

ABSTRACT

Characterization of Fundamental Adsorption Behavior of Pesticides on Polar Organic Chemical Integrative Sampler (POCIS)

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Determination of accurate time weighted average concentrations (TWACs) of chemicals in water using polar organic chemical integrative sampler (POCIS) is still unsatisfactory, due to the limited understanding of environmental factors impact on POCIS uptake. The objective of this research was to improve understanding of environmental factors effects on POCIS uptake by performing laboratory POCIS exposure experiments. The research mainly focused on 12 pesticides, including common types of pesticides used in the US, with a range of physico-chemical properties. A UPLC-MS/MS method was developed for water and POCIS extract sample analyses of select pesticides. The effects of change in hydrodynamic conditions as well as change in temperature on POCIS sampling rate (R_s) were investigated. Flow velocities at the surface of POCIS devices were determined using a novel method based on the measurement of mass transfer coefficients of the water boundary layer near the surface of POCIS devices. Hydrodynamic conditions effects on POCIS R_s were mainly observed between stagnant flow conditions and 6 cm/s. An Arrhenius model was used to describe the linear relationship between temperature and

R_s and the use of temperature-corrected R_s to accurately calculate TWAC was evaluated in field settings. The investigation of suspended sediment effects on POCIS uptake suggested that suspended sediment do not have an effect on POCIS R_s for most compounds, but it may affect transport processes across POCIS membrane for compounds with relatively high hydrophobicity and relatively high affinity to POCIS membrane. The investigation of concentration exposure effects on POCIS uptake demonstrated that concentration exposure has no effect on POCIS R_s or on POCIS integrative capability for concentrations ranging from 3 to 60 $\mu\text{g/L}$ over a 21-day exposure period. However, POCIS integrative capabilities may be shortened for POCIS exposures to concentrations higher than 60 $\mu\text{g/L}$. Additionally, there was an interesting increase in POCIS R_s observed between constant concentration and pulse concentration exposures.

Characterization of Fundamental Adsorption Behavior of Pesticides
on Polar Organic Chemical Integrative Sampler (POCIS)

by

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Thank you.

DEDICATION

To my sweet children Osei, Tunie, and Cean; my beloved husband Ferdinand; and my
dearest parents Felix and Jacqueline Toteu.

Je ne saurais exprimer ma gratitude envers vous. Je vous aime!

CHAPTER ONE

Introduction

The use of pesticides such as herbicides, insecticides and fungicides in the agricultural sector has significantly contributed to the increase in crop production and the improvement of crop products quality. For instance, average corn yield has increased from 80 bushels per acre in 1988 to over 180 bushels per acre in 2018. Similarly, average soybean yield has increased from 25 bushels per acre in 1988 to over 52 bushels per acre in 2018.¹ Proper usage of pesticides on crops provides several benefits to farmers including the control of weed growth, plant pathogens and insect damage, while reducing the amount of labor, fuel, and machinery used for pest control.² The use of pesticides also provides several benefits to consumer products including the availability and affordability of fresh produce all year round.

A total of 438 pesticides with a total high estimated mass of 3 million tons were used between 2012 and 2016 for United States (US) crops including corn, soybean, wheat, cotton, vegetables & fruits, rice, orchards & grapes, alfalfa, pasture & hay, and others.³ Atrazine, azoxystrobin, bicyclopyrone, cyproconazole, fomesafen, mesotrione, S-metolachlor, propiconazole, sedaxane, simazine, solatenol and thiamethoxam represent a wide class range of pesticides used in the US, with different modes of action and crop usage, as illustrated in Table 1.1. Atrazine and S-metolachlor were among the most used with an estimated 0.2 and 0.1 million tons, respectively. This corresponds to over 6% and 4%, respectively, of total pesticides usage between 2012 and 2016 in the US. Corn,

Table 1.1. Chemical classification, usage, mode of action and ecological risk assessment for select pesticides.

	Compound	Chemical Family	Top 3 Crops use	Average* (tons)	Range* (tons)	Mode of action	Aquatic ecological risk assessment for chronic exposure
Insecticide	Thiamethoxam	neonicotinoids	Soybeans, corn and cotton	481	162-754	acetylcholine receptor agonist	survival, growth, emergence, mobility, and behavior of aquatic invertebrates. ^{4, 5}
	Atrazine	triazine	Corn, vegetables & fruits and pasture & hay	36421	35177-38234	Inhibition of photosystem II	survival, growth or reproduction of aquatic animals and plants ⁶
Herbicides	Simazine	triazine	Corn, orchards & grapes and soybeans	3393	2963-4135	Inhibition of photosystem II	
	Bicyclopyrone	triketone	Corn and vegetables & fruits	23	0-112	Inhibition of 4-hydroxyphenylpyruvate dioxygenase	
	Mesotrione	triketone	Corn, vegetables & fruits and orchards & grapes	1458	1290-1768	Inhibition of 4-hydroxyphenylpyruvate dioxygenase	
	Fomesafen	diphenylether	Soybeans, cotton and vegetables & fruits	2139	1506-3329	Inhibition of protoporphyrinogen oxidase	
Fungicides	S-Metolachlor	chloroacetanilide	Corn, soybeans and cotton	25324	21736-30462	Inhibition of very long chain fatty acid synthesis	survival, growth, emergence, of fish and aquatic invertebrates. ⁷
	Azoxystrobin	strobilurins	Corn, soybeans and wheat	1167	1101-1218	Inhibition of the QoL site	
	cyproconazole	triazole	Soybeans, corn and wheat	57	9-91	Inhibition of ergosterol-biosynthesis	
	Propiconazole	triazole	Wheat, corn and soybeans	1101	1034-1227	Inhibition of ergosterol-biosynthesis	
	Sedaxane	pyrazole	Wheat and soybeans	3	0-11	Inhibition of succinate dehydrogenase	
	Solatenol	pyrazole	Corn, soybeans and orchards & grapes	10	0-50	Inhibition of succinate dehydrogenase	

*Calculated from total high estimate mass of pesticides use in the US between 2012 to 2016

soybeans, and vegetables & fruits were the crops with the most pesticide usage in the US and contributed to over 28%, 18% and 18%, respectively, of total pesticides usage between 2012 and 2016.¹

Despite significant progress in pesticide research and development, pesticides are still not fully selective to target specific organism and may cause unintended environmental effects. Most pesticide usage for agricultural purpose is intended for the control of pests on above-ground plant parts. However, a significant portion of the applied pesticides (80 to 99%) drift into the atmosphere, soil, ground and surface water.^{8, 9 10} Furthermore, pesticides can be transported from their intended sites into ground and/or surface water via leakage from the soil as well as runoff following precipitation.^{8, 11} Pesticides that reach the soil may cause adverse effects to the soil flora and fauna (including fungi and algae), insects and earthworms; all of which contribute to the maintenance of soil fertility and are an integral portion of the terrestrial food webs.⁸ The occurrence of pesticides in the aquatic environment may also affect the aquatic flora and fauna, and cause disruptions in the aquatic food webs. Additionally, occurrence of pesticides in the aquatic environment can cause a reduction in the dissolved oxygen level of water due to the decomposition of aquatic flora by pesticides, which can be detrimental for the aquatic system overall¹². While the use of pesticides can improve crop production, they may have counterproductive effects on soil quality over time and can also have repercussions on terrestrial as well as aquatic food chains and biodiversity. Moreover, ground and surface water are both important drinking water sources. Thus, occurrence of pesticides in surface and ground water may have direct effects on human health.

Potential effects of pesticides on the aquatic environment as well as on human health has caused increasing concerns. Worldwide regulation agencies have been working on regulating pesticide standard values in drinking water, surface water, groundwater, soil and air for years. The US Environmental Protection agency (EPA) process for evaluating the potential health and ecological effects of a pesticide include the determination of human and aquatic organisms exposure to pesticides from water, i.e., the concentration, frequency and duration of pesticides occurrence in water.^{6, 13} Exposure measurements are primarily derived from field monitoring data. Alternatively, exposure measurements can also be derived from models that estimate environmental concentration, especially for new pesticides with no field monitoring data available.

