKA Works, Wilmington, NC) at 180 rpm at 23°C for three one-hour repeats. The 35 current-use pesticides (AccuStandard, New Haven, CT, USA) were selected to represent the wide range of chemical properties in environmental exposure (Table 1). Other solvents used included GC$^{2®}$–grade ethyl acetate (Burdick & Jackson, Muskegon, MI, USA) and GC-grade methanol (Burdick & Jackson, Muskegon, MI, USA). All materials were solvent rinsed and baked at 300˚C overnight.

System Design and Calibration Experiment. A stock solution of 10 µg/L was prepared using the 35 selected current use pesticides in a 4L amber glass bottle. A flow-through system was constructed using an HP 1512 HPLC pump (Hewlett Packard) to mix the concentrated stock solution with water to produce a constant flow of 6mL/min diluted solution into second 4L amber glass bottle which acted as a reservoir to hold the uPSDs; ultimately the exposure concentration was diluted to 100ng/L using D.I. water. The reservoir bottle was sealed air-tight with a stopper through which the feeding line and an effluent line were connected. The effluent line led to a sink for discharge and water sample collection. The pump and transfer lines were all made of non-absorption materials (diamond pump piston, stainless steel pump, Teflon tubes) and were flushed with acetone for 10 min to clean the flow contacting surfaces. The exposure bottle was fastened to an HS 501 D shaker table (Janke & Kunkel, Stauffen, Germany) set at a constant speed of 150rpm (23°C) to simulate the turbulence of the aquatic environments for the duration of the exposure. At this shaking speed the shear flow across the uPSD surface is approximately 20 cm s^{-1}. The uptake experiment spanned 30 days, with uPSDs sampled in triplicate after 1, 5, 10, 15, 20, 25, and 30 day cumulative exposures. Water samples (1 L) were collected in triplicate every 48 hours.

Sample Preparation and Processing. Prior to extraction, excess water was removed from uPSDs by centrifugation at 3000 rpm for 20 minutes at 23°C. Individual uPSDs were extracted twice using a total of 40mL of dichloromethane (DCM) for a total extraction time of 2 hours, shaking in 20mL vials at 180rpm, dried through a column containing anhydrous sodium sulfate (Na_2SO_4), and then concentrated to an autosampler vial by nitrogen evaporation at 35°C under 5psi for two one-hour repeats prior to analysis. Water samples collected for laboratory calibrations were extracted 3M Empore®C18 (47mm) disks using methanol to prepare the disk. Dichloromethane was used to extract the disk, using a Whatman® UNIPREP (0.45µm PTFE membrane) to further filter the sample prior to transfer to autosampler vials. Water samples collected in the field were processed in the same way except they were first filtered through a 0.7 µm glass fiber filter (Whatman GF/C).

Instrumental Analysis. Samples were analyzed for current use pesticides using an Agilent 6890 GC equipped with a Restek RTX-5MS 30m × 0.25mm (0.25µm film thickness) 5m Integra-Guard column, connected to an Agilent 5973 mass selective detector operated in selected ion monitoring (SIM) mode. After one minute, injection carrier gas pressure was dropped and flow was kept constant for the duration of the run at 1mL/min. The temperature program for the current use pesticides was as follows: initial temperature 40ºC for one minute with ramps of 30ºC/min to 100ºC, 5ºC/min to 250ºC, and 30ºC/min to a final temperature of 310, held for 5 minutes; transfer line temperature 300ºC; MS source heated to 230ºC; quadrupole heated to 150ºC. The SIM ions (m/z) monitored are provided in supplementary materials.

Competition Experiment. In order to address the potential for competition of adsorption sites on the Oasis HLB, a second 30-day uptake experiment was conducted concurrently under identical conditions as the first. Materials, system design, uPSD preparation and processing and instrumental analysis were all identical to that of the calibration experiment. To simulate a competition scenario the stock solution consisted of 10 ug/L of the 35 selected current use pesticides and 1 mg/L malathion (AccuStandard, New Haven, CT, USA) as the competitive sorbate, diluted for an ultimate exposure concentration of 100 ng/L current use pesticide and 100 ug/L malathion. This experiment was followed by an uptake experiment of all 35 pesticides conducted as above with DI water, except using water collected from a freshwater pond instead to simulate the potential competition from natural organic matter (DOC = 8.4 mg/L) and possible uPSD pore blockage by suspended solids (TSS = 8.2 mg/L).

Data Quality Assessment. Surrogate internal standards (SIS) were fortified into every sample to help assess the recovery of target analytes and thus the accuracy of the analytical method. The recoveries of the SIS ranged from 68-104%, indicating that the method very likely adequately recovered all target analytes. Analytical data were not corrected for the SIS recoveries. Procedural blanks and matrix spikes were run with each batch of 10-15 uPSD and water samples in order to determine background contamination and to help assess precision and accuracy of the analytical methods. All procedural blanks contained non-detectable target pesticides. The matrix spikes showed acceptable recovery with a range of 40 – 90%, with most being above 85%. Matrix spike duplicates and samples duplicates all had relative percent differences less than 16%, indicating excellent precision.

Field Deployment. The uPSDs were deployed at several sites in China and this work is described in detail elsewhere [15]. Briefly, the uPSDs were deployed in triplicate in surface waters receiving agricultural drainage for 29 days while single grab samples were collected every other day during the deployment. For this paper, we focused on an area of high atrazine use where 13 sites were sampled along a gradient from the atrazine source downstream to diluted waters. Water samples were placed on ice or in a refrigerator at 4ºC and were filtered and extracted as described above with 48 hours of collection. The uPSDs were placed in clean foil and polyethyelene bags and on ice. They were stored frozen at -20ºC until extraction and analysis as described above within 30 days of sample collection.

Results and Discussion

Uptake of current use pesticides by uPSDs. Table 1 presents some of the physicochemical properties and the sampling rates of the 35 selected current use pesticides. These pesticides were selected because they are commonly detected in surface waters and offer a broad range of log K_{ow} values. The uPSDs performed exceptionally well and this range demonstrates the nearly universal nature of the uPSD to detect chemicals with varying physicochemical properties. The use of PSDs to estimate aqueous concentrations requires them to be calibrated by measuring uptake rate constants for the device under controlled conditions and then estimating the dissolved concentrations using the following equation that has been derived by others [14]:

$$C_{W,fd} = C_{PSD} / k_e t \qquad (1)$$

where $C_{W,fd}$ is the concentration of the chemical freely dissolved in water (ngL^{-1}), C_{PSD} is the concentration of the chemical in the PSD (ngL^{-1}), k_e is the first-order exchange (uptake) rate constant ($Lg^{-1}d^{-1}$), and t is the time period the PSD is deployed.

Equation 1 assumes linear uptake. For equation 1 to be valid, deployments must occur over a sufficient duration to reduce the contribution of initial uptake demonstrating nonzero intercepts. All 35 current-use pesticides investigated demonstrated linear uptake across the 30-day period (Table 1). Uptake curves for six representative pesticides ranging in log K_{ow} from 1.49 to 7.43 are shown in Figure 2 with some variability among curves. Water concentrations remained relatively constant throughout the duration of the experiment as confirmed by analysis of water samples. Additional uptake graphs are shown in Supplementary Materials.

Previous work conducted in our lab has demonstrated that flow rate has little to no effect on uptake kinetics (k_e) of the uPSD until very high flows (>50 cm/s) are achieved (X. Kong, personal communication). Due to the design, the porous stainless steel cartridge and the water boundary layer do not have specific selectivity towards any compound, therefore the exchange does not occur on the surface membrane of the uPSD but rather in the slurry mixture of sorbent inside the sampler. This design also offers a novel protection against biofouling. Since the exchange is happening inside and not at the surface of the uPSD, biofouling will not affect the sampling rate as long as water can still penetrate the sampler.

Sampling Rates. Sampling rates (R_s) measured in L/d were calculated using the equation:

$$C_{w,fd} = N_{uPSD}/R_s t \qquad (2)$$

where N_{uPSD} (ng) is the amount of chemical taken in by the uPSD. Calculating a R_s in this manner assumes a constant C_w. This assumption was verified by collecting and measuring water samples every other day (Figure 2). The sampling rates ranged 0.282 – 1.14 Ld^{-1} (Table 1 and Figure 3) with an average sampling rate of 0.464 Ld^{-1}. Sampling rates were generally constant and demonstrated low variability overall indicating that sampling rate does not appear to be a function of the log K_{ow} and results will be reproducible in the field.

The relatively low range of sampling rates compared to other PSDs, approximately a factor of four, indicates that semi-quantitative analysis could be performed on other chemicals for which sampling rates have yet to be determined.

Competition Experiments. The results of the competition experiments are shown in Figures 4 and 5. In the presence of 100 μg/L of malathion as the competitive sorbate, there was generally a decrease in the sampling rate (Figure 4) but this effect was not statistically significant for any of the pesticides (using one-way ANOVA, $p < 0.05$). Although statistically not significant, there was an apparently greater effect with the more hydrophilic pesticides of lower log K_{OW} values (those toward the left side of Figure 4). This would be consistent with the hypothesis that if competition were to occur, it would be most evident for those chemicals whose sorption mechanism were influenced most by surface adsorption compared to those more hydrophobic chemicals whose sorption would be dominated by partitioning into the hydrophobic phase of the sorbent (those pesticides toward the right side of Figure 4). The competitive sorbate malathion would have significant surface adsorption versus hydrophobic partitioning.

The competition experiments using natural lake water fortified with the pesticides (Figure 5) also exhibited no statistically significant difference compared to uptake experiments using deionized water (using one-way ANOVA, $p < 0.05$). Again, what small effect that was visually apparent was somewhat greater with the more hydrophilic pesticides, but this effect was more variable than with that seen for just the malathion.

In summary, given no statistically significant competitive effect for very high concentrations of malathion or for relatively high DOC and TSS in natural lake water. It appears that sampling rates for these pesticides are not affected by competition under conditions that would be expected in natural waters. Given the wide range of log K_{OW} values for the chemicals tested, this indicates that the uPSD should be unaffected by competition for most other organic chemicals as well.

Comparison of uPSDs to Grab Samples in the Field. The concentration of atrazine measured in grab samples collected every other day was compared to the mean of triplicate uPSDs deployed over the same period at a single location (Figure 6). Two rain events are indicated that resulted in runoff of atrazine to the stream where samples were collected. While the grab samples exhibited a nearly 1000-fold range in measured concentrations, the mean of these grab samples was not statistically different from the mean of the three uPSD replicates (using one-way ANOVA, $p < 0.05$). This illustrates the temporal changes that can take place and the temporal information that repeated grab sampling can provide. However, given that even the highest atrazine concentration measured was well below known acute toxicity thresholds, it is the chronic exposure that is of greatest interest and the uPSD provided a statistically equivalent estimate of chronic exposure compared to the repeated grab sampling – at a fraction of the effort and cost. We estimate that the cost associated with the repeated grab sampling and analysis of those samples was approximately 10-fold higher than that of the uPSD sampling and analysis. This graph also illustrates the substantial error in the chronic exposure estimate that would exist if one were to sample only at times of lowest or highest exposure.

The data in Figure 6 were from the sampling site closest to the source of atrazine. We also deployed uPSDs for one month and sampled the water every two days at 12 other sites on a gradient downstream from this source of atrazine. The results are shown in Figure 7, where the mean and standard deviation of the 15 grab samples collected over 29 days are plotted on the x-axis and the mean and standard deviation of the uPSDs deployed for the same 29 days are plotted on the y-axis. There is about a two order of magnitude difference in the concentration of atrazine as you move away from the source (from the upper right to lower left in the graph). There is a good linear relationship between the grab sample means and the uPSD means (r^2 = 0.9235). The slope is 0.76 indicating that the uPSD is estimating approximately 75% of the mean from the grab samples. This is not a statistically significant difference, but it is consistent with a general slightly lower estimate using uPSDs compared to grab samples. One very important feature that also is evident is the much greater variability associated with the grab samples compared to the uPSDs. This is indicative of the temporal changes noted above and in Figure 5.

Conclusions

The uPSD we have developed and reported on here has been calibrated in the laboratory for 35 current-use pesticides with log K_{ow} values ranging from 1.49-8.15 and yielding sampling rates with low variability. Competitive sorption from other pesticides or natural DOC or TSS does not appear to effect these sampling rates. A field comparison of the uPSDs with sequential grab sampling over one month in atrazine contaminated waters resulted in excellent agreement on estimated chronic exposure with the uPSD having approximately 10% of the cost of the grab sampling. Given the wide range of physicochemical properties embodied within these 35 pesticides, we believe this new uPSD should have very broad application to most organic chemicals and has the potential to offer a significant advance in decreasing the uncertainty in risk assessment by increasing our capability to estimate chronic exposure of chemicals in water.

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Table 1. Summary of sampling rates for 35 current use pesticides. These were determined by solving for the sampling rate (R_s) using $C_{w,\,fd} = N_{uPSD}/R_s t$ where $C_{w,\,fd}$ is the freely dissolved pesticide concentration (ng/L) in water, N_{uPSD} is the mass (ng) of pesticide sorbed by the uPSD at time t (days).