Monitoring Methods for the Occurrence of Pesticides in Surface Water

Active water sampling techniques have been traditionally used for the monitoring of pesticide occurrence in water. Active water sampling techniques are typically carried out by manual or automatic collection of discrete volumes of water at one point in space and time. These methods provide simple and straightforward calculations of pesticides average concentration for a given sampling time period. Yet, active water sampling methods have a number of shortcomings. Active water sampling methods usually require a large volume of water and pre-concentration steps for pesticides occurring at relatively low concentration and/or the use of highly sensitive instruments during sample analysis. Additionally, active water sampling methods may provide limited information on pesticides time weighted average concentrations (TWACs) during short temporal variations of pesticide concentrations in water, especially when the sampling frequency is low. Automatic discrete water samplers such as ISCO can be used to increase water sample

collection frequency and improve the robustness of the data.¹⁴ However, this option is labor-intensive and expensive. Automatic continuous water sampler such as continuous low-level aquatic monitoring (CLAM) is another relatively cheaper and less labor-intensive alternative.^{15, 16} However, the collection duration is limited to 36 hours due to the low capacity of the extraction disk and the battery life time.

Integrative passive sampling methods are possible alternatives to overcome the limitations of active water sampling methods and have gained increasing interest for the monitoring of pesticides in water. Some advantages of these integrative passive samplers over conventional water sampling methods include simple handling and deployment procedures, longer deployment periods, high detection limits, and relative cost effectiveness. Several integrative passive sampling devices have been developed for the monitoring of pesticides in surface water. These include polar organic chemical integrative sampler (POCIS) for polar pesticides;¹⁷ chemcatcher for both polar and non-polar pesticides;¹⁸ semi-permeable membrane devices (SPMD) for non-polar pesticides;¹⁹ trimethyl-pentane containing passive sampler (TRIMPS) for both polar and non-polar pesticides;²⁰ and membrane enclosed sorptive coating (MESCO) for non-polar pesticides.²¹ However, POCIS, chemcatcher, and SPMD are the most commonly used for the monitoring of pesticides in surface water and are commercially available. SPMD is a well-established and implemented passive sampling device. POCIS and chemcatcher, on the other hand, are relatively newer passive sampling devices with ongoing research to define the mechanisms of sorption. The focus of this work is the use of POCIS for the monitoring of pesticides in water.

POCIS Description

POCIS was developed by Alvarez et al.¹⁷ for the monitoring of polar organic chemicals in water. A typical POCIS device used for the monitoring of pesticides in water consists of Oasis HLB resin (200 mg), the sorbent, which is enclosed between two polyethersulfone (PES) membranes (90 mm diameter and 0.1 μm pore size) and held together by two stainless-steel rings, as illustrated in Figure 1.1. The PES membrane acts as a semi-permeable barrier, allowing freely dissolved molecules to diffuse through to the sorbent while excluding particulates, microorganism, and macromolecules with a cross-sectional diameter greater than 0.1 μm . POCIS, as described in Figure 1.1, works best for chemicals with a log K_{ow} of less than four. The sorbent (Oasis HLB) and the membranes (PES) have been modified in several studies in order to further optimize the accumulation of specific classes of chemicals.²²⁻²⁷

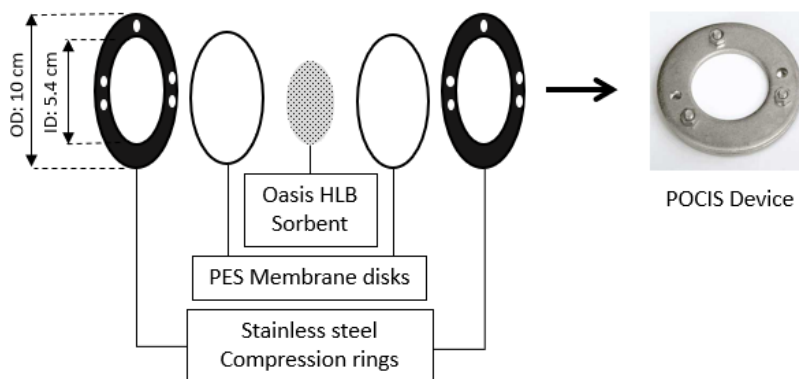


Figure 1.1. Schematic of a typical polar organic chemical integrative sampler (POCIS) used for the monitoring of pesticides in surface water.

POCIS devices have been used in several field applications including chemical screening,²⁸ coupling with bioassay,²⁹ and determination of TWACs of chemicals in

water.³⁰ An example of the work flow in field application for the determination of TWACs is illustrated in Figure 1.2.

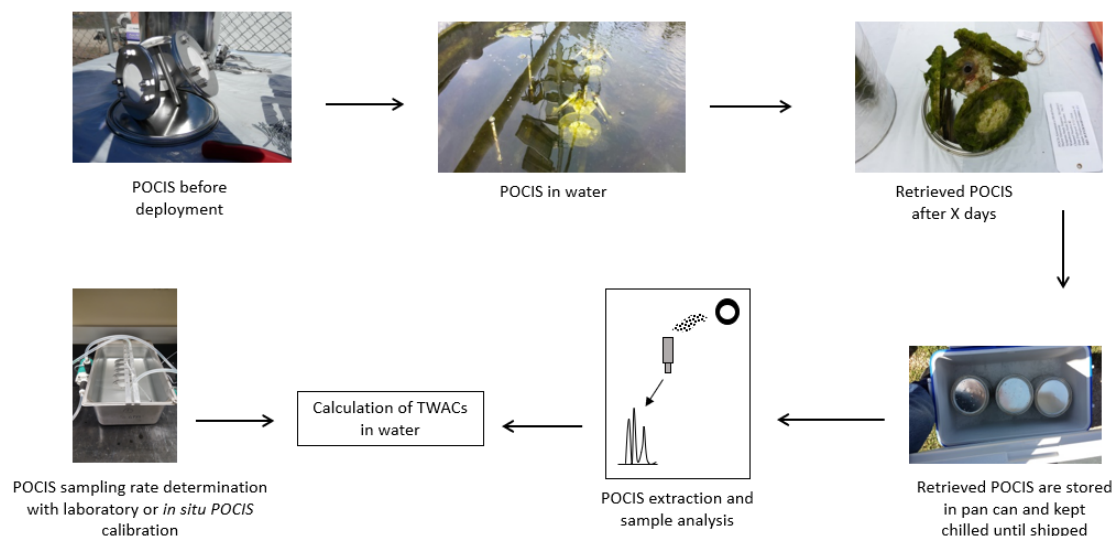


Figure 1.2. Typical work flow for chemical monitoring and TWAC determination in water using POCIS.

Theory and Modeling

POCIS is based on the free movement of chemicals from the water to the sorbent of the passive sampling device. A first order kinetic model is typically used to describe POCIS accumulation of chemicals over time, where accumulation is first integrative, then curvilinear, and finally reaches equilibrium as illustrated in Figure 1.3.^{31, 32} The net flow of chemicals from water to the sorbent occur until equilibrium is reached or until the sampling is terminated. The determination of TWACs in water with POCIS can only be carried out within the linear or integrative uptake phase. Previous studies have demonstrated that POCIS linear uptake phase is compound-dependent and can last up to two months.^{17, 33}