Chemical	log K_{ow}	Sampling Rates Rs ($L\ d^{-1}$)	Overall H2O Average (ng/L)
Metribuzin	1.49	0.34 ± 0.19	33.58 ± 9.06
Methidathion	1.58	0.48 ± 0.25	31.48 ± 9.08
Malathion	2.29	0.44 ± 0.25	47.28 ± 12.35
Carbofuran	2.30	0.35 ± 0.19	22.14 ± 6.14
Carbaryl	2.35	0.37 ± 0.20	46.09 ± 11.92
Simazine	2.40	0.28 ± 0.15	47.87 ± 12.24
Phosmet	2.48	0.57 ± 0.34	27.08 ± 8.23
Captan	2.74	1.14 ± 1.00	1.08 ± 1.96
Methyl Parathion	2.75	0.39 ± 0.22	20.95 ± 5.45
Atrazine	2.82	0.30 ± 0.12	47.98 ± 12.32
Ethoprop	3.14	0.28 ± 0.15	40.31 ± 9.66
Metolachlor	3.24	0.30 ± 0.15	49.45 ± 12.52
Fenamiphos	3.29	0.81 ± 0.50	6.88 ± 5.08
Phorate	3.37	0.41 ± 0.24	13.53 ± 4.92
Alachlor	3.37	0.33 ± 0.15	41.57 ± 10.34
Chlorothalonil	3.66	0.31 ± 0.15	33.60 ± 9.03
Prometryn	3.73	0.31 ± 0.14	43.61 ± 11.46
Diazinon	3.86	0.31 ± 0.10	40.27 ± 8,74
Disulfoton	3.86	0.34 ± 0.18	15.32 ± 5.90
Propiconazole	4.13	0.92 ± 0.62	18.12 ± 7.52
Terbufos	4.24	0.41 ± 0.20	11.92 ± 3.75
Chlorpyrifos	4.66	0.32 ± 0.13	36.77 ± 7.75
Pendimethalin	4.82	0.41 ± 0.24	19.50 ± 4.94
Ethalfluralin	5.23	0.37 ± 0.14	19.57 ± 4.43
Trifluralin	5.31	0.39 ± 0.16	18.91 ± 4.65
Benfluralin	5.31	0.38 ± 0.16	19.31 ± 4.85
Fenpropathrin	5.62	0.34 ± 0.21	24.01 ± 8.49
Cyfluthrin	5.74	0.45 ± 0.22	13.54 ± 6.74
Tribufos	5.75	0.41 ± 0.21	24.23 ± 9.23
Deltamethrin	6.18	0.73 ± 0.39	4.17 ± 1.63
Cypermethrin	6.38	0.51 ± 0.26	11.42 ± 5.95
Esfenvalerate	6.76	1.13 ± 1.31	3.65 ± 2.32
Cyhalothrin (lambda)	6.85	0.57 ± 0.34	4.21 ± 2.43
Permethrin	7.43	0.53 ± 0.19	9.71 ± 4.24
Bifenthrin	8.15	0.31 ± 0.16	3.26 ± 1.31

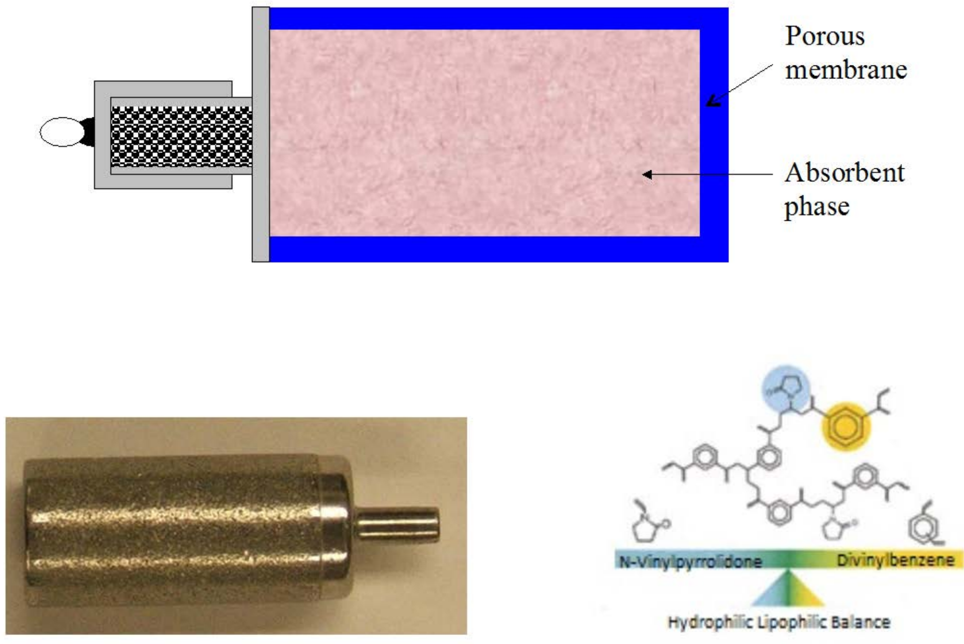


Figure 1. Diagram and picture of the uPSD, with chemical structure of the sorbent phase (lower right).

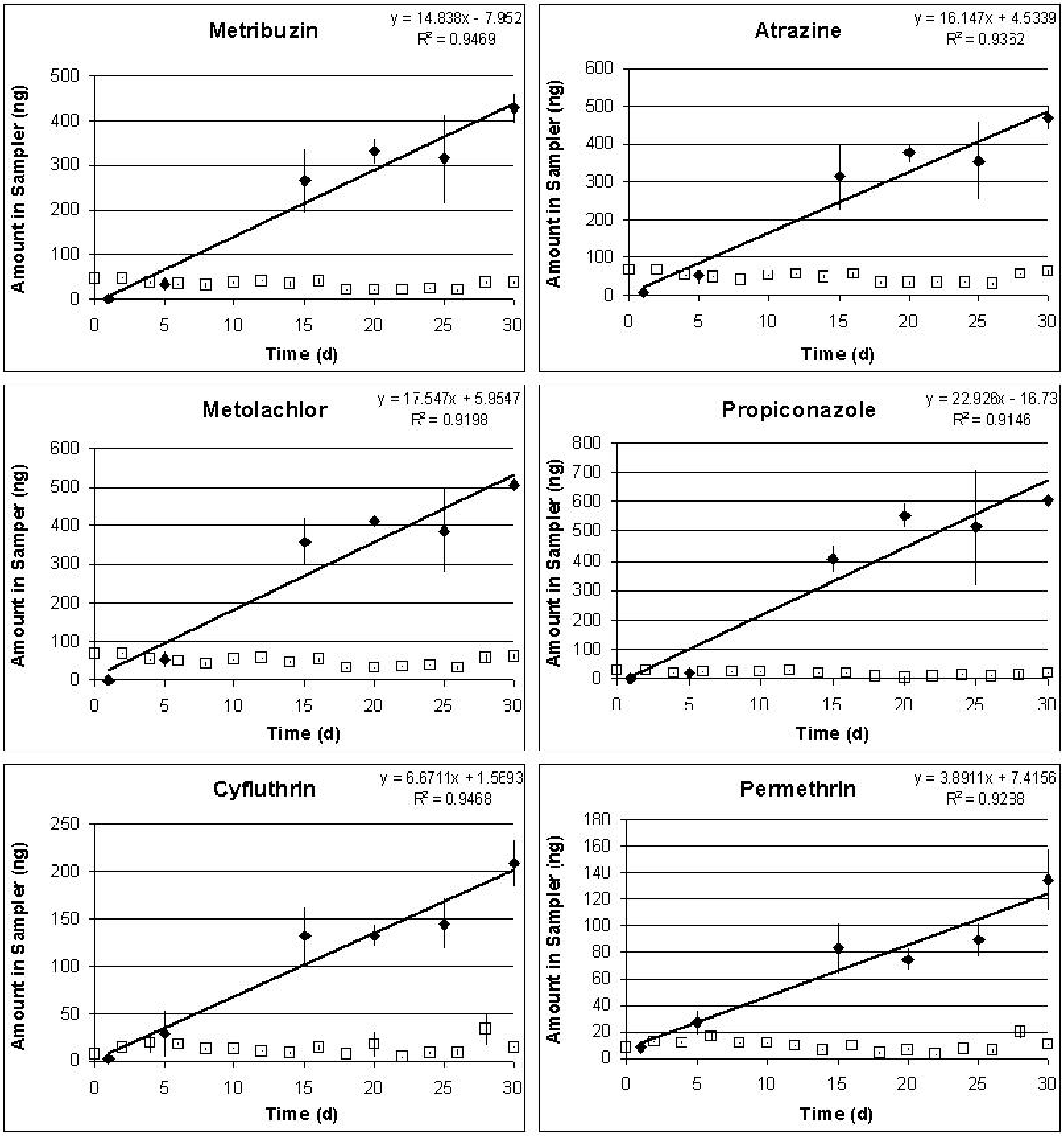


Figure 2. Uptake curves and exposure concentrations in water for six representative pesticides: Metribuzin, Atrazie, Metolachlor, Propiconazole, Cyfluthrin, and Permethrin. Solid diamonds (♦) represent the mean concentration in the uPSD (n = 3) and open squares (□) represent the exposure concentrations (n = 3). Additional uptake curves are provided in supplementary material.

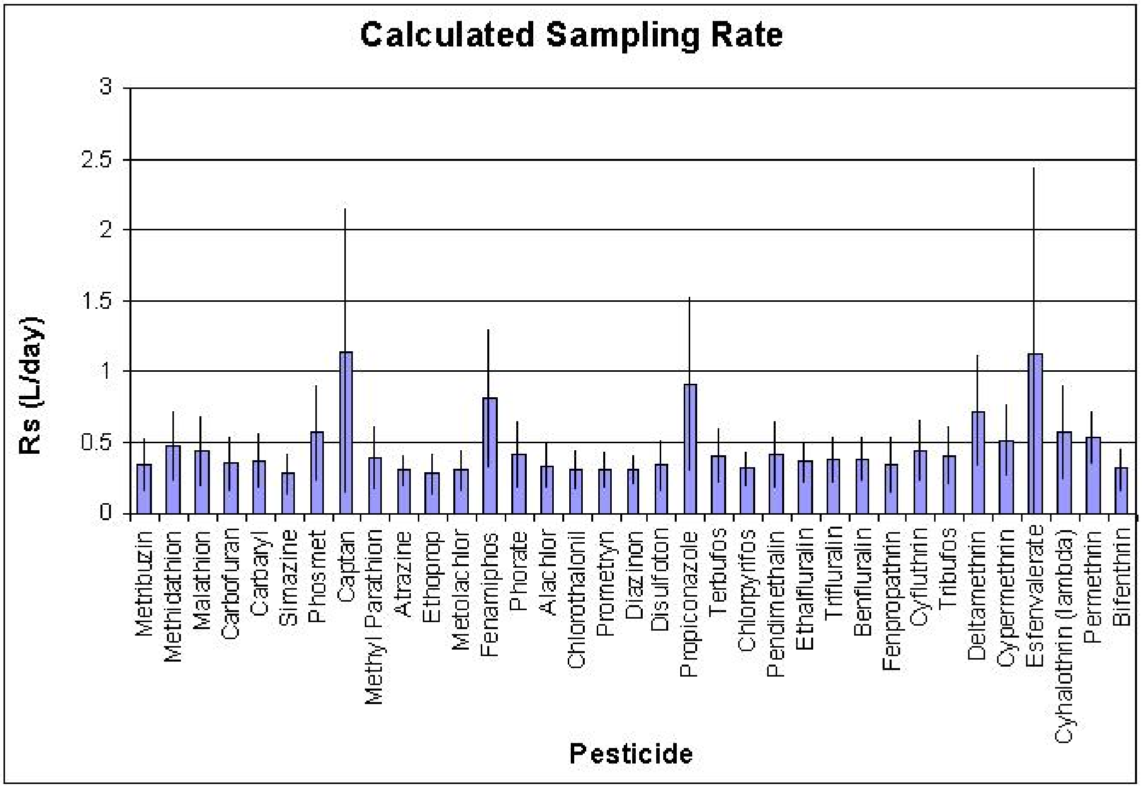


Figure 3. Sampling Rates for 35 current use pesticides arranged in order of increasing log K_{ow}.

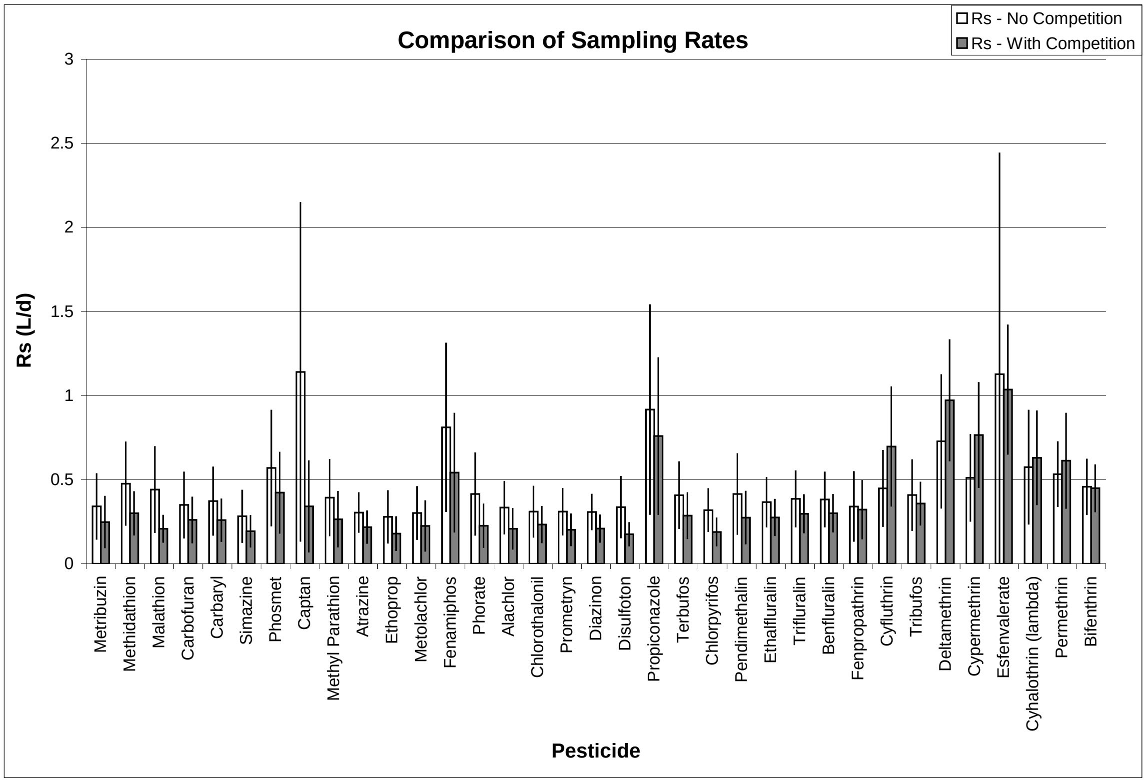


Figure 4. The effect of potential competition for surface adsorbent sites using 100 μg/L of malathion as the competitive sorbate.