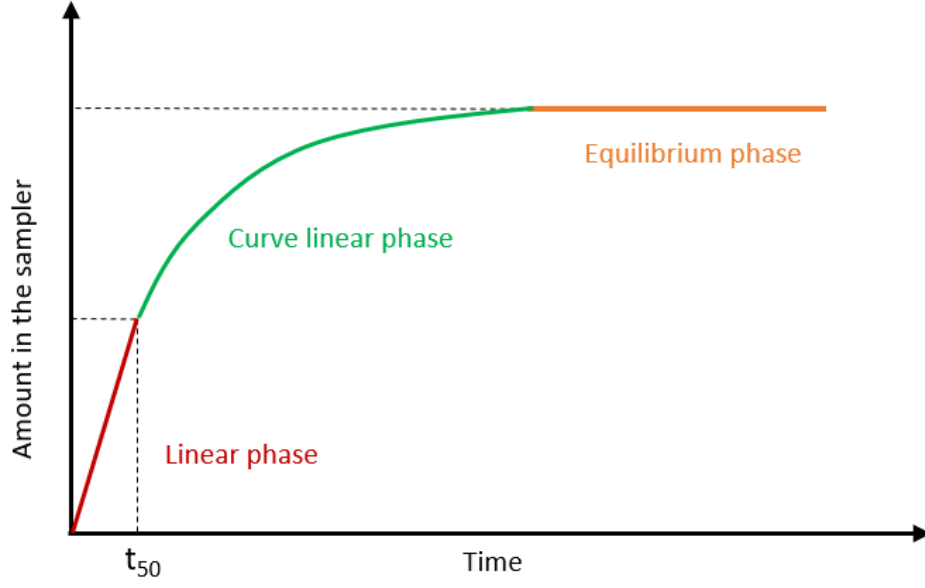


Figure 1.3. Uptake phases of POCIS accumulation. t_{50} is the time needed for POCIS to accumulate half of the equilibrium amount of chemicals.

Overall chemical uptake into POCIS is described as follows:³⁴

$$\frac{dC_s}{dt} = \frac{Ak_0}{V_s} \left(C_w - \frac{C_s}{K_{sw}} \right) \quad (1)$$

Where C_s and C_w are the concentrations of chemical in the sampler and water, respectively, K_{sw} is the sampler-water partition coefficient, k_0 the overall mass transfer coefficient, A is the sampler surface area and V_s the sampler volume.

Chemical concentration in the sampler (C_s) at a given time t from Eq. (1) is as follows:

$$C_s = K_{sw}C_w(1 - e^{-k_e t}) \quad (2)$$

Where k_e , the elimination rate constant, is as follows:

$$k_e = \frac{Ak_0}{K_{sw}V_s} \quad (3)$$

Within the linear or integrative phase, it is assumed that chemical concentration in POCIS is very small compared to chemical concentration at equilibrium ($C_s \ll K_{sw}C_w$), leading to the simplification of Eq. (1) after integration over time to:

$$C_w = \frac{C_s V_s}{A k_0 t} \quad (4)$$

Where $A k_0$ is equivalent to the apparent water sampling rate (R_s) over a given exposure time t and the amount of chemical adsorbed by the sampler (N_s) equals to $C_s V_s$, leading to Eq. (5):

$$C_w = \frac{N_s}{R_s t} \quad (5)$$

Where C_w is the time-weighted average concentration for a given exposure time t within the linear uptake phase.

Limitation of POCIS in Field Studies

POCIS used for the monitoring of chemical TWACs in surface water has several advantages over conventional discrete or continuous grab water sampling methods. However, previous studies have reported significant inconsistencies between TWACs calculated from POCIS and from high frequency automatic grab sampling.^{35, 36} These inconsistencies in TWACs are attributed to the dependence of POCIS sampling rate on environmental conditions such as temperature, flow velocities, and biofouling.

The overall mass transfer coefficient (k_0) is the only variable in Equation 4, which enables the calculation of TWAC in water (Eq.4). k_0 includes mass transfer of chemicals from bulk water to the sorbent as described in Figure 1.4 and is expressed as follows:³⁴

$$\frac{1}{k_0} = \frac{\delta_w}{D_w} + \frac{\delta_f}{D_f K_{fw}} + \frac{\delta_m}{D_m K_{mw}} \quad (6)$$

Where D_w , D_f and D_m are the diffusion coefficient in the water boundary layer (WBL), the fouling layer (FL) and the membrane layer (ML), respectively; K_{fw} and K_{mw} are the fouling layer-water partition coefficient and the membrane-water partition coefficients, respectively; δ_w , δ_f and δ_m are the thickness of the water boundary layer and the membrane layer, respectively. The diffusion of molecules through a given solution or materials and the partition of molecules between two given phases are both significantly dependent on temperature,³⁷⁻³⁹ hence the dependence of POCIS sampling rate on temperature. The dependence of POCIS sampling rate on hydrodynamic conditions is related to the thickness of the WBL, which changes with hydrodynamic conditions. In stagnant conditions, the WBL thickness is at its maximum and decrease with increasing turbulence.^{34, 40}

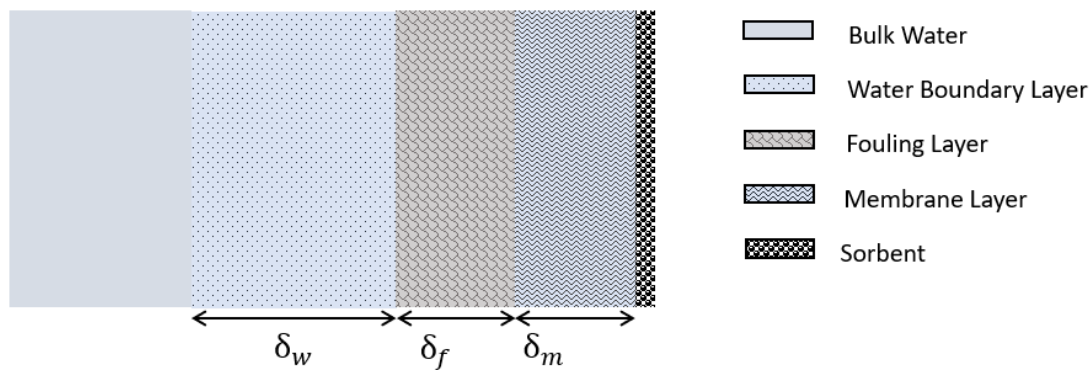


Figure 1.4. Representation of different barriers to chemical uptake into POCIS.

One alternative to overcome this issue is to perform *in situ* POCIS calibration for the determination of the sampling rate. But, the use of such derived *in situ* POCIS sampling rates is limited to sites with similar environmental conditions. Another alternative to bridge the gap between TWACs calculated from grab sampling and POCIS in order to have a

better fundamental understanding of the effects of changing environmental factors on each component of k_0 (i.e., WBL, FL and ML) and to derive models that can be applied in field studies in order to account for changes in environmental factors.

Analytical Instrumentations Used for Water Monitoring Samples Analysis

Analytical instrumentation plays a key role in the monitoring of pesticides in water, as they are the determining factors of analytical method detection limits and throughput. High performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) is one of the most common analytical instrumentations used for the analysis of pesticides in water. As illustrated in Figure 1.5, sample analysis with HPLC-MS/MS typically goes through four major steps including analyte separation, ion generation, mass analysis and detection.

First, analytes are separated in a chromatographic column based on interactions with the mobile and stationary phases, depending on the analytes chemical and/or physical properties. Analysis of pesticides in water is typically performed with reverse phase chromatography, where analyte interaction occurs between non-polar stationary phases such as C-18 and an aqueous polar mobile phase. Analytes with higher polarity interact more with the polar mobile phase and move faster through the column, while analytes with lower polarity interact more with the stationary phase and move more slowly through the column. Analyte separation can be optimized by using a mobile phase with decreasing polarity. This can be achieved by using a mixture of polar (aqueous) and non-polar solvents such as methanol or acetonitrile for the mobile phase.

Second, gas-phase ions are produced from the analyte solution exiting the column. Electrospray ionization (ESI) is one of the most common ion sources used for the analysis

of pesticides in water, where gas-phase ions are produced under atmospheric-pressure conditions from a sample solution directed through a capillary needle that is maintained at a high electric potential.^{41, 42} Proposed mechanism for the generation of gas-phase ions for small molecules such as pesticides is the ion evaporation model and is illustrated in Figure 1.5.⁴¹ Basically, as the solvent evaporates from a given droplet, the charge density in that droplet increases and reaches a threshold where the repulsive force between the charges in the droplet exceeds the surface tension of the droplet, leading to fission and the formation of smaller droplets until gas-phase ions are produced.

Third, the produced gas-phase ions are analyzed based on the mass to charge ratio (m/z) by a mass analyzer. Tandem quadrupole is one of the most commonly used mass analyzers for analysis of pesticides in water. Quadrupoles are mass analyzers which consist of four rods with a range of DC and RF voltages applied, enabling gas-phase ions to be filtered based on m/z . As illustrated in Figure 1.5, tandem quadrupole consists of three sets of quadrupoles. Multiple Reaction Monitoring is the most commonly used mode of a tandem quadrupole for quantitative analysis. The first quadrupole (Q1) works as a mass filter, allowing only a specific precursor ion to move on to the second quadrupole. Next, the selected precursor ion is fragmented in the second quadrupole (Q2) or collision cell with an inert gas such as nitrogen. Finally, the ions produced from the collision cell are transferred into the third quadrupole (Q3), which also works as a mass filter and allows only product ions with a specific m/z to pass.

Fourth, the transmitted product ions are detected. The signal is amplified, digitized and processed to produce chromatogram as illustrated in Figure 1.5. Photomultiplier tube (PMT) is one of the most commonly used detectors for mass spectrometry.

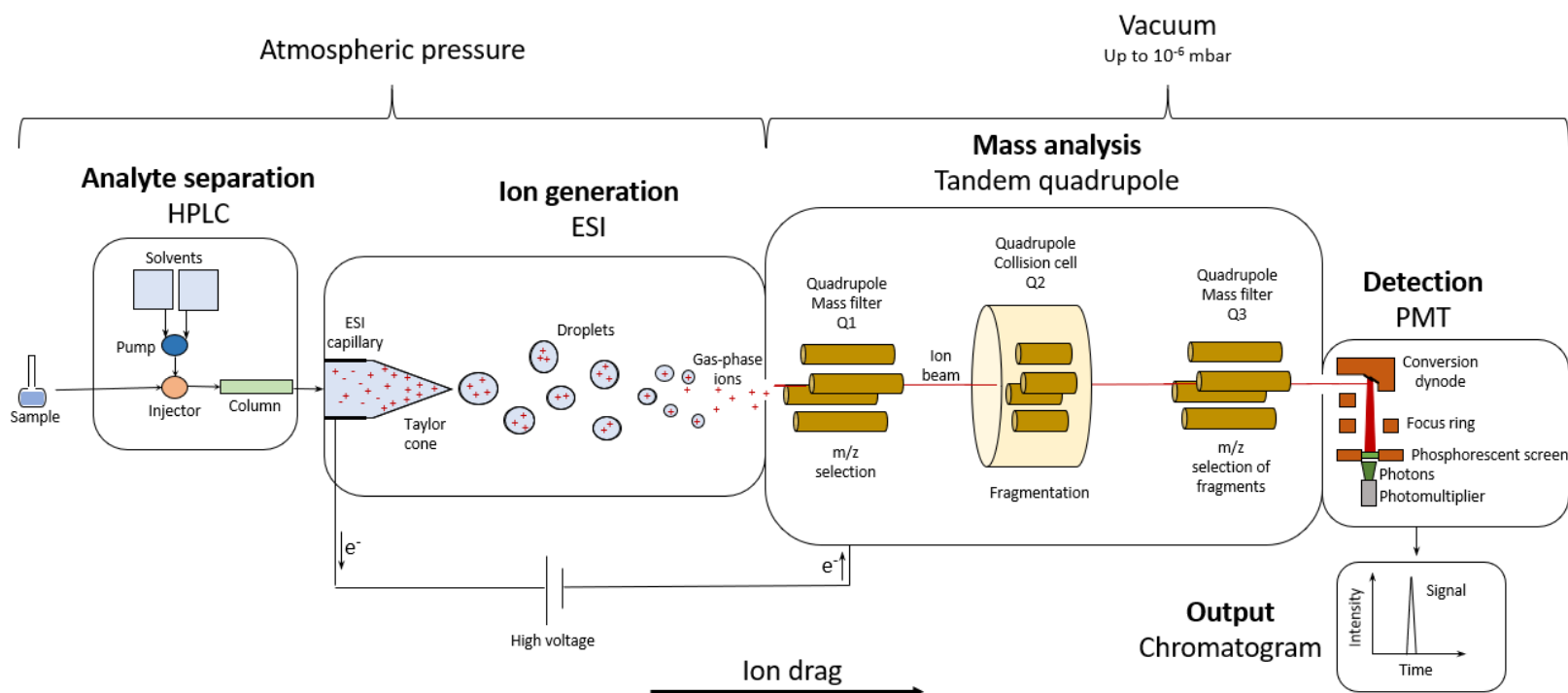


Figure 1.5. Schematic representation of commonly used high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) for pesticides analysis in water.

The ions exiting Q3 strike a conversion dynode, which results in electron emission. These electrons then strike the phosphorous screen, which in turn releases a burst of photons. The photons then pass into the photomultiplier tube where amplification occurs.

Scope of the Present Work

The overall goal of this work is to provide improved fundamental understanding of POCIS sampling rates to bridge the gap between data derived in laboratory versus field settings. The objectives of this work are to investigate the effects of changes in environmental conditions on POCIS sampling rates for 12 pesticides (atrazine, azoxystrobin, bicyclopyrone, cyproconazole, fomesafen, mesotrione, S-metolachlor, propiconazole, sedaxane, simazine, solatenol and thiamethoxam) with a range of physico-chemical properties, using UPLC-MS/MS analysis for water and POCIS extracts. Independent laboratory POCIS experiments were carried out with a given environmental condition including flow velocity, temperature, total suspended solid (TSS) sediment concentration and pesticide concentration exposure. These environmental factors were selected for the above pesticides based on typical environmental conditions observed in agricultural streams.

The main objective in chapter two was to develop and validate a multi-residue UPLC-ESI-MS/MS method for the select pesticides in surface water. The development of this method was necessary to support quantitative targeted trace analysis of water and POCIS extract samples in chapter three, four and five. Standard operating procedure (SOP) of analytical method from sample collections in the field through sample analysis was developed and internally published in Syngenta (report number: TK0180337). This SOP will be used to support ongoing and future Syngenta studies. I am the primary author of

this chapter, performing all the method development, validation and analysis of the select compounds. Dr. Sunmao Chen and Dr. Kevin Chambliss were involved in all aspects of this work.

The main objective in chapter three was to investigate the effect of hydrodynamic conditions and temperature on POCIS sampling rates. Changes in hydrodynamic conditions is one of the most common changes in environmental factors observed in field studies. Several studies have investigated the effect of changes in hydrodynamic conditions on POCIS sampling rates and have demonstrated that there is significant increase in POCIS sampling rates from stagnant to flow conditions. However, there were still some uncertainties regarding the effect of increasing flow velocity on POCIS sampling rates. One possible contributing factor to such uncertainty is the lack of a standard method to characterize flow velocities in the laboratory, making the comparison of results among studies difficult. We have developed an independent method to determine flow velocity at/near the surface of POCIS devices. This approach represents a step forward in terms of standardizing estimations of flow rate in passive sampling experiments. We then investigated the effect of hydrodynamic conditions including stagnant and five flow velocities ranging from 6 to 21 cm/s, using corrected flow velocities. Temperature is another environmental factor subject to significant changes. Yet, only one study has investigated the effects of temperature on POCIS sampling rates and proposed an Arrhenius model to describe the dependence of POCIS sampling rates and temperature. However, the study only evaluated three temperature points over a relatively small temperature range (18 to 30 °C), making the proposed model not statistically robust. We have assessed the temperature dependence of POCIS sampling rate for five temperatures

ranging from 8 to 39 °C. These temperatures span the range most commonly observed in field monitoring applications. Finally, the significance of using temperature-corrected sampling rates in a field study was evaluated by comparing TWACs calculated from POCIS and from daily composite water sampling. This work is published in *Environmental toxicology and chemistry*. I am the primary author of this chapter, designing the experimental procedure and apparatus used for POCIS exposure, performing sample analysis and data interpretation. Raegyn Taylor also assisted with the development of the method to determine flow velocity near the surface as well as daily water renewal and POCIS extraction. Dr. Kees Booij, assisted with the development of the method to determine flow velocity near the surface of POCIS as well as the writing and editing of the manuscript. Dr. Sunmao Chen and Dr. Chambliss were involved in all aspects of this work.