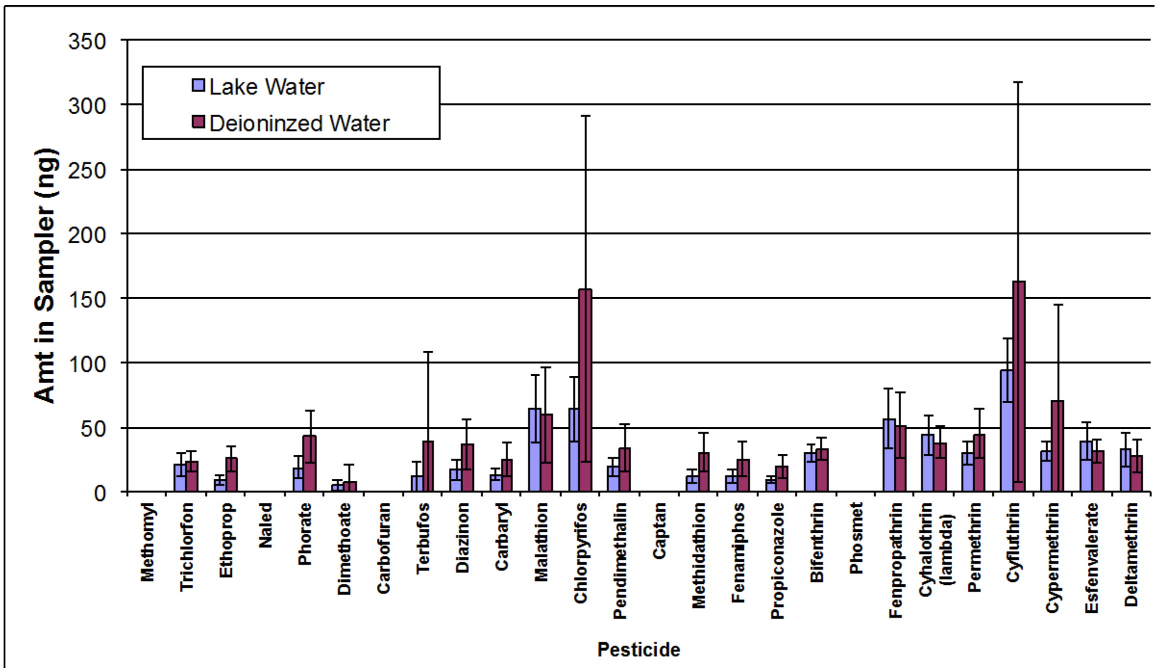


Figure 5. The effect of potential competition of naturally occurring organic matter (DOC = 8.4 mg/L) and suspended solids (TSS = 8.2 mg/L) in natural lake water on the amount of pesticide sorbed by the uPSD.

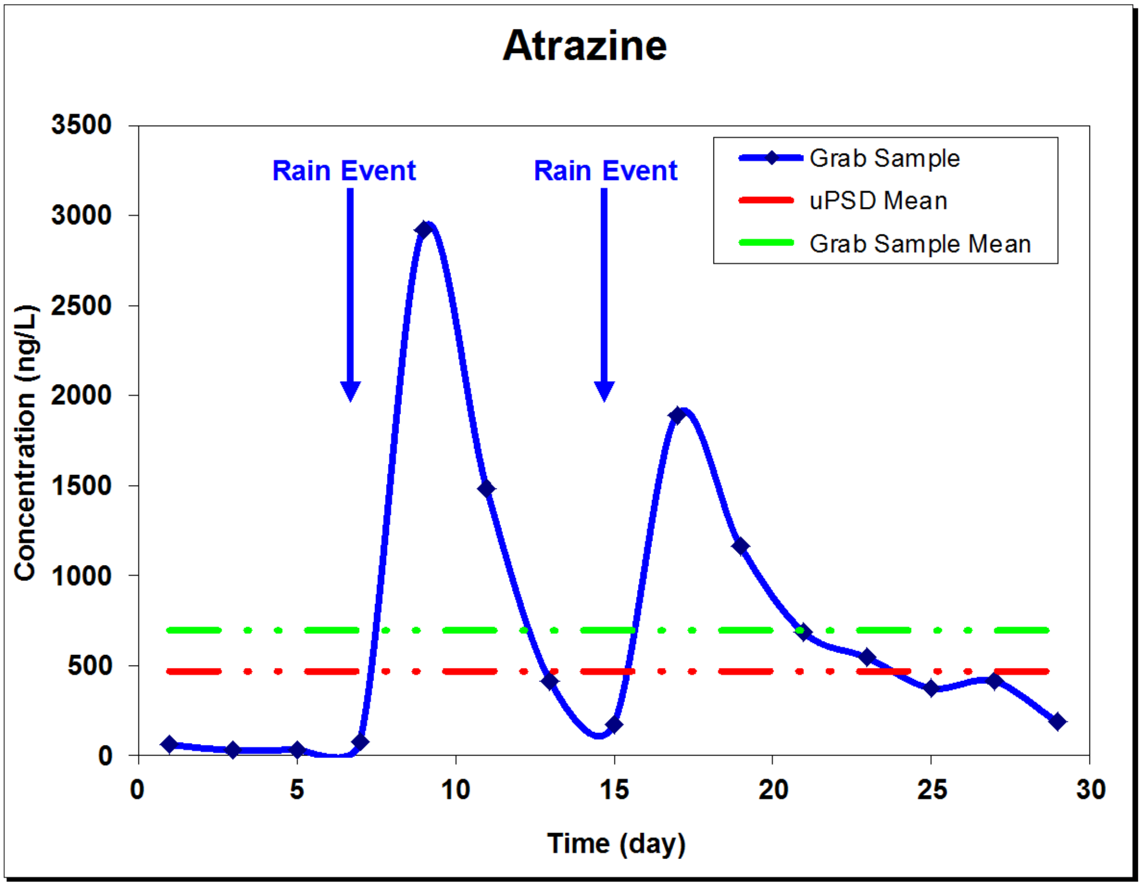


Figure 6. Comparison of the atrazine concentration measured in grab samples collected every other day to the mean of triplicate uPSDs deployed over the same period at a single location. Two rain events are indicated that resulted in runoff of atrazine to the stream where samples were collected.

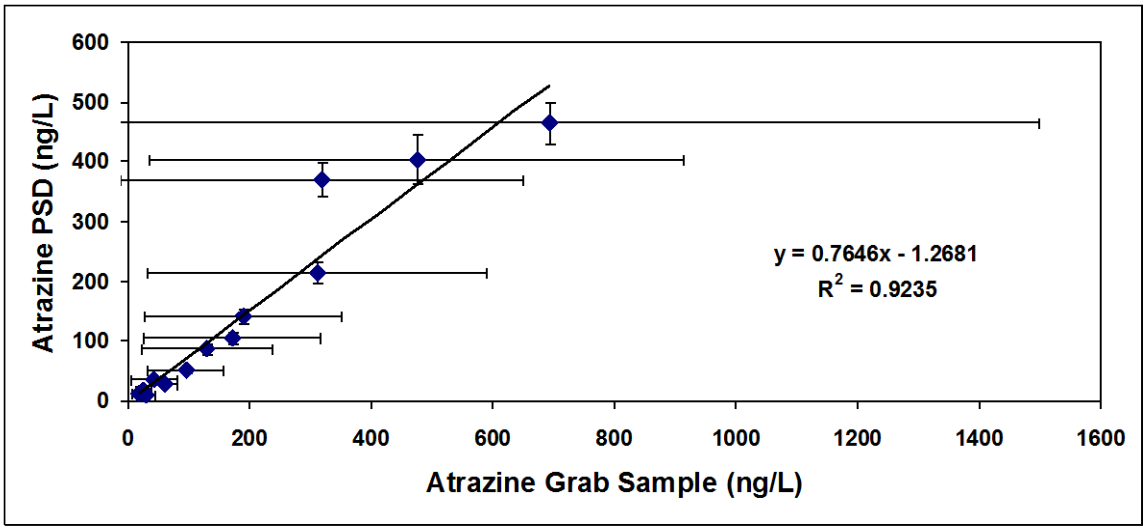
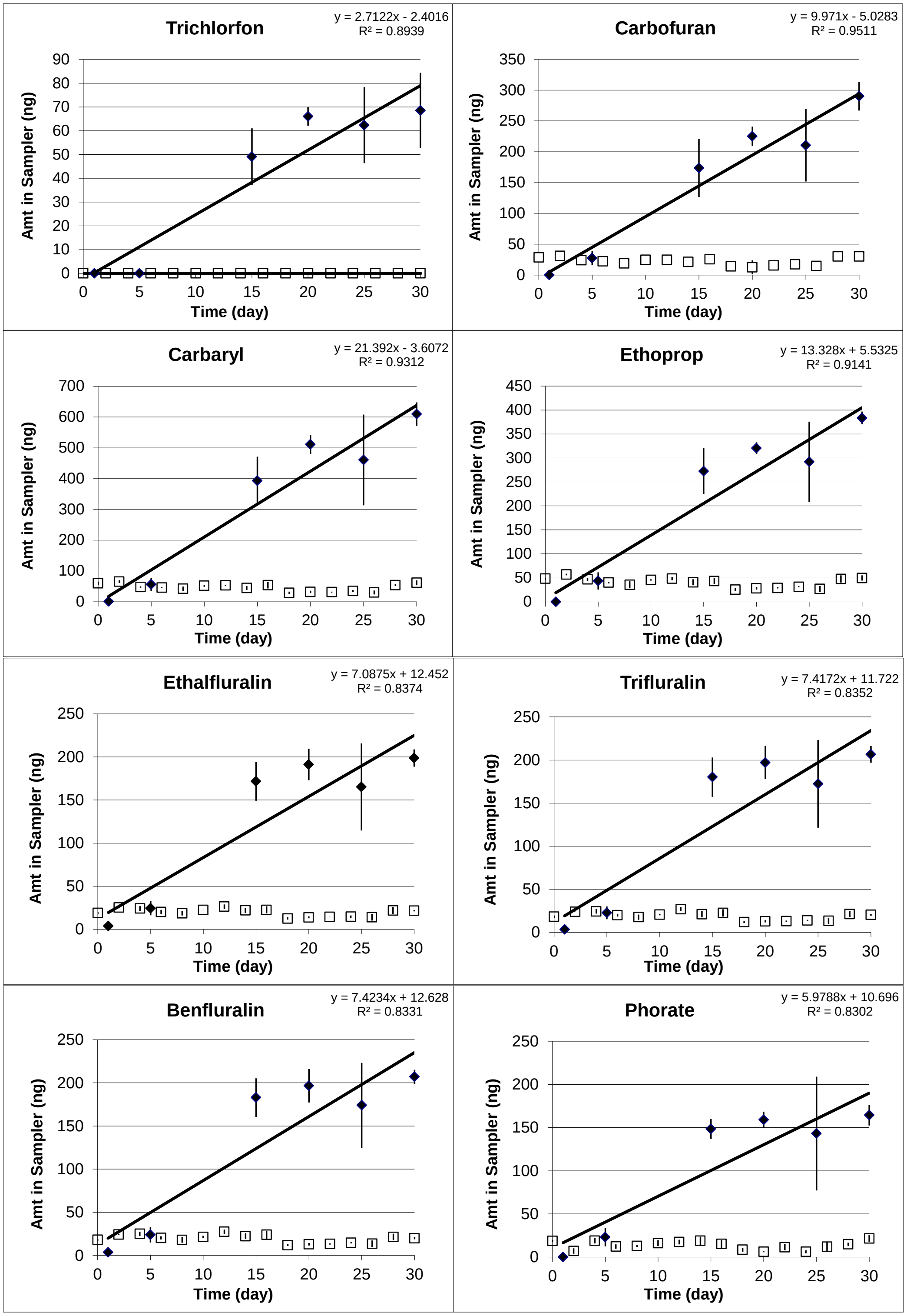
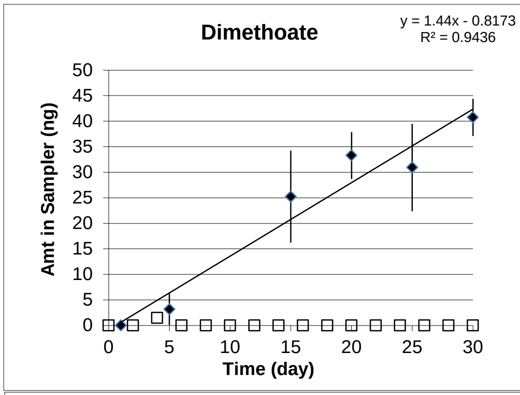
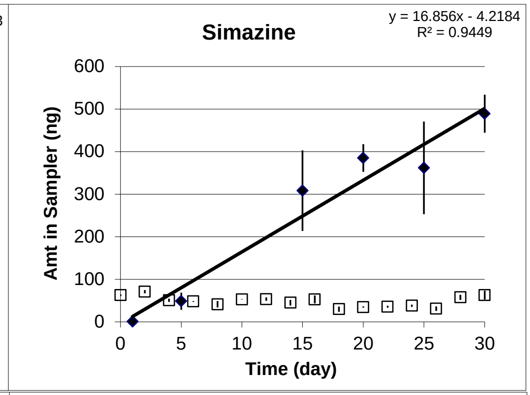


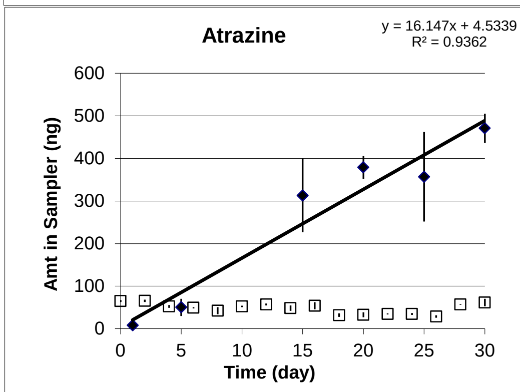
Figure 7. Comparison of the means and standard deviations of atrazine measurements in grab samples versus the uPSDs over a 29-day uPSD deployment and grab sampling every other day for the same period. Each data point represents the means at individual sampling sites. The highest concentration value (upper right of graph) represents all of the data shown in Figure 6. The other data points are from 12 additional sites located downstream of this atrazine source.