The main objective in chapter four was to investigate the effects of suspended sediment on POCIS sampling rates. POCIS devices used for the monitoring of pesticides in field studies are typically made of Oasis HLB sorbent sandwiched between two porous polyethersulfone (PES) membranes that are tightly held in place with two stainless steel rings. Diffusion of chemicals into POCIS occur through the PES membranes can occur via water filled-pores or via the PES matrix. Environmental factors such as microorganisms or sediment can potentially foul and/or alter the PES membrane structure, which may affect the transport of chemicals across the membranes and subsequently affect the uptake of chemicals by the sorbent. Total suspended solid (TSS) concentration in some agricultural streams can be as high as 18,000 ppm during heavy runoff events, with median concentration ranging from 500 to 2000 ppm. Additionally, heavy sediment deposits have been observed on the surface of POCIS devices deployed in those streams. We are, to the

best of our knowledge, the first to investigate and report effects of PES fouling by sediment on POCIS uptake. POCIS uptake of the 12 select pesticides was evaluated in parallel experiments for POCIS exposure to water containing sediment (daily average TSS concentration of 3600 ppm) and water containing no sediment (as a control). The amount of each pesticide adsorbed onto Oasis HLB sorbent and PES membranes was assessed. These data were interpreted in the context of a common mass transport model for movement of chemicals across the PES membrane. I am the primary author of this chapter, designing the experimental procedure and apparatus used for POCIS exposure, performing sample analysis and data interpretation. Dr. Sunmao Chen and Dr. Chambliss were involved in all aspects of this work.

The main objective in chapter five was to investigate the effects of concentration exposure on POCIS uptake. Pesticides concentration in agricultural streams are known to significantly fluctuate by up to several orders of magnitudes with time. The use of traditional discrete grab water sampling methods for pesticides monitoring in those streams may fail to integrate peak events and derive TWACs that are not representative of actual concentrations. This can be significantly improved by using high sampling frequency automatic grab samplers such ISCO. However, the latter method is very expensive and labor intensive. A more convenient and relatively low-cost alternative is the use of POCIS. However, determination of TWACs using POCIS in field studies is carried out with the assumption that the POCIS devices operate within the linear phase during the period of deployment and thus should integrate concentration peaks. Few studies have evaluated the ability of POCIS to accurately provide TWAC of chemicals in water with temporal fluctuation in concentrations and reported full integration of concentration peaks by

POCIS. However, the studies investigated the effect of concentration exposure of POCIS uptake for only relatively low concentrations and/or short exposure duration, thus, did not have a challenging enough temporal fluctuation of concentrations as observed in some agricultural streams. To the best of our knowledge, we are the first to investigate and report effects of concentration exposures on POCIS uptake for environmentally relevant high concentrations. POCIS devices in series of 41 independent experiments, were exposed to seven constant concentrations ranging from 3 to 60 $\mu\text{g/L}$ and five pulse concentrations ranging from 5 to 150 $\mu\text{g/L}$. This concentration range was selected to reflect concentrations observed in some agricultural streams. In this work, the effects of Oasis HLB redistribution and settling between the PES membranes, a phenomenon that has been observed in previous experiments in our research group and also reported in the literature, was also investigated in junction with unexpected change in POCIS sampling rates observed for some pulse experiments. Though Oasis HLB redistribution and settling between PES membranes has been reported in the literature, to the best of our knowledge, we are the first to investigate the effect of random Oasis HLB redistribution and settling between PES membranes on POCIS sampling rates. I am the primary author of this chapter, designing the experimental procedure and apparatus used for POCIS exposure, performing sample analysis and data interpretation. Raegyn Taylor and Dr. Jonathan Bobbitt assisted with experimental procedure, sample analysis and data interpretation. Dr. Sunmao Chen and Dr. Chambliss were involved in all aspects of this work. The overall conclusion of the dissertation and future work are discussed in chapter seven.

CHAPTER TWO

Development of a Multiresidue UPLC-MS/MS Method for Direct Injection Analysis of 10 Pesticides in Water using Internal Standards

Abstract

An analytical method using ultra-performance liquid chromatography with electrospray ionization and tandem mass spectrometry (UPLC-ESI/MS/MS) was successfully developed to determine pesticide (atrazine, azoxystrobin, bicyclopyrone, cyproconazole, fomesafen, mesotrione, *S*-metolachlor, propiconazole, simazine and thiamethoxam) residues in water using internal standards. The developed UPLC method enabled elution of the pesticides in less than 2.5 minutes with base line resolution of most of the compounds. The detection limit ranged from 0.02 to 0.1 µg/L. The calibrated linear range for target analytes extended from 0.02 to 5 µg/L. Three criteria were used to validate the linearity of calibration curves: correlation coefficients (R^2) for analyte response vs. concentration plots, corresponding log-log plots ($R^2 > 0.99$) and relative standard deviation (RSD) of relative response factors (RRF) for a given set of calibration standards ($\leq 10\%$). Mean analyte recoveries, derived from analysis of continuing calibration verification (CCV) samples, ranged from 91 to 107% with standard deviations $\leq 11\%$. Matrix effects were evaluated for three surface water samples by comparing slopes of solvent-based and matrix-matched calibration curves. Negligible matrix interference was observed for all compounds evaluated in this method except azoxystrobin, fomesafen and mesotrione. Matrix had a small, but identifiable, effect on the analytical response observed for these

compounds. Matrix effects were offset using stable isotope internal standards. The method was validated *via* direct injection of fortified river water samples.

Introduction

The use of pesticides has tremendously improved the agricultural sector worldwide by increasing food production to feed a growing population as well as other benefits such as reducing insect-borne diseases. In order to monitor the potential occurrence of pesticides in the environment, the focus has been on the development of analytical tools enabling reliable detection and quantification of a wide range of pesticides at low concentration. A variety of liquid chromatography-mass spectrometry (LC-MS) or gas chromatography-mass spectrometry (GC-MS) analytical methods have been developed to meet such criteria. However, many of these methods require an additional sample preparation step for clean-up and sample pre-concentration in order to lower the limit of detection to environmentally relevant concentrations. These sample preparation techniques include liquid-liquid extraction,⁴³ solid-phase extraction,⁴⁴ solid-phase microextraction,⁴⁵ liquid-phase microextraction,⁴⁶ dispersive liquid-liquid microextraction,⁴⁷ single drop microextraction,⁴⁸ and ultrasound assisted emulsification-microextraction.⁴⁹ Although these techniques have been proven to be effective for pesticide analysis in water, they can be laborious, time consuming and/or expensive. In recent years, significant progress has been made with the development of new techniques that enable direct sample injection for multiresidue analysis of chemicals in water at sub-parts per billion concentrations. Ultra-performance liquid chromatography (UPLC) coupled to tandem mass spectrometry has shown to be an excellent analytical tool for this purpose.^{44, 50}

In this study, a new multiresidue analytical method using ultra-performance liquid chromatography with electrospray ionization and tandem mass spectrometry (UPLC-ESI/MS/MS) was successfully developed for analysis of 10 pesticides in surface water. These pesticides were selected not because there is a regulatory requirement or safety concern leading to the need to monitor but to take advantage of a wide range of polarity characteristics and chemical properties thus allowing evaluation of the applicability of the analytical method as a potential multiresidue method. Additionally, they are representative of the main pesticide uses in the US including herbicides, fungicides and insecticides. The developed method presents a distinct advantage compared to other UPLC-MS/MS methods for analysis of pesticides in that sample preparation and preconcentration are not required. This method offers low detection limits, high precision and excellent accuracy, using only 9 μ L of sample.

Experimental

Chemicals and Reagents

Atrazine, azoxystrobin, bicyclopyrone, cyproconazole, fomesafen, mesotrione, S-metolachlor, propiconazole, simazine and thiamethoxam were provided by Syngenta Crop Protection, LLC at > 96% purity and used as received. Atrazine-d5, 4-Chloro-2-(methyl-d3) phenoxyacetic acid (MCPA-d3), metolachlor-d6, simazine-d10 and thiamethoxam-d3 were purchased from CDN isotopes (Quebec, Canada) at > 98% purity. Formic acid and HPLC grade acetonitrile (ACN) were purchased from Fisher Scientific (Fair Lawn, New Jersey, USA). A Thermo Branstead Nanopure (Dubuque, Iowa, USA) Diamond UV water purification system was used to provide 18 M Ω water for preparation of samples and UPLC eluents.

UPLC-MS/MS Analysis

Samples were analyzed directly *via* an Acquity UPLC system coupled to a Xevo TQ-S mass analyzer equipped with an electrospray ionization (ESI) source (Waters Corp., Manchester, England). The system was controlled by MassLynx 4.1 software. The Acquity UPLC system consisted of a degasser, a binary solvent pump, an autosampler (10 °C) and a column oven (35 °C). Analytes were separated on an Acquity UPLC BEH C18 column (2.1 x 50 mm x 1.7 µm) connected to a VanGuard pre-column (Acquity UPLC BEH C18 2.1 x 5 mm x 1.7 µm Waters, Milford, USA). The binary step gradient developed for optimal separation of analytes is illustrated in Table A1. 10 µL of each sample (i.e., 9 µL water sample plus 1 µL internal standards mixture) were injected and column effluent was diverted to waste during the first 0.5 min of each chromatographic run to prevent salts and highly polar compounds from contaminating the ESI source and potentially affecting the ionization of target analytes. The mass analyzer was operated in multiple reactions monitoring (MRM) mode throughout the analysis. Mass spectrometry parameters held constant during analysis were as follows: capillary voltage = 2.00 kV; source offset = 50 V; desolvation temperature = 600 °C; desolvation gas flow = 900 L/Hr; Cone gas flow = 150 L/Hr; nebulizer gas flow = 7 bar; collision gas flow = argon @ 0.15 mL/min.

Instrument Calibration and Performance Metrics

Calibration standards were prepared in 5/95 (v/v) ACN/water with 0.1% formic acid and contained isotopically labeled internal standards at 0.5 µg/L each and target analytes at concentrations ranging from 0.005 to 5 µg/L. Samples were prepared by adding 100 µL of internal standards mixture to 900 µL of each water sample. Analyte-specific calibration curves were constructed by plotting analyte response [i.e., analyte peak area x

(internal standard concentration/internal standard peak area)] on the y-axis versus analyte concentration on the x-axis. Calibration data were fit to a linear regression with 1/X weighting. A representative calibration curve is illustrated in Figure A1.

Linearity was verified by inspection of log-log transformations of each calibration plot. Additionally, the relative response factor (RRF) was calculated for each point and the precision of the RRF across the calibration range was assessed by calculating the coefficient of variation (CV). Criteria for acceptable calibration were that the relative standard deviation (RSD) of the RRF was $\leq 15\%$ and R^2 for the linear regression with 1/X weighting exceeded 0.99. The limit of detection (LOD) and limit of quantification (LOQ) were calculated for each analyte as 3 times and 10 times, respectively, the standard deviation of signal observed in the corresponding analyte retention time window following injection of a blank sample (i.e., 5:95 (v/v) ACN-water with 0.1% formic acid).

Method Validation

Water samples collected from the North Bosque River in Waco, Texas were spiked with standard solutions of pesticides at 0.05, 0.1 and 0.5 $\mu\text{g/L}$. Spike recoveries were calculated as the difference between observed concentrations in spiked and unspiked samples divided by the spiking level. Continuing calibration verification (CCV) samples were prepared and analyzed at three concentration levels, 0.05, 0.1 and 0.5 $\mu\text{g/L}$, to assess method performance characteristics.

Matrix effects were evaluated on surface waters collected from three different sources: North Bosque River in Waco Texas, Branch of Boeuf River, Louisiana and West Fork Cuivre River, Missouri. Solvent-based and matrix-matched calibration curves were prepared with pesticide concentrations ranging from 0.02 to 3 $\mu\text{g/L}$. Standards for the

solvent-based approach were prepared by dissolving target analytes and corresponding internal standards in 5/95 (v/v) ACN-water containing 0.1% formic acid. For the matrix-matched approach, 3 sets of standards containing the same amounts of target analytes and internal standards were prepared using surface water instead of nanopure water as the aqueous solvent. All standards were analyzed in triplicate. Statistical comparisons of slopes resulting from matrix-matched and solvent-based calibration were performed using a two-tailed Student's *t*-test at the 95% confidence level.⁵¹

Results and Discussion

Optimized UPLC-MS/MS Method

To determine the optimum conditions for MS/MS analysis of target analytes, each compound was infused individually into the mass spectrometer at concentrations ranging from 0.1 to 1 µg/mL in 5:95 ACN-water with 0.1% formic acid (v/v). The flow rate in these experiments was 10 µL/min. MS/MS transitions for each compound and their optimum collision cell energies and cone voltages were initially generated using IntelliStart, which is a program in MassLynx 4.1 that allowed the system to automatically tune MS/MS parameters for each compound. However, manual tuning of collision energies was required to identify suitable monitoring parameters for fomesafen and mesotrione.

Unique precursor-to-product ion transitions were identified for each pesticide (Figure 2.1). One precursor ion and two product ions were monitored for each analyte in the final method. The MS/MS transition including the most abundant and stable product ion was used for analyte quantification, and the transition including the second most abundant product ion provided a secondary confirmation of analyte identity. In general,

the quantitation ion should have the highest m/z ratio.⁵² However, this rule was not followed for cyproconazole, azoxystrobin and fomesafen. A relatively low-mass product ion (m/z 70) was selected for quantitative analysis of cyproconazole because its intensity exceeded that of the second most abundant product ion (m/z 125) by more than 10-fold. Similarly, product ions selected for quantitative analysis of azoxystrobin, fomesafen and simazine also had a lower m/z than their corresponding qualification ions but greater signal intensity (by at least 2-fold). All pesticides were ionized in positive mode except fomesafen and mesotrione, which were ionized in negative mode.

Even though good mass separation was achieved with MS/MS analysis, an UPLC method was developed to further optimize the separation and ionization of each pesticide. A step gradient resulted in baseline resolution of most analytes in less than 2.5 min as illustrated in Figure 2.2. Note that chromatographic peaks in this figure do not translate to equivalent analyte concentrations. Baseline separation of pesticides was targeted in this method to minimize potential ion suppression/enhancement effects caused by other analytes of interest, especially when isotopically-labelled internal standards are not available. Note that baseline resolution of target analytes also decreases the probability of more general matrix interference that could be caused by non-target compounds present in a given sample.