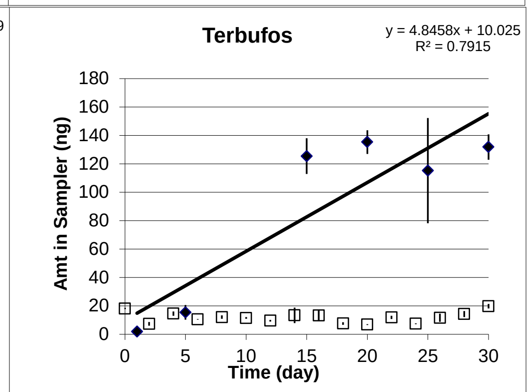
Figure 8. Supplementary figure of uptake curves and exposure concentrations in water for thirty seven pesticides. Solid diamonds (♦) represent the mean concentration in the uPSD (n = 3) and open squares (□) represent the exposure concentrations (n = 3).

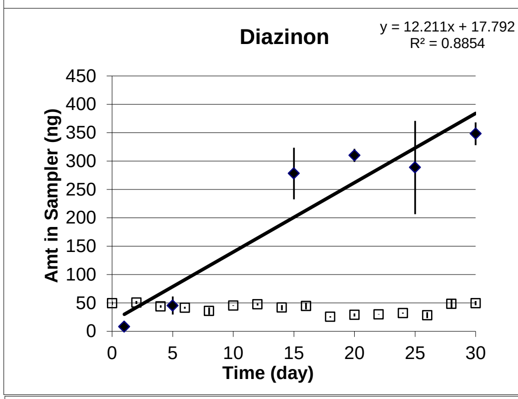

Trichlorfon
y = 2.7122x - 2.4016
R² = 0.8939
Amt in Sampler (ng)
Time (day)
Carbofuran
y = 9.971x - 5.0283
R² = 0.9511
Amt in Sampler (ng)
Time (day)
Carbaryl
y = 21.392x - 3.6072
R² = 0.9312
Amt in Sampler (ng)
Time (day)
Ethoprop
y = 13.328x + 5.5325
R² = 0.9141
Amt in Sampler (ng)
Time (day)
Ethalfluralin
y = 7.0875x + 12.452
R² = 0.8374
Amt in Sampler (ng)
Time (day)
Trifluralin
y = 7.4172x + 11.722
R² = 0.8352
Amt in Sampler (ng)
Time (day)
Benfluralin
y = 7.4234x + 12.628
R² = 0.8331
Amt in Sampler (ng)
Time (day)
Phorate
y = 5.9788x + 10.696
R² = 0.8302
Amt in Sampler (ng)
Time (day)

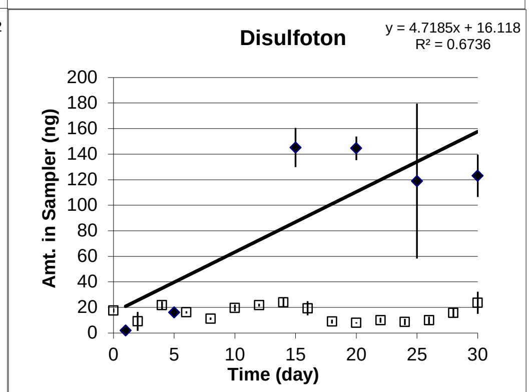

Dimethoate
y = 1.44x - 0.8173
R² = 0.9436
Amt in Sampler (ng)
Time (day)

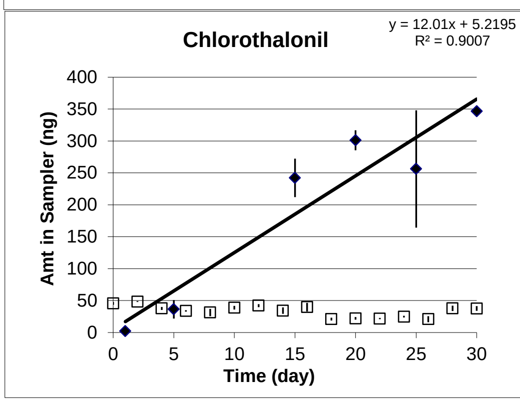

Simazine
y = 16.856x - 4.2184
R² = 0.9449
Amt in Sampler (ng)
Time (day)

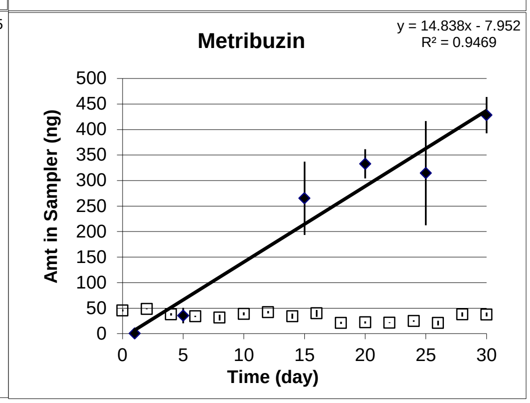

Atrazine
y = 16.147x + 4.5339
R² = 0.9362
Amt in Sampler (ng)
Time (day)

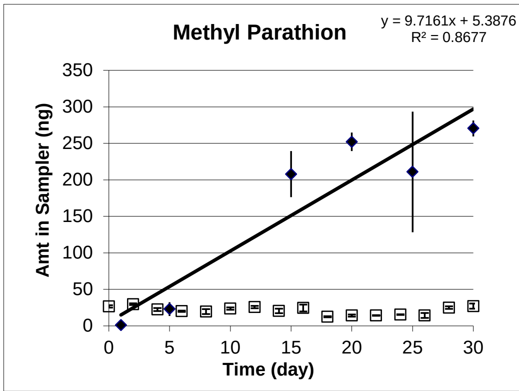

Terbufos
y = 4.8458x + 10.025
R² = 0.7915
Amt in Sampler (ng)
Time (day)


Diazinon
y = 12.211x + 17.792
R² = 0.8854
Amt in Sampler (ng)
Time (day)

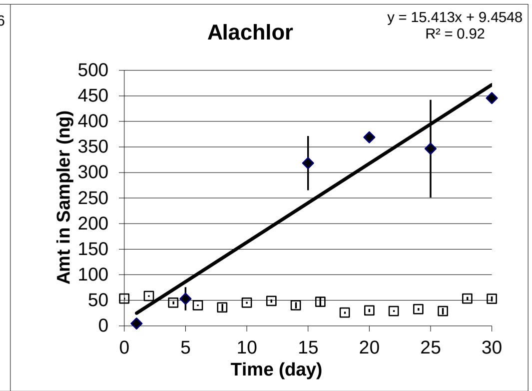

Disulfoton
y = 4.7185x + 16.118
R² = 0.6736
Amt. in Sampler (ng)
Time (day)


Chlorothalonil
y = 12.01x + 5.2195
R² = 0.9007
Amt in Sampler (ng)
Time (day)

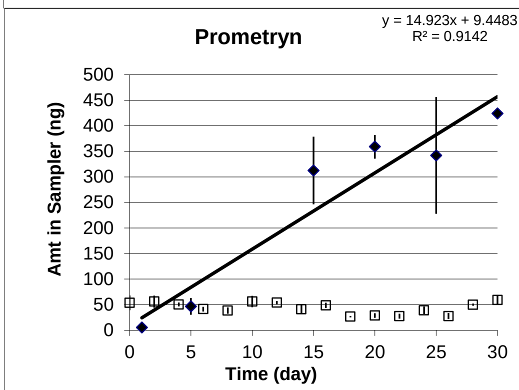

Metribuzin
y = 14.838x - 7.952
R² = 0.9469
Amt in Sampler (ng)
Time (day)



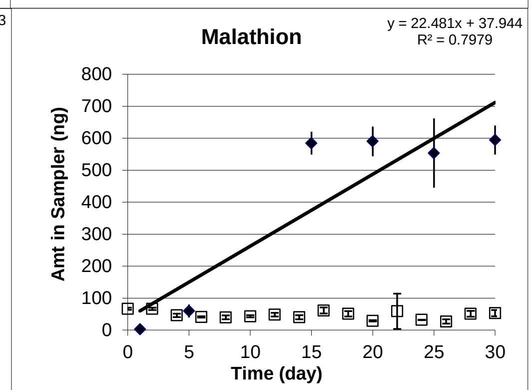
Methyl Parathion
y = 9.7161x + 5.3876
R² = 0.8677
Amt in Sampler (ng)
Time (day)



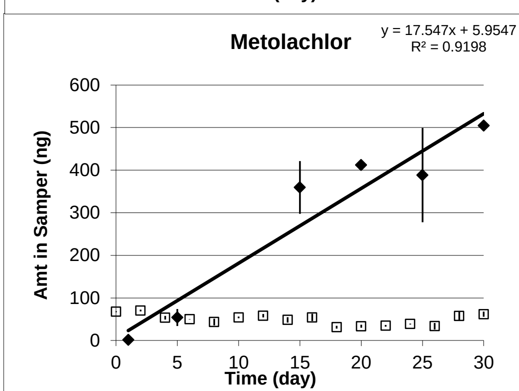
Alachlor
y = 15.413x + 9.4548
R² = 0.92
Amt in Sampler (ng)
Time (day)



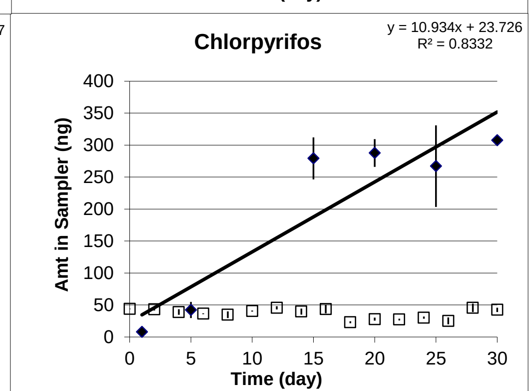
Prometryn
y = 14.923x + 9.4483
R² = 0.9142
Amt in Sampler (ng)
Time (day)



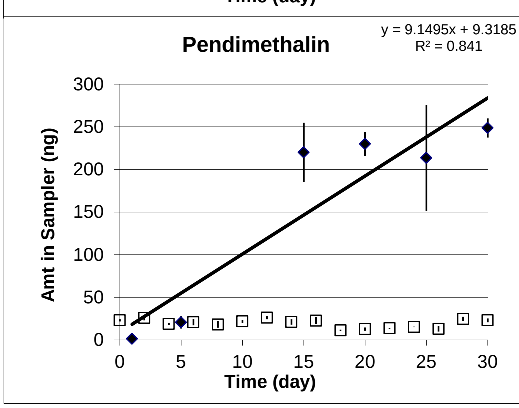
Malathion
y = 22.481x + 37.944
R² = 0.7979
Amt in Sampler (ng)
Time (day)



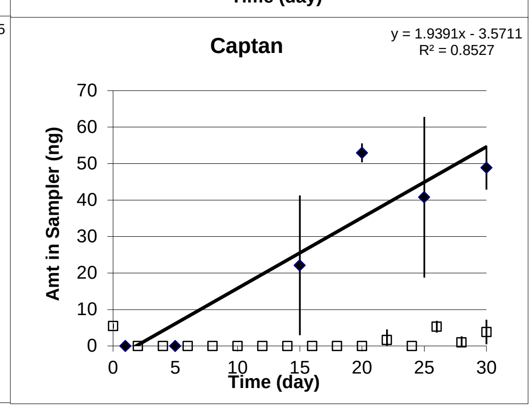
Metolachlor
y = 17.547x + 5.9547
R² = 0.9198
Amt in Samper (ng)
Time (day)



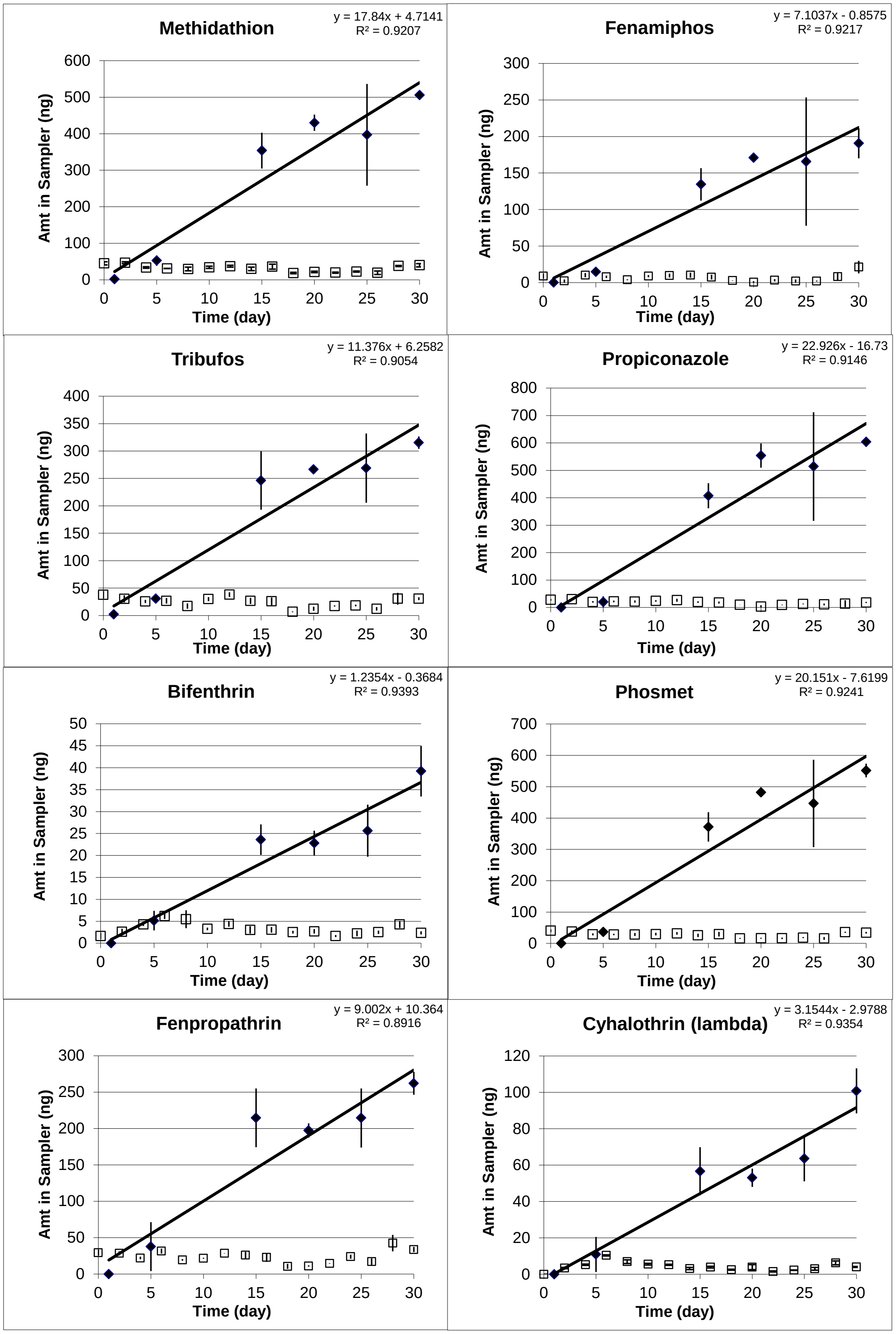
Chlorpyrifos
y = 10.934x + 23.726
R² = 0.8332
Amt in Sampler (ng)
Time (day)