The UPLC method was divided into 4 steps. During step 0, column effluent was diverted to waste in order to exclude salts and highly polar compounds from the ESI source, which otherwise could have potentially affected the ionization of target analytes. Chromatographic separation of pesticides occurred during steps 1, 2 and 3, with an increasing non-polar mobile phase composition as illustrated in Figure 2.2. Selected

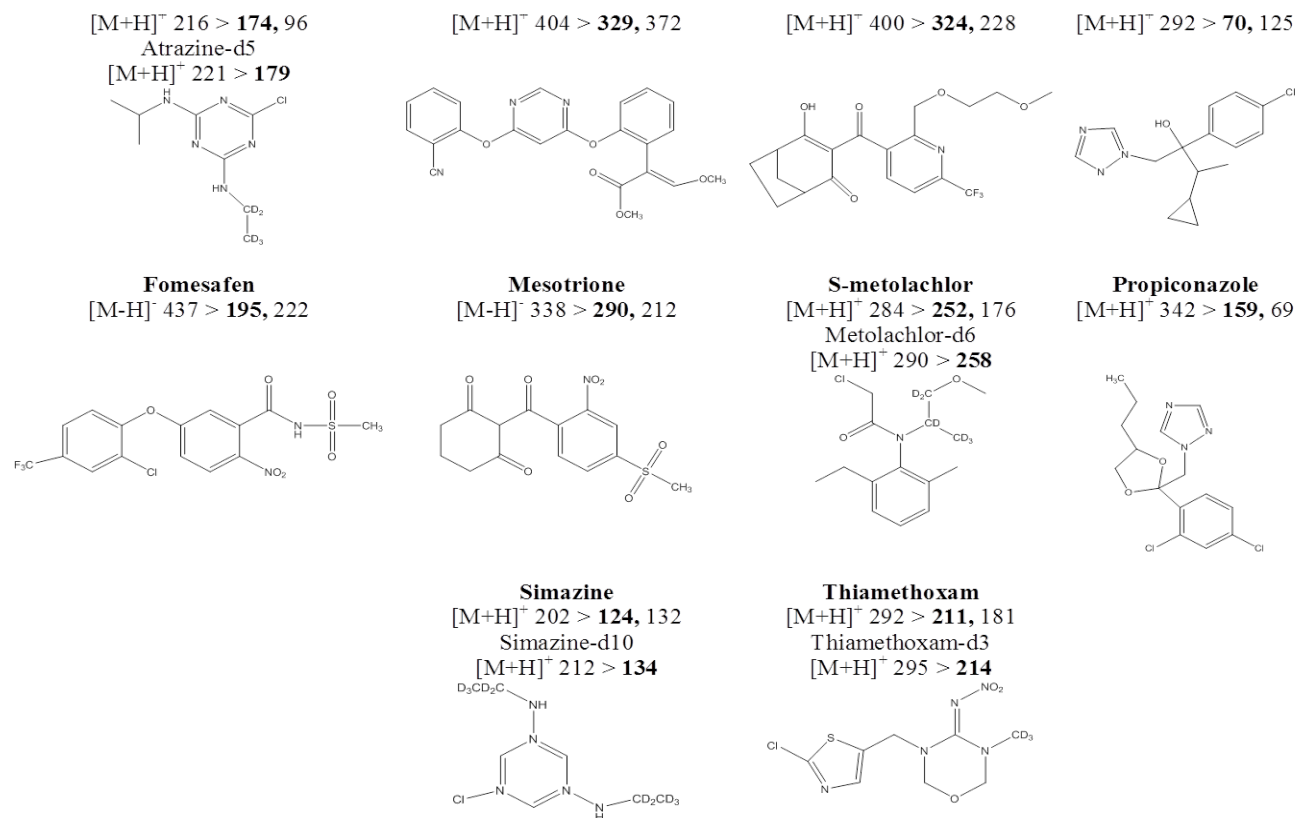


Figure 2.1 Common name, optimized MS/MS transitions (precursor ion > quantification ion, qualifier ion; $[M + H]^+$ and $[M - H]^-$ represent protonated and deprotonated molecular ions, respectively) and chemical structure of monitored analytes. Deuterium positions are shown on analytes for which isotopically-labeled internal standards were available.

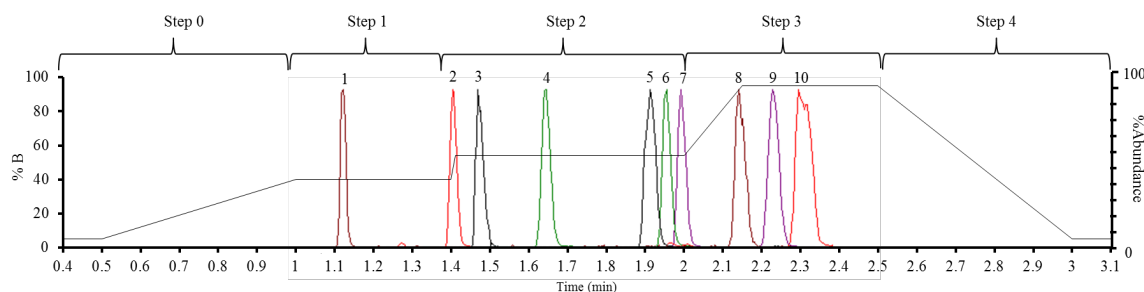


Figure 2.2. Chromatographic separation of target analytes with a binary mobile phase gradient. Elution order is as follows: (1) thiamethoxam, (2) simazine, (3) mesotrione, (4) atrazine, (5) cyproconazole, (6) bicyclopyrone, (7) azoxystrobin, (8) fomesafen, (9) S-metolachlor, and (10) propiconazole.

pesticides covered a wide range of polarity characteristics with octanol-water partition coefficients ($\text{Log } K_{ow}$) ranging from -0.13 to 3.72 . $\text{Log } K_{ow}$ was a good parameter to characterize analyte polarities in this study because, based on their pK_a values, the neutral form of each compound is expected to predominate throughout the separation. Thiamethoxam, which is the most polar analyte ($\text{Log } K_{ow} = -0.13$) eluted first during step 1. Fomesafen, S-metolachlor and propiconazole were the least polar ($\text{Log } K_{ow} = 2.9, 3.13$ and 3.72 , respectively) and eluted last during step 4. These results demonstrate that the separation followed general principles of reverse phase chromatography.^{53 53 53 53}

Step 4 was added to the UPLC method to ensure re-equilibration of the system before the next sample injection. The incorporation of a system re-equilibration step is generally very important when developing any liquid chromatography method involving a gradient. It ensures that initial mobile phase, column, and back pressure conditions are restored before the next sample is injected. Failure to allow for adequate re-equilibration can cause analyte retention time shifts and, consequently, lead to errors in analyte peak attribution and MS/MS analysis.⁵⁴

Even though fomesafen and mesotrione were completely resolved from the other pesticides, a decline of their analytical response was observed when MRM monitoring included all 10 pesticides compared to the signal observed when only these two analytes were monitored. Fomesafen and mesotrione are both ionized in negative mode, and the high throughput UPLC method developed in this work enabled elution of all compounds in less than 2.5 min. The relatively short time period of elution limited the capability of the mass analyzer to efficiently switch back and forth between positive and negative modes to generate ions. To resolve this issue, each sample was analyzed twice (first in positive mode and then in negative mode), resulting in a total duty cycle of 11 min per sample, which is still less time than many multiresidue methods.

Peak splitting of propiconazole and cyproconazole was observed during UPLC method development because they were provided as a mixture of diastereoisomers. Peak splitting of diastereoisomers has been previously reported for HPLC analyses.⁵⁵⁻⁵⁷ However, the final gradient resulted in baseline resolution of pesticides and alleviated peak splitting that was observed for other eluent compositions. Therefore, the method will detect and quantify all isomers as a single chromatographic peak.

Method Performance Characteristics

The linear range of analytical response for each analyte was investigated by plotting the log of analytical response versus the log of concentration for concentrations ranging from 0.005 to 5 µg/L. An example of this plot is illustrated for thiamethoxam in Figure A2. Correlation coefficients derived from linear regressions with $R^2 > 0.99$ were the only calibration points retained. In initial evaluations of linear range, the relative response factor (RRF) of each calibration point was plotted against its respective concentration. A

representative plot of RRF versus concentration is shown for thiamethoxam in Figure A3. Calibration points falling at or outside $\bar{X} \pm 2s$ (where \bar{X} is the mean RRF and s the standard deviation) were excluded from the linear range. In subsequent analyses, the criterion used to verify initial instrument calibration required that the relative standard deviation of RRFs for all calibration points was $\leq 15\%$. Results in Table 2.1 demonstrate that linear ranges for pesticides extended from 0.02 to 5 $\mu\text{g/L}$. LOD and LOQ were investigated by measuring the signals of selected pesticides in injection blanks. The LOD and LOQ were defined as 3 times and 10 times respectively, the standard deviation of the measured signal. Results in Table 2.2. illustrate the LOD and LOQ for the selected pesticides.