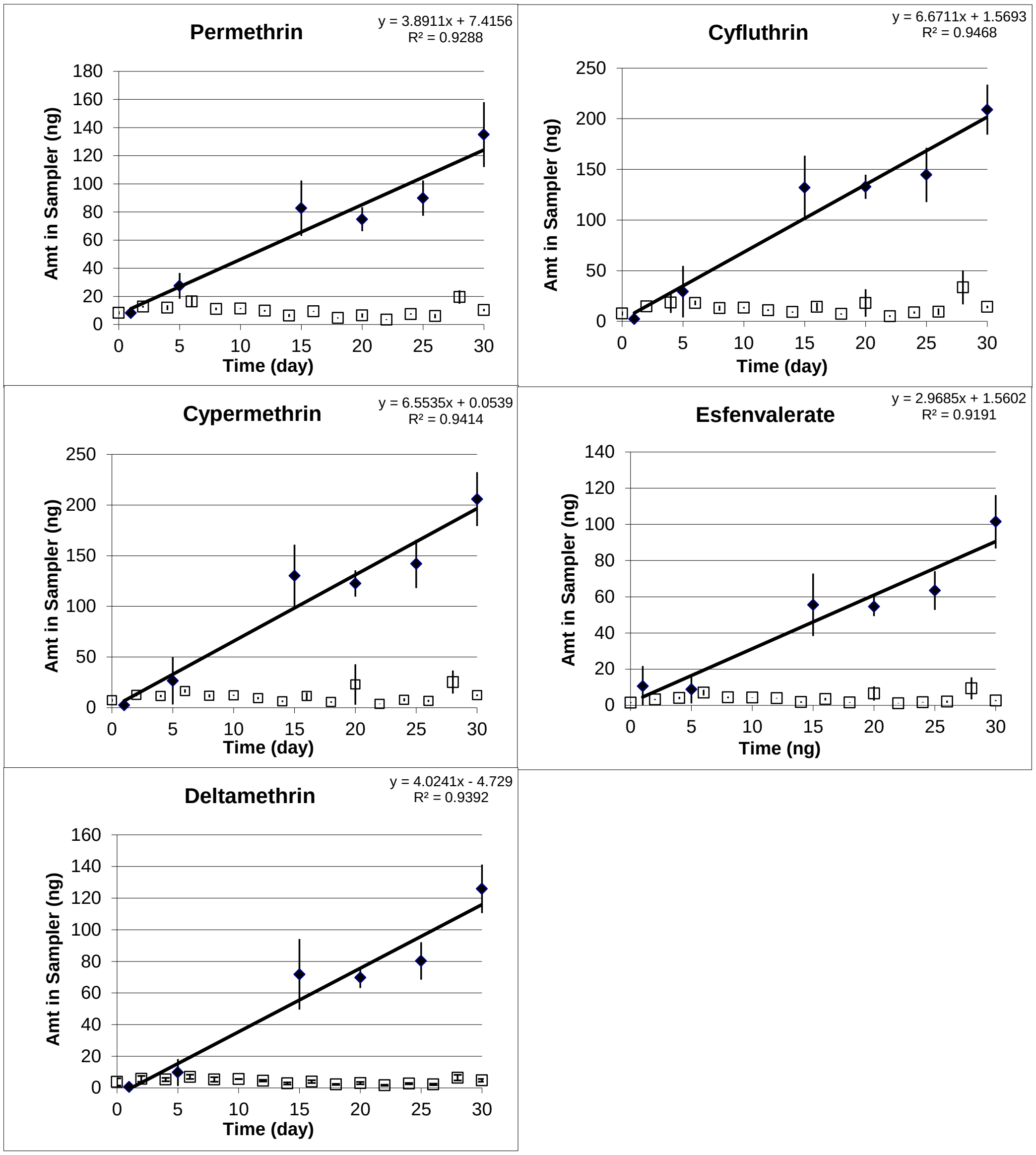


Pendimethalin
y = 9.1495x + 9.3185
R² = 0.841
Amt in Sampler (ng)
Time (day)



Captan
y = 1.9391x - 3.5711
R² = 0.8527
Amt in Sampler (ng)
Time (day)


Methidathion
y = 17.84x + 4.7141
R² = 0.9207
Amt in Sampler (ng)
Time (day)
Fenamiphos
y = 7.1037x - 0.8575
R² = 0.9217
Amt in Sampler (ng)
Time (day)
Tribufos
y = 11.376x + 6.2582
R² = 0.9054
Amt in Sampler (ng)
Time (day)
Propiconazole
y = 22.926x - 16.73
R² = 0.9146
Amt in Sampler (ng)
Time (day)
Bifenthrin
y = 1.2354x - 0.3684
R² = 0.9393
Amt in Sampler (ng)
Time (day)
Phosmet
y = 20.151x - 7.6199
R² = 0.9241
Amt in Sampler (ng)
Time (day)
Fenpropathrin
y = 9.002x + 10.364
R² = 0.8916
Amt in Sampler (ng)
Time (day)
Cyhalothrin (lambda)
y = 3.1544x - 2.9788
R² = 0.9354
Amt in Sampler (ng)
Time (day)



Supplementary Figure 1. Uptake curves and exposure concentrations in water for thirty seven pesticides. Solid diamonds (♦) represent the mean concentration in the uPSD (n = 3) and open squares (□) represent the exposure concentrations (n = 3).

CHAPTER 3. A Passive Sampling Device to Measure Chlorothalonil and the 4-Hydroxy Metabolite in Water

Introduction

Acute pesticide poisoning events are becoming increasingly rare with decreasing application rates and lower acute toxicities of pesticides, with the predominant environmental concern shifting to more long-term, chronic exposures at very low concentrations [1]. This presents the challenge of measuring or estimating chronic low-level environmental exposure and assessing human and ecological risks associated with pesticides. In aquatic systems, water has traditionally been collected with grab sampling, but this only gives an exposure estimate of a single point in time. With pesticide exposures often varying several orders of magnitude with time, obtaining an estimate of chronic exposure in this manner would require extensive sampling and analysis over the exposure period and this often proves too expensive and highly impractical [1, 2]. Obtaining an accurate and low-cost estimate of chronic exposure in water remains a universal challenge in risk assessment. One of the most promising solutions to this challenge is the use of passive sampling devices (PSDs) that can provide a time-weighted-average measurement of exposure using a sorptive phase with an infinite capacity to accumulate the chemical over the time of deployment [3-7]. Successful use of PSDs can reduce the uncertainty and cost associated with exposure assessment, thereby reducing the uncertainty and cost of the overall risk assessment.

Since their development roughly 20 years ago, passive sampling devices have greatly improved environmental monitoring efforts providing both qualitative and quantitative data to describe the extent of environmental exposure [3-9]. Several types of passive sampling devices (PSDs) have been developed for monitoring chronic chemical exposure in aquatic systems, however their use is largely limited to hydrophobic chemicals [3, 7, 9-11]. Very few samplers have been developed to estimate aquatic exposure to polar compounds with the exception of the organic version of the Chemcatcher and the polar organic chemical integrative sampler (POCIS) [6, 12]. The development of a more universal passive sampling device that is capable of monitoring both highly water soluble and insoluble compounds concurrently would be an advantage, especially with current use pesticides that span a very broad range of log K_{ow} values. We recently developed a new and more universal passive sampling device (uPSD) that is capable of accumulating chemicals covering a log K_{ow} range of 1-8 and that appears ideally suited for measuring both parent pesticides and their degradation products in water [13]. The uPSD concentrates very low concentrations of chemicals to detectable levels while providing a time-weighted-average sample, and this work has demonstrated these uPSDs to have linear uptake rates with similar, consistent sampling rates. This uPSD also benefits from having a relatively simple extraction procedure and its stainless steel casing offers a more durable alternative to what is currently available.

In this study, we wanted to evaluate the utility of using the uPSD to look at both a parent pesticide and its degradation product, capitalizing on the ability of the uPSD to accumulate polar chemicals from water. We choose to study the widely used systemic fungicide chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile, CHT) and its primary degradation product, 2,5,6-trichloro-4-hydroxyisophthalonitrile (4OH-CHT), because the 4OH-CHT is more water soluble, more stable, and more toxic (by some measures) than the parent compound [14-17]. This work included a laboratory study of uptake rates of CHT and 4OH-CHT into the uPSD under controlled conditions where environmental parameters that could influence uptake rates were varied. We examined the effects flow rate can have on the sampling rate of CHT and 4OH-CHT and four different scenarios where the sampling rates of both CHT and 4OH-CHT might be impacted through saturation or competition for adsorption sites in the sampler including 1) increasing concentrations of dissolved organic carbon (DOC), 2) increasing pesticide concentration, 3) increasing total suspended solids (TSS) and 4) decreasing particle size of TSS. Finally, a field validation study was conducted at an experimental turf grass site in Guangdong Province, China. Although this work was not intended to be a comprehensive assessment of CHT fate and exposure, it is the first report to our knowledge of using a passive sampling device to measure exposure to both parent CHT and its primary degradation product, 4OH-CHT.

Experimental Section

Materials. The uPSDs were constructed as described previously and is depicted in Figure 1. Briefly, the uPSDs consisted of 10-µm inlet HPLC solvent filters (Alltech Associates, Deerfield, IL, USA), packed with 200 mg Oasis® HLB sorbent with a particle size of 60 µm and specific surface area of 810 m^2/g (Waters Corporation, Milford, MA, USA), filling approximately half of the total volume of the stainless steel cartridge and allowing free flow of water through the cartridge[13]. The uPSDs had an external diameter of 1.25 cm and were 2.8 cm in length, resulting in an internal surface area of approximately 6.19 cm^2. Prior to use, uPSDs were washed three times with ~20 mL (60 mL total) Ultra Resi-Analyzed® Dichloromethane (DCM) (J. T. Baker, Deventer, The Netherlands) in 20 mL vials and shaken on a digital orbital shaker (IKA Works, Wilmington, NC) at 180 rpm at 23°C for one hour each time (3 hours total). Analytical standards of chlorothalonil (CHT), 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4-D methyl ester, 2,4,5,6-tetrachloro-m-xylene (TCMX), 4,4'-dibromooctafluorobiphenyl (DBOFB), with purities of over 97% were obtained from ChemService Inc. (West Chester, PA) and d8-naphthalene was obtained from Cambridge Isotopes (Cambridge, MA). 4-hydroxy-2,5,6-trichloroisophthalonitrile (metabolite II, 97%) was obtained from the EPA National Pesticide Standard Repository (Fort Meade, MD). Hexane, dichloromethane (DCM), 2-propanol, methanol (MeOH), isooctane, ethyl acetate, diethyl ether, acetonitrile (ACN) and acetone (HPLC grade) were from Burdick & Jackson, (Muskegon, MI, USA). Distilled methyl tert-butyl ether (MtBE) was purchased from EM Science (Gibbstown, NJ). Ammonium formate, acetic, formic and sulfuric acids, sodium chloride (NaCl), sodium sulfate (Na_2SO_4) and ammonium hydroxide (NH_4OH) were purchased from Fisher Scientific (Pittsburgh, PA). Disposable 1-mL OASIS® HLB solid-phase extraction (SPE) cartridges were obtained from Waters Inc. (Milford, MA). Diazald and carbitol for diazomethane generation were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI, USA). HPLC-grade water was from a Milli-Q system (Millipore, Bedford, MA, USA). Stock standards of each pesticide were prepared in acetonitrile, methanol or hexane. For spiking of samples, stock solutions were diluted in acetone. All the solutions were kept in the freezer (-20 °C) and replaced approximately every month. All materials were solvent rinsed and baked at 300˚C overnight.

Laboratory Exposure Experiment. The laboratory calibration of the uPSDs was performed as described previously [13]. A stock solution of ~10 µg/L was prepared using the analytical standards in a 4L amber glass bottle. A flow-through system was constructed using an HPLC pump to mix the concentrated stock solution with DI water to produce a constant flow of 5 mL/min diluted solution into a second 4L amber glass bottle which acted as a reservoir to hold the uPSDs, yielding ~100 ng/L of each chemical. The reservoir bottle was sealed air-tight with a stopper through which the feeding line and an effluent line were connected. The effluent line led to a sink for discharge and water sample collection. The pump and transfer lines were all made of non-absorption materials (diamond pump piston, stainless steel pump, Teflon tubes) and were flushed with acetone for 10 min to clean the flow contacting surfaces. The exposure bottle was fastened to a shaker table set at various speeds (23°C) to simulate the turbulence of the aquatic environments for the duration of the exposure. A flow meter was used in a similar open container at the same shaking speeds to estimate actual flow rates in the system (10, 29, and 93 cm/s). The uptake experiments were for 30 days, with uPSDs sampled in triplicate after the 30-day cumulative exposures and water samples (250 mL) were collected every 2 days.

The possible effect of DOC on uptakes rates was tested by repeating the uptake experiment with natural waters containing 2.3, 6.7, 16.1, and 23.5 mg/L DOC, with DOC measured using high temperature combustion (Shimadzu TOC 5000 instrument, Kyoto, Japan) after filtering with a 0.7 μm glass-fiber filter (GF/F). The possible effect of other chemicals competing with or saturating sorption sites in the uPSD was tested using different concentrations (1, 10, and 100 mg/L) of a pesticide mixture comprised of equal amounts of atrazine, diazinon, malathion, metalochlor, and chlorpyrifos (SinoHarvest, Shanghai, China). The possible effect of particles blocking the pores of the uPSD was tested using quartz particles (Powder Technology, Inc., Burnsville, MN, USA), separated into size fractions: 0-8 µm, 8-53 µm, and 53-106 µm.

Field Sampling. All fieldwork was conducted at an experimental turf grass site in Guangdong Province, China. Application of CHT was made at a rate of 11.3 lb a.i./A corresponding to the maximum single application rate for turf use in the USA. Applications were made on days 1, 6, 13, 18, and 26 with natural rainfall, augmented by simulated rainfall as needed, to yield ~ 2.5 cm/d rainfall each day. The application rates and rainfall were designed to provide a very high rate of CHT runoff to an adjacent small pond. Water samples were collected every two days from the pond (no replicates) and triplicate uPSDs were deployed in the pond at approximately equal distance apart.

Sample Preparation and Processing. Prior to extraction, excess water was removed from uPSDs by centrifugation at 3000 rpm for 20 minutes at 23°C. Individual uPSDs were extracted twice using a total of 40mL of dichloromethane (DCM) for a total extraction time of 2 hours, shaking in 20mL vials at 180rpm, dried through a column containing anhydrous sodium sulfate (Na_2SO_4), and then concentrated to an autosampler vial by nitrogen evaporation at 35°C under 5psi for two one-hour repeats prior to analysis. Water samples were processed as described previously [15, 18]. Samples were collected in 250-mL amber jars and filtered through a 0.7 µm GF/F (Whatman). The filtrate was extracted using solid-phase extraction (OASIS HLB) after adjusting the pH <2.0. After the nitrogen evaporation step, the solvent was split into two fractions: one for analysis of CHT and one for analysis of 4OH-CHT that was derivatized to the methyl ester [18].

Instrumental Analysis. Samples were analyzed for current use pesticides using an Agilent 7890 GC equipped with a Restek RTX-5MS 30m × 0.25mm (0.25µm film thickness) 5m Integra-Guard column, connected to an Agilent 5975 mass selective detector operated in selected ion monitoring (SIM) mode. The oven was programmed from 90 °C (3 min) to 185 °C at 10 °C/min, held for 4 min and then ramped to 265 °C at 20 °C/min and held for 2 min. The carrier gas was helium at 1 ml/min. The temperature of the injector and the detector was set at 270 °C. For all extracts, the MS was operated in the selected ion monitoring mode (SIM) using *m/z* 266 for CHT and *m/z* 260 for the 4OH-CHT methyl ester and using TCMX as the quantitation internal standard. Surrogate internal standards were d8-naphthalene for CHT and 2,4-D for 4OH-CHT.

Data Quality Assessment. Procedural blanks were run for both water and uPSDs and no analytes were detected in any blanks. Matrix spike recoveries ranged from 86-102% for CHT and 66-91% for 4OH-CHT. Surrogate recoveries ranged from 78-92% for d8-naphthalene and 77-96% for 2,4-D. Data were not corrected for these recoveries.

Results and Discussion

The use of PSDs to estimate aqueous concentrations of dissolved chemicals requires them to be calibrated by measuring uptake rate constants for the PSD under controlled conditions and then estimating the dissolved concentrations using the following equation that has been derived by others (3):

$$C_{W,fd} = N_{PSD} / R_S t \qquad (1)$$

where $C_{W,fd}$ is the concentration of the chemical freely dissolved in water (ngL^{-1}), N_{PSD} is the mass of the chemical in the PSD (ng), R_S is the first-order exchange (uptake) rate constant converted to units of a sampling rate ($L\ d^{-1}$), and t is the time period (days) the PSD is deployed. Equation 1 assumes linear uptake and deployments must occur over a sufficient duration to reduce the contribution of initial uptake demonstrating nonzero intercepts. These assumptions were previously proven to be valid for CHT and many other chemicals using these uPSDs for a 30-day deployment (Shea et al., in prep). Therefore, all uptake experiments were conducted for 30 days and assumed to also be in the linear uptake phase, allowing the use of equation 1 to estimate the dissolved chemical concentration in water.

There are, however, other environmental variables that could influence the uptake rates of chemicals into the uPSD. It has been previously shown that temperature, biofouling, and shear flow across a membrane-type PSD can influence uptake rates. The temperature primarily has an effect on diffusion rate of the chemical through the aqueous boundary layer on the surface of the PSD and through the sorptive polymer. Biofouling creates an additional physical substrate for the chemical to diffuse through, effectively creating additional impedance. Shear flow across the PSD affects the thickness of the aqueous boundary layer on the PSD and for chemicals whose rate-limiting step is diffusion across the boundary layer, this would effect the kinetics of uptake. The more commonly used hydrophobic PSD, such as the SPMD or PE strips, can be fortified or infused with deuterated performance reference compounds (PRCs), during calibration and in the field, to correct for these variables, however a similar PRC method for a mixed-mode of sorption that includes surface adsorption is complicated by potential non-linear and non-isotropic kinetics [19, 20]. There remains the challenge of developing a PRC method for PSDs that includes surface adsorption, such as the POCIS and the uPSD used in this study. Until a PRC method is developed for the uPSD, it is important to test the effects of environmental variables on the uptake rates and recognize whatever limitation (i.e., variability) there may be when estimating dissolved chemical from the residue in the PSD using equation 1.

Although shear flow across the surface of a membrane-type PSD has been shown to be important, the porous structure of the uPSD is likely to contain a stagnant layer of water in the pores of the stainless steel potentially making flow across the uPSD much less important. We tested this hypothesis for both CHT and 4OH-CHT in a static system and at shear flow rates of approximately 10, 29, and 93 cm/s (Figure 2). There was no difference in uptake rates between 0 and 10 cm/s, but increasing flow to 29 cm/s caused a statistically significant increase ($p < 0.01$) of ~ 30% for 4OH-CHT and ~50% for CHT. The uptake rates increased further at 93 cm/s, however the maximum difference was still less than a factor of two. Most PSD deployments utilize a protective cage that also baffles the flow and the cages we use typically reduce flow to less than 20 cm/s even in highly turbulent waters. Therefore, we would expect little or no difference in uptake rates between those derived in our primary calibration experiments (~10-20 cm/s) and the actual rates during field deployment.

As discussed previously, the uPSD mixed-phase polymer (Oasis HLB) has a mixed mode of sorption for chemicals: absorption or partitioning of hydrophobic chemicals into the hydrophobic phase and adsorption onto the polar surfaces for more hydrophilic and polar chemicals [13]. This mixed mode of sorption provides the advantage of a more universal capacity of this uPSD, but there is the potential for the polar surface functional groups to become saturated or to otherwise have competition for these sites from chemicals other than those of interest. Two sources of these competing chemicals could be from natural organic matter dissolved in the water or anthropogenic chemicals including other pesticides. We tested this previously and found no statistically significant difference in the sampling rates under the conditions tested [13]. However, there was visually an apparent consistent small decrease in sampling rates for the more polar water-soluble chemicals in the presence of high concentrations of potentially competing sorbates. Given that the 4OH-CHT is rather polar, we decided to test the potential for surface adsorption competition more completely than we did previously [13].

The results of all of the competition experiments can be seen in Table 1 and Figures 3 and 4. From this we are able to conclude that increasing concentration of pesticide mixture does not significantly change the sampling rate for the uPSD for either Chlorothalonil or its metabolite, 4OH-CHT, indicating that at concentrations up to 100mg/L there is not competition for adsorption or absorption sites in the chosen polymer. An Analysis of Variance (ANOVA) confirmed that there is not a significant difference between the means of each concentration ($p < 0.05$).

We also saw in Figure 4 that increasing concentrations of dissolved organic carbon (DOC) does not affect the sampling rate of the uPSD. The sampling rates remained consistent with increasing concentrations of DOC, from 2.3mg to 23.5mg. An ANOVA again confirmed that there is not a statistical difference between the sampling rates for Chlorothalonil or 4OH-CHT.

Increasing concentration of total suspended solids (TSS) does not affect the sampling rate of the uPSD until concentrations of 150mg/L are reached (Figure 5). At a concentration of 150 mg/L the sampling rate for CHT becomes significantly lower than those of distilled water, 5 mg/L TSS or 20 mg/L TSS. However no significant difference is observed prior to that indicating that under typical conditions the uPSD is not likely impacted by concentration of total suspended particles.

The sampling rate of the uPSD was impacted by the size of total suspended solid. At a very high total TSS of 150 mg/L, as the particle size decreased so did the sampling rate, Figure 6. Consequently, we hypothesize that small particles (0-8 µm) might be capable of blocking the pores on the samplers thereby altering the sampling rates. The pore size of the stainless steel cartridges used for these uPSDs is 10 µm. Although the experimental results shown in Figure 6 represent an extreme environmental condition, it is possible that the uPSD, as constructed here, might not be an effective sampler in situations with very high concentrations of very fine particles.

Finally to help confirm that the calibrated uPSD adequately represents chronic exposure in the field, the uPSD was deployed in a small pond adjacent to an experimental turf grass field site with known amounts of chlorothalonil applied and simulated rainfall designed to move applied chemicals into the pond. Grab water samples were taken every other day and uPSDs were deployed for 30 days. The results of this experiment can be seen in Figures 7 and 8. The grab samples demonstrate the cyclical nature of pesticide runoff and exposure (in this case driven by application followed by simulated rainfall); nicely illustrating that depending upon when the system was sampled it could either greatly overestimate or underestimate the average chronic exposure. The uPSD measured an average CHT concentration of 61 ng/L in the receiving water while the average of the grab samples was 118 ng/L. The mean concentration of 4OH-CHT in the uPSD was 112 ng/L compared to 189 ng/L in the grab samples. These differences were not statistically significant, although they are consistent with previous work on atrazine indicating that the uPSD slightly underestimates exposure measured with grab samples by as much as a factor of two [13]. Thus, these differences may just be due to the highly variable nature of this system (and the grab sampling) or that the uPSD only measures the truly dissolved portion whereas the grab samples, even after filtering, might have some particulate/colloid bound chemical being measured. The latter feature of the uPSD is by design – the uPSD is intended to measure only the truly dissolved and presumably bioavailable fraction of chemical in the water. Regardless of whether this difference is real or not, the factor of two agreement between the uPSD and the repeated grab samples is remarkable and this work demonstrates the ability of this new PSD design to capture both the parent pesticide and the more polar degradation product using a single device.

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Table 1. Sampling rates (L/day) from 30 day competition experiments

	Chlorothalonil					4OH-CHT				
	Rep 1	Rep 2	Rep 3	Mean	Std	Rep 1	Rep 2	Rep 3	Mean	Std
deionized water	0.138	0.155	0.165	0.153	0.014	0.160	0.141	0.185	0.162	0.022
natural water, 2.3 mg/L DOC	0.159	0.162	0.181	0.167	0.012	0.183	0.178	0.147	0.169	0.020
natural water, 6.7 mg/L DOC	0.159	0.172	0.185	0.172	0.013	0.163	0.155	0.137	0.152	0.013
natural water, 16.1 mg/L DOC	0.176	0.144	0.149	0.156	0.017	0.187	0.157	0.167	0.170	0.015
natural water, 23.5 mg/L DOC	0.141	0.16	0.168	0.156	0.014	0.179	0.143	0.160	0.161	0.018
deionized water	0.138	0.155	0.165	0.153	0.014	0.160	0.141	0.185	0.162	0.022
Pesticide mixture, 1 mg/L	0.144	0.168	0.172	0.161	0.015	0.169	0.128	0.157	0.151	0.021
Pesticide mixture, 10 mg/L	0.158	0.177	0.188	0.174	0.015	0.183	0.133	0.182	0.166	0.029
Pesticide mixture, 100 mg/L	0.13	0.125	0.179	0.145	0.030	0.128	0.132	0.170	0.143	0.023
deionized water	0.138	0.155	0.165	0.153	0.014	0.160	0.141	0.185	0.162	0.022
TSS, 5 mg/L	0.18	0.161	0.185	0.175	0.013	0.177	0.184	0.142	0.168	0.023
TSS, 20 mg/L	0.166	0.121	0.104	0.130	0.032	0.139	0.150	0.128	0.139	0.011
TSS, 150 mg/L	0.089	0.062	0.115	0.089	0.027	0.135	0.110	0.130	0.125	0.013
TSS, 150 mg/L mix	0.089	0.062	0.115	0.089	0.027	0.135	0.110	0.130	0.125	0.013
TSS, 150 mg/L 0-8 uM (4.1)	0.026	0.014	0.033	0.024	0.010	0.017	0.030	0.022	0.023	0.007
TSS, 150 mg/L 8-53 uM (21.1)	0.126	0.099	0.104	0.110	0.014	0.087	0.065	0.081	0.078	0.011
TSS, 150 mg/L 53-106 uM (72)	0.144	0.175	0.186	0.168	0.022	0.160	0.180	0.188	0.176	0.014

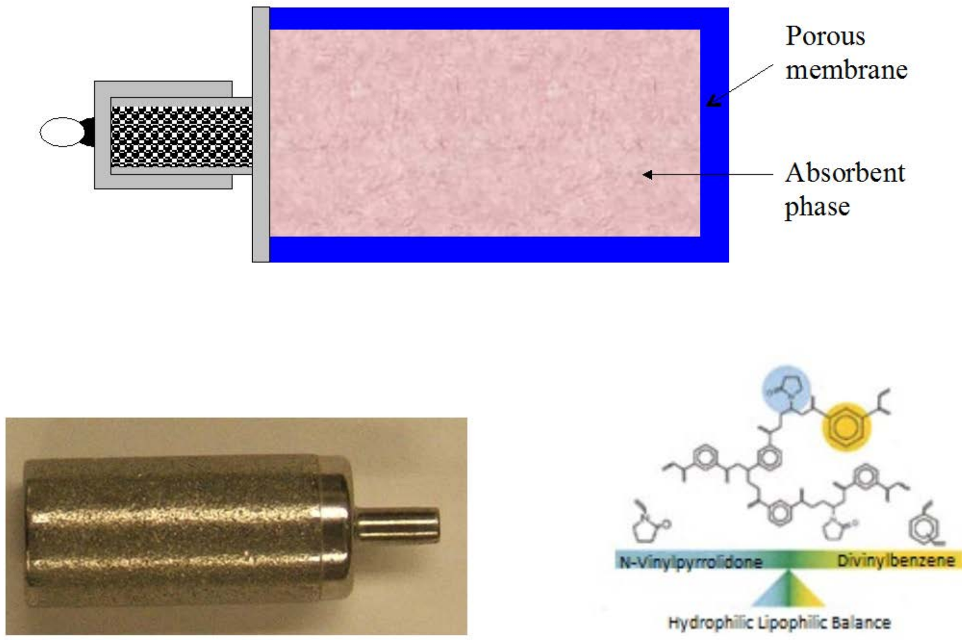

Figure 1. Diagram and picture of the uPSD, with chemical structure of the sorbent phase (lower right).

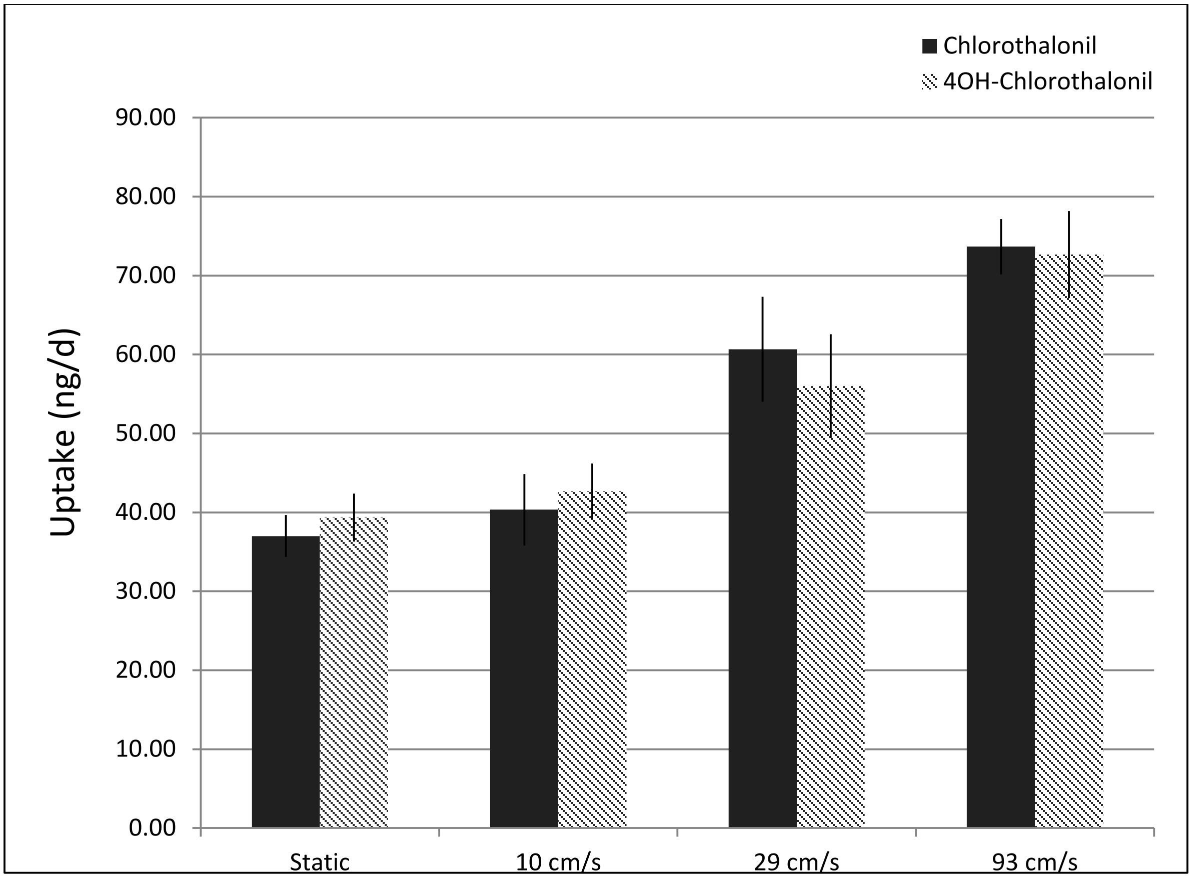

Figure 2. Effects of flow rate on the uptake of CHT and 4OH-CHT.

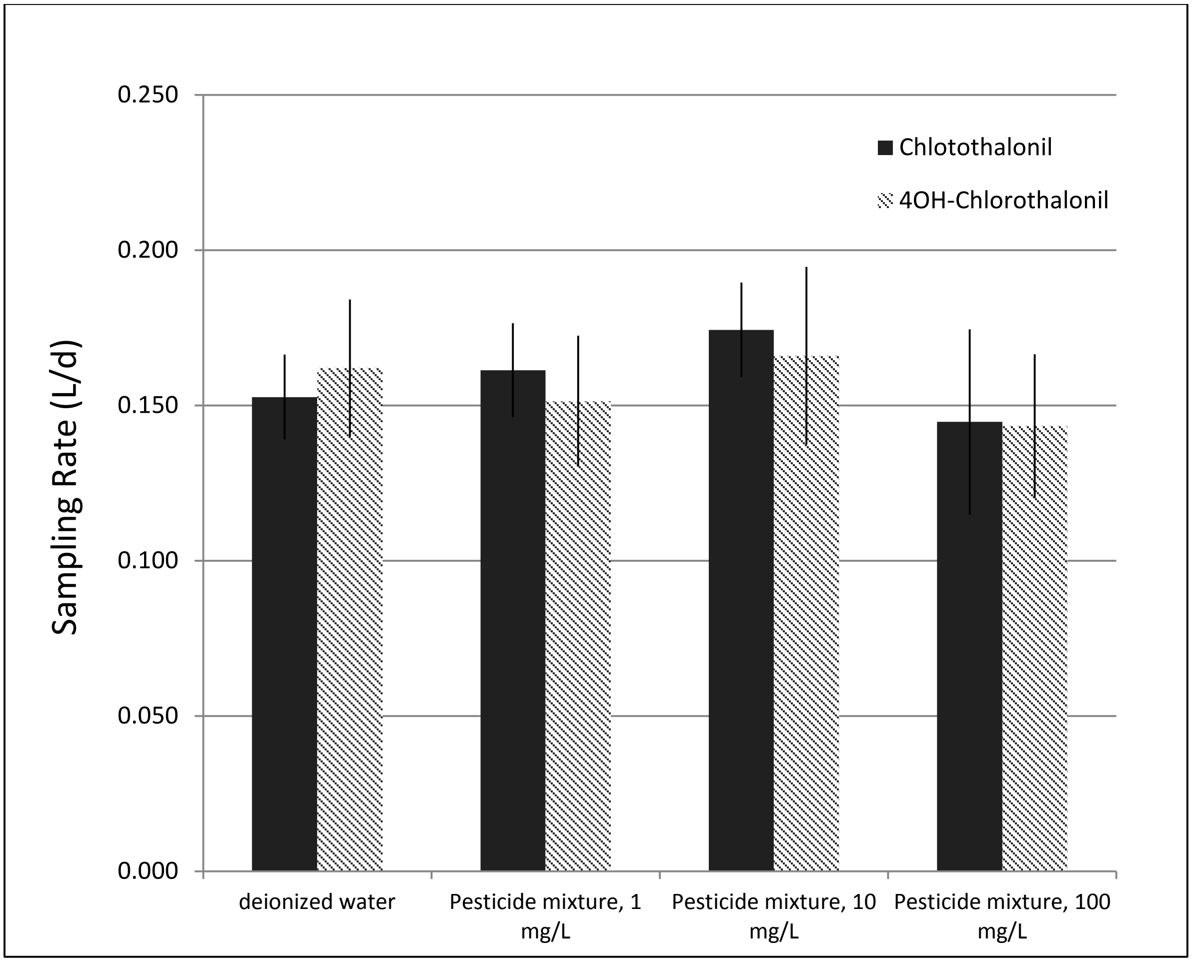

Figure 3. Effects of increasing pesticide concentration on sampling rate.

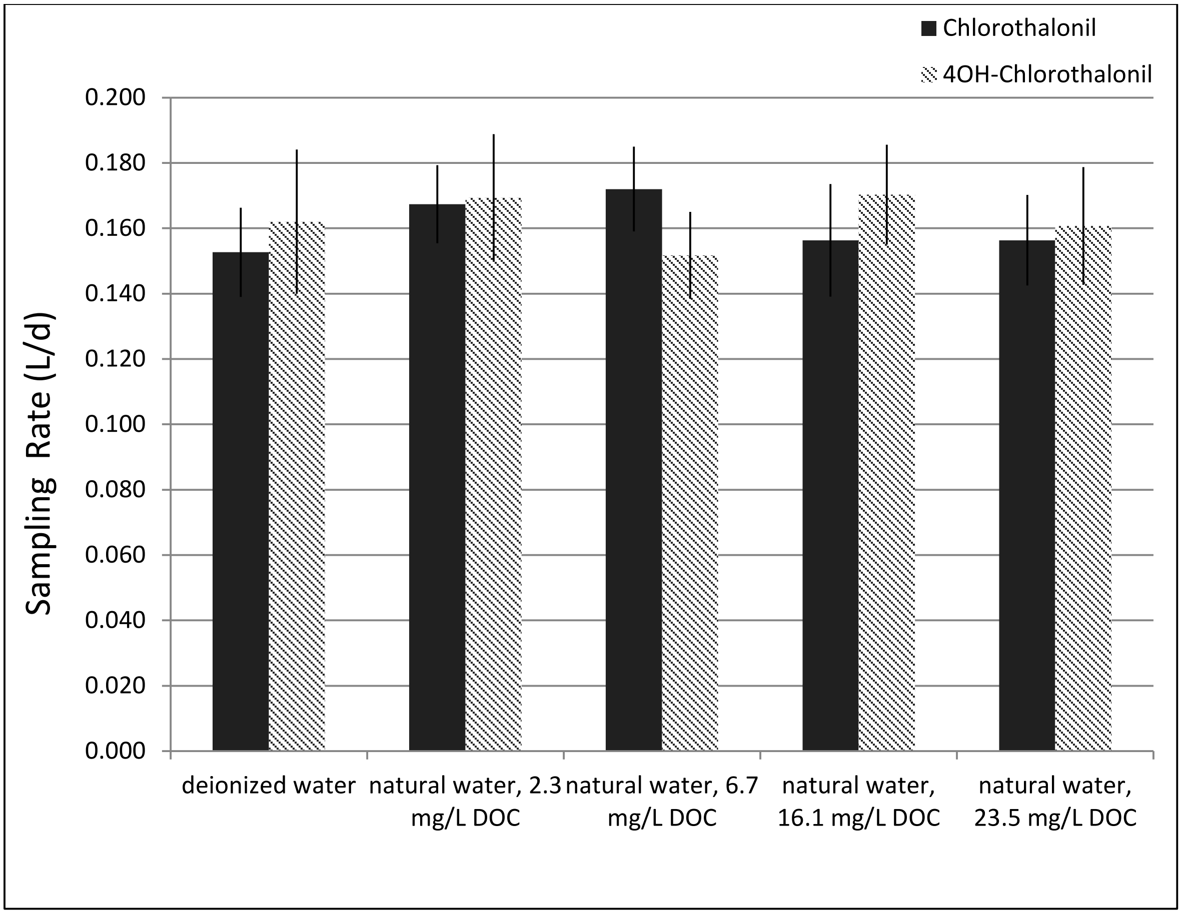

Figure 4. Effect of increasing DOC on sampling rate.

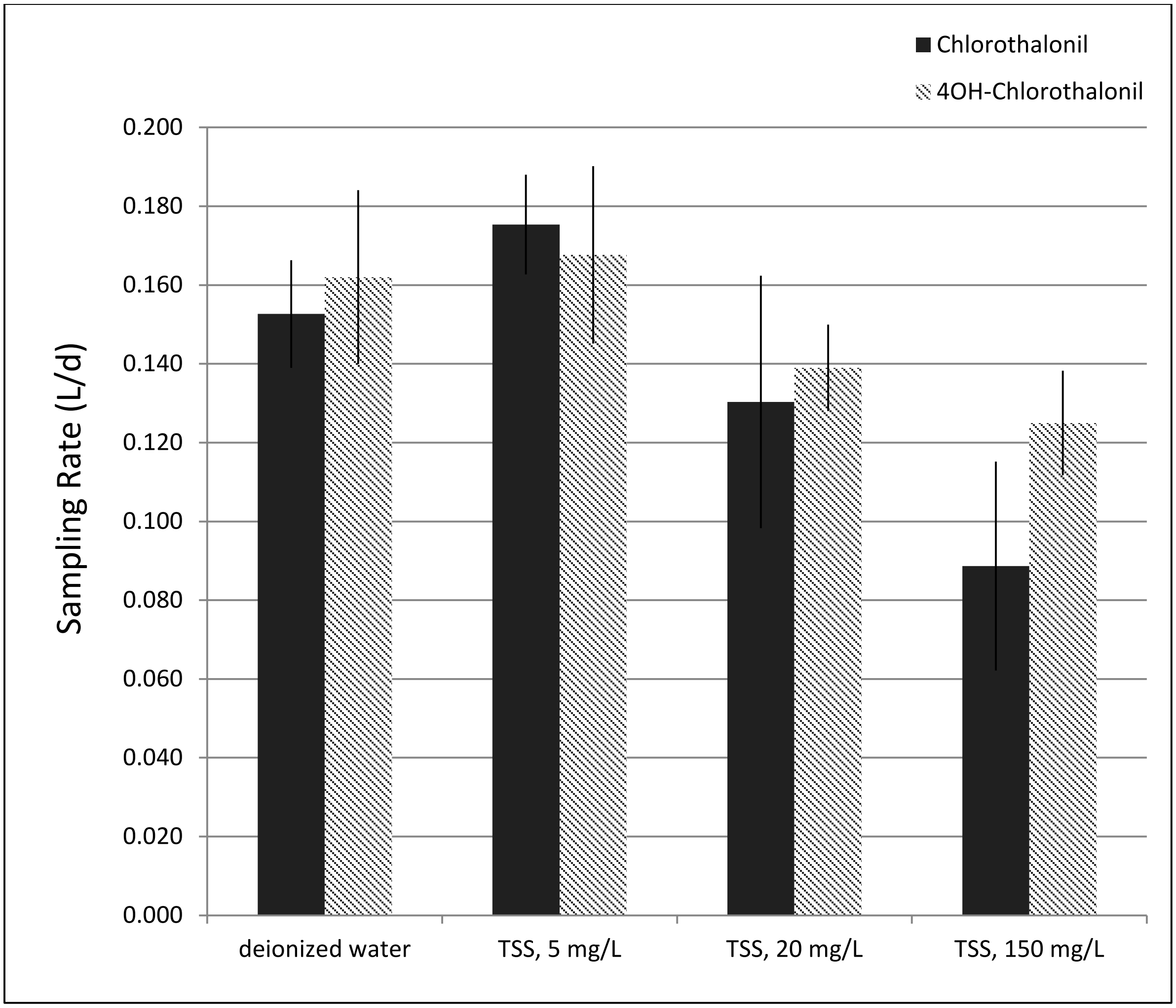

Figure 5. Effect of increasing TSS concentration on sampling rate

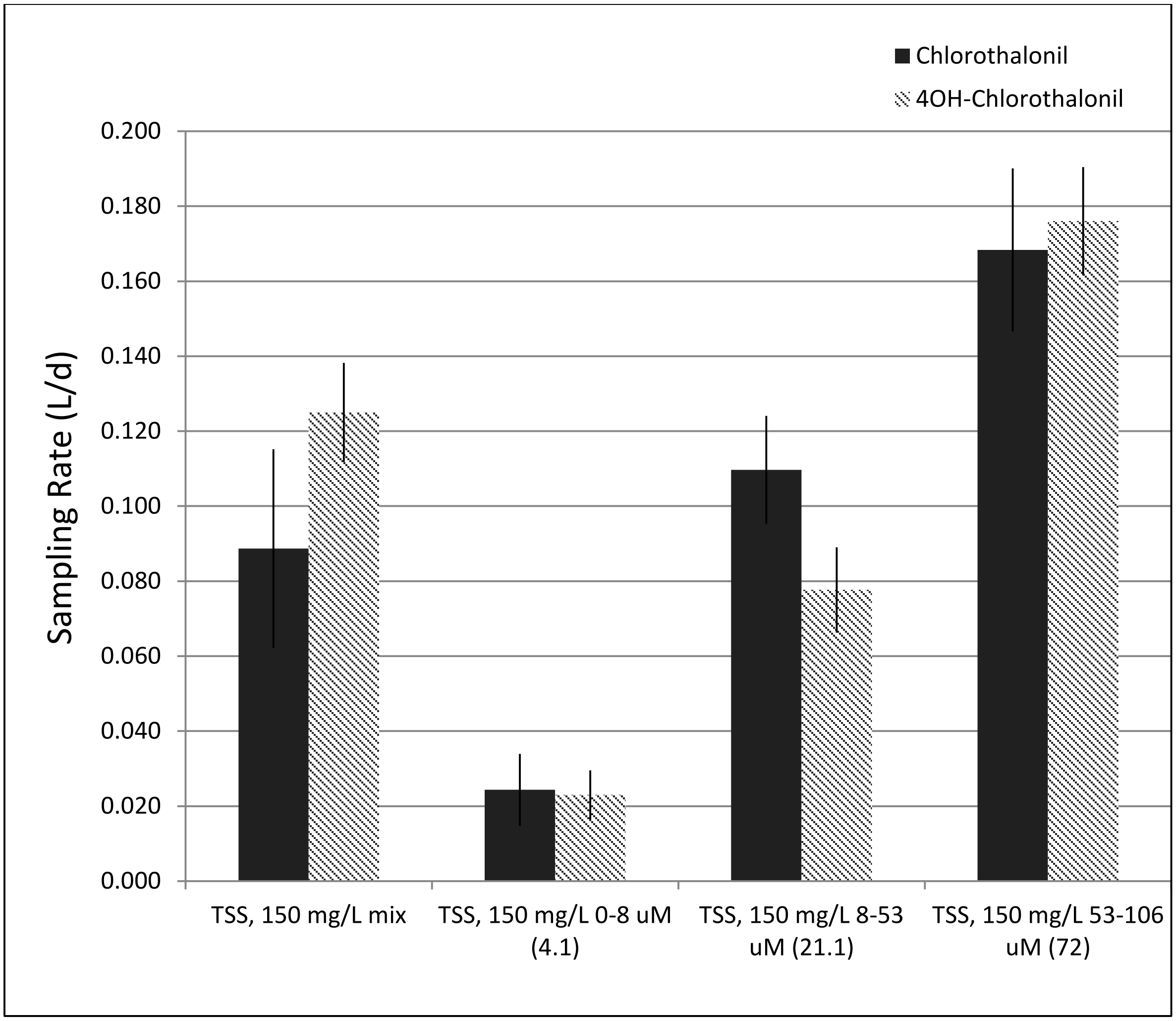

Figure 6. Effect of particle size of TSS on sampling rate

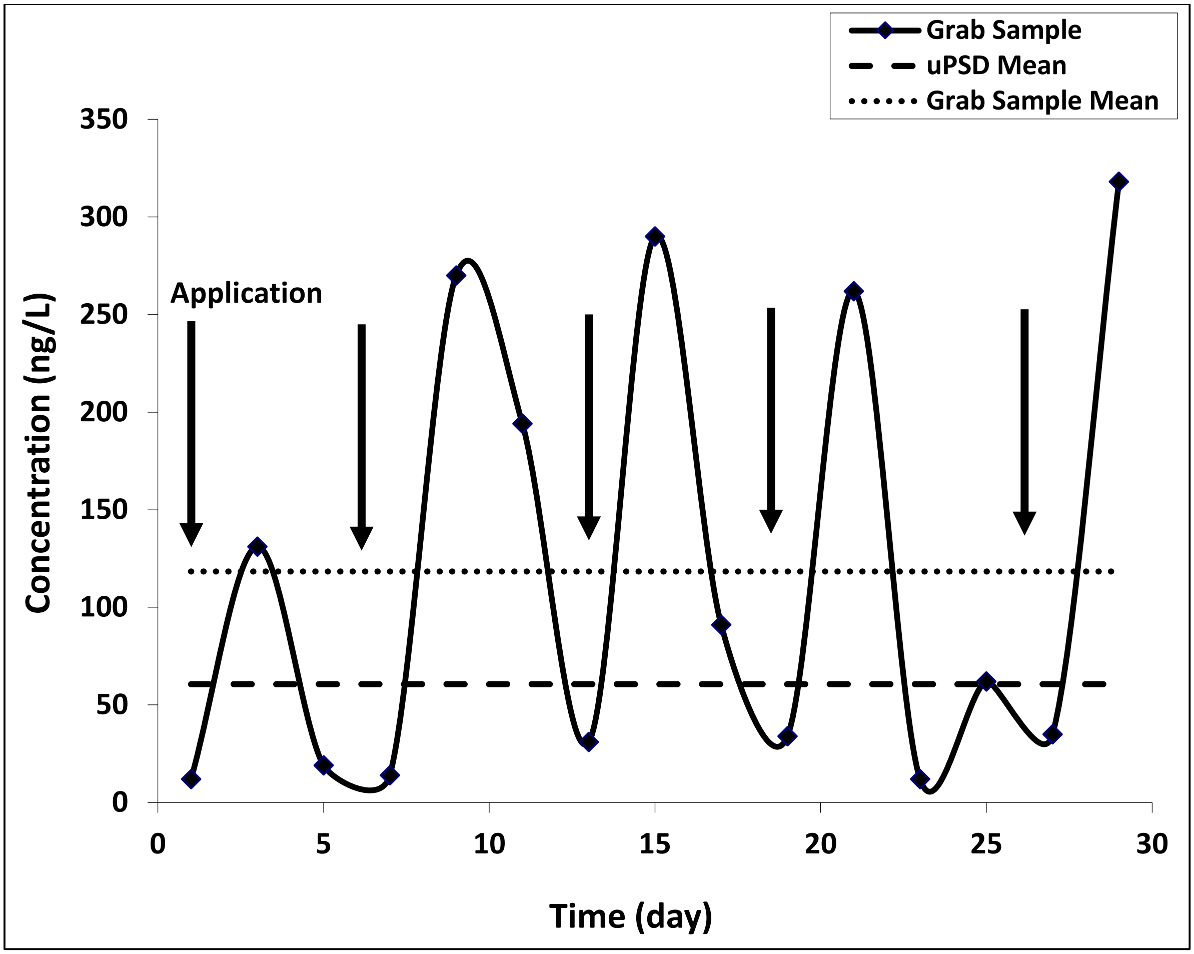

Figure 7. Chlorothalonil measured through grab sampling and uPSD estimations.

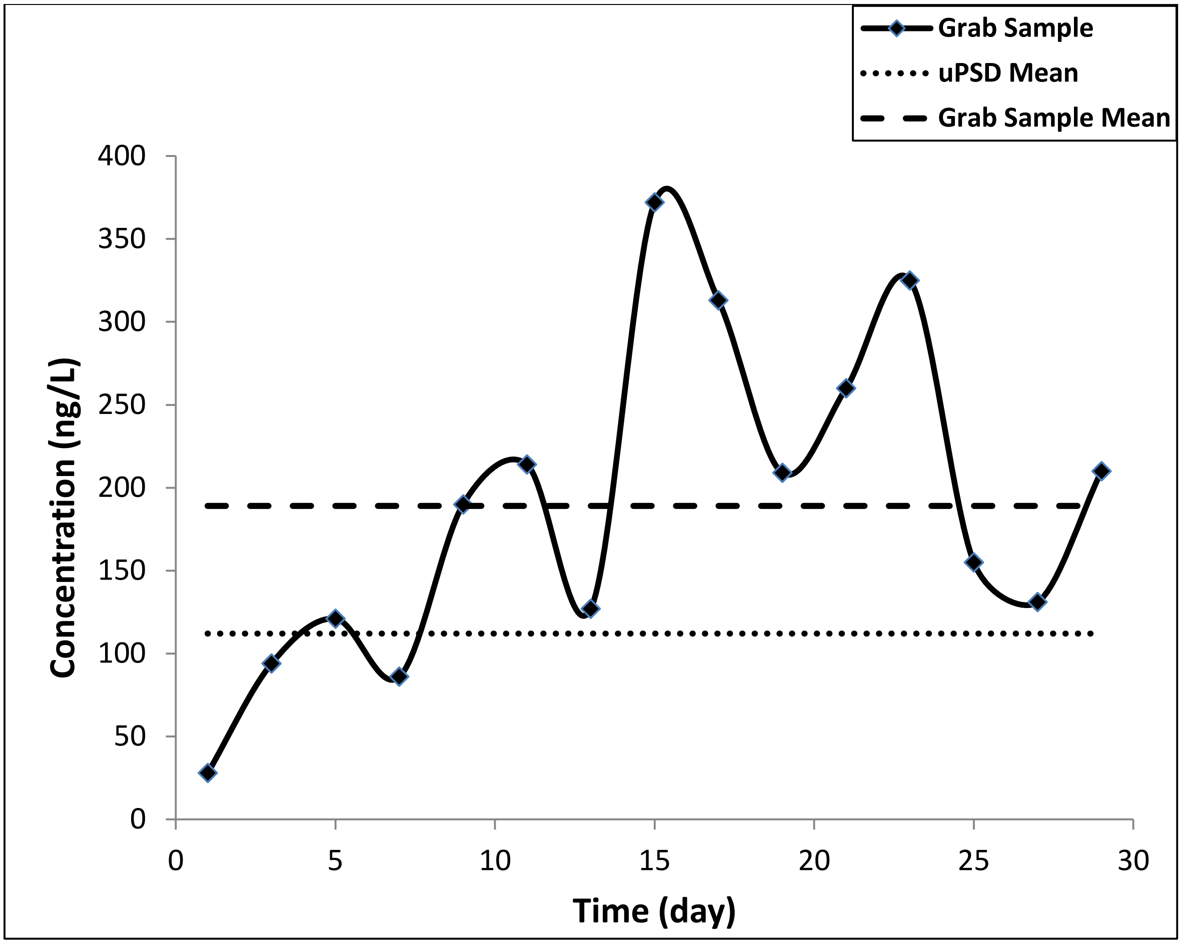

Figure 8. 4OH-CHT measured through grab sampling and uPSD estimations.