Continuing calibration verification (CCV) samples, consisting of concentrations near the LOQ (0.05, 0.1 $\mu\text{g/L}$) and near the mid-point of the calibrated range (0.5 $\mu\text{g/L}$) were analyzed over a period of 15 days to assess the method performance characteristics for daily calibrations. Mean analyte recoveries and the corresponding standard deviations ($n = 45$) were calculated for each pesticide concentration. Upper control limits (UCL) and lower control limits (LCL) were calculated for each concentration level as the mean recovery plus or minus 3 standards deviations, respectively. Mean recoveries and the corresponding control limits are reported in Table 2.2. Recoveries ranged between 91 and 107% with standard deviations below 11%. Data in Table 2.2 support the general conclusion that control limits determined for all analytes fall within $\pm 30\%$ of the mean recovery observed for each pesticide.

Surface water samples collected from the North Bosque River were filtered with 0.2 μm nylon membrane filters and spiked with pesticides at 0.05, 0.1 and 0.5 $\mu\text{g/L}$ to

Table 2.1. Linear range; limit of detection (LOD) and limit of quantification (LOQ) for direct injection of blank samples (n = 21); and analyte recoveries for fortified surface water samples (mean \pm standard deviation; n = 3).

Compound	Linear Range $\mu\text{g/L}$	LOD $\mu\text{g/L}$	LOQ $\mu\text{g/L}$	Recovery (%)		
				0.05 $\mu\text{g/L}$	0.1 $\mu\text{g/L}$	0.5 $\mu\text{g/L}$
Atrazine	0.02 - 3	0.005	0.02	108 \pm 3	106 \pm 2	99 \pm 2
Azoxystrobin	0.02 - 2	0.01	0.04	84 \pm 5	94 \pm 11	94 \pm 5
Bicyclopyrone	0.02 - 3	0.005	0.02	101 \pm 7	91 \pm 3	104 \pm 8
Cyproconazole	0.01 - 4	0.005	0.02	92 \pm 4	90 \pm 3	100 \pm 2
Fomesafen	0.08 - 5	0.02	0.08	95 \pm 3	98 \pm 4	102 \pm 4
Mesotrione	0.08 - 5	0.03	0.1	91 \pm 9	88 \pm 4	94 \pm 3
S-Metolachlor	0.02 - 2	0.005	0.02	102 \pm 5	102 \pm 1	100 \pm 5
Propiconazole	0.02 - 3	0.015	0.05	104 \pm 3	106 \pm 2	106 \pm 4
Simazine	0.01 - 4	0.005	0.02	93 \pm 2	98 \pm 3	112 \pm 7
Thiamethoxan	0.01 - 4	0.005	0.02	98 \pm 6	94 \pm 5	103 \pm 5

Table 2.2. Recoveries resulting from repeated analysis of continuing calibration verification (CCV) samples and preliminary control limits for method performance at concentrations near the LOQ [0.05 and 0.1 $\mu\text{g/L}$ (*)] and near the middle of the calibration range (0.5 $\mu\text{g/L}$). \bar{X} is the mean and s the standard deviation for n = 45; LCL and UCL are the lower and upper control limits, respectively.

Recovery Range	CCV % at 0.05 $\mu\text{g/L}$			CCV % at 0.5 $\mu\text{g/L}$		
Compound	$\bar{X} \pm s$	LCL	UCL	$\bar{X} \pm s$	LCL	UCL
Atrazine	97 \pm 6	78	116	98 \pm 4	86	109
Azoxystrobin	105 \pm 9	79	130	107 \pm 6	89	126
Bicyclopyrone	92 \pm 9	66	118	94 \pm 7	72	116
Cyproconazole	102 \pm 7	82	123	98 \pm 5	84	112
Fomesafen*	100 \pm 10	71	129	99 \pm 8	76	123
Mesotrione*	98 \pm 9	71	125	98 \pm 9	71	125
S-Metolachlor	100 \pm 4	87	113	99 \pm 3	90	108
Propiconazole	99 \pm 7	79	120	96 \pm 7	74	118
Simazine	100 \pm 9	72	128	99 \pm 6	81	116
Thiamethoxan	91 \pm 7	69	112	99 \pm 5	85	114

evaluate the accuracy of the method. These concentrations represent the LOQ and the approximate mid-point of the calibration range for each analyte. As shown in Figure 2.3, mean recoveries ranged from 89 to 106%, demonstrating acceptable accuracy of the developed method for analysis of surface water.

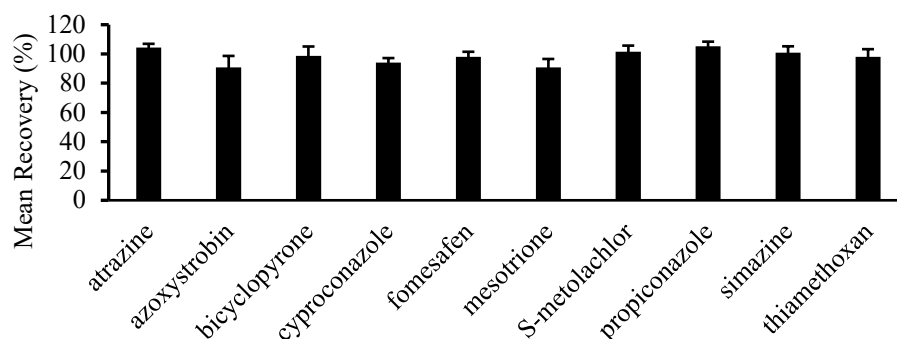


Figure 2.3. Mean recoveries from surface water. Error bars represent the standard deviation ($n = 9$) for three concentrations, specified in Table 1. Surface water was collected from the North Bosque River in Waco TX.

Evaluation of Matrix Effects

Matrix effects were evaluated for three environmental water samples, collected from the North Bosque River in Waco Texas, the Branch of Boeuf River, Louisiana and the West Fork Cuivre River, Missouri. The graph in Figure 2.4A illustrates a comparison of slopes resulting from external calibrations (i.e., no internal standard was employed in these data treatments) using standards prepared in solvent and in each of the three environmental matrices. Asterisks in this figure designate instances where the slope of a given matrix-matched calibration curve was found to be statistically different than the slope observed for the corresponding solvent-based calibration. Calculated t values are reported in Table A2. Identifiable matrix effects were observed for seven analytes in the Missouri sample (i.e., thiamethoxam, propiconazole, mesotrione, S-metolachlor, atrazine,

azoxystrobin, and cyproconazole), six analytes in the Louisiana sample (i.e., thiamethoxam, propiconazole, mesotrione, simazine, S-metolachlor, and azoxystrobin), and 4 analytes in the sample collected from the North Bosque River (i.e., propiconazole, thiamethoxam, simazine, and mesotrione).

Matrix effects are common in quantitative ESI methods,⁵⁸⁻⁶² and several strategies have been reported for reducing matrix effects in water analysis. These methods include effective sample clean-up, optimization of the chromatographic method to achieve complete separation of target analytes, dilution of sample extracts, standard addition and the use of internal standards.⁶³⁻⁶⁸ The use of a structurally-identical, isotopically-labeled internal standard for each analyte is often the preferred approach for combating matrix interference, but isotopically-labeled standards were only available for 4 of 10 pesticides monitored in the present study.

Figure 2.4B illustrates a comparison of slopes similar to that shown in Figure 2.4A, but in this case, an internal standard calibration approach was used. Isotopically-labeled internal standards were used for atrazine, metolachlor, simazine and thiamethoxam. Atrazine-d5 was also used as the internal standard for azoxystrobin, bicyclopyrone and cyproconazole. Metolachlor-d6 was used as the internal standard for propiconazole, and MCPA-d3 (eluting at 1.71 min) was used as the internal standard for fomesafen and mesotrione. These internal standard pairings were selected to minimize statistically relevant differences between calibration slopes resulting from matrix-matched and solvent-based calibration. Results in Figure 4B demonstrate an approximate 40% reduction in the total number of instances where a matrix effect was identified (i.e., from 17 in Fig. 2.4A to 10 in Fig. 2.4B). As expected, the use of an isotopically-labeled analog considerably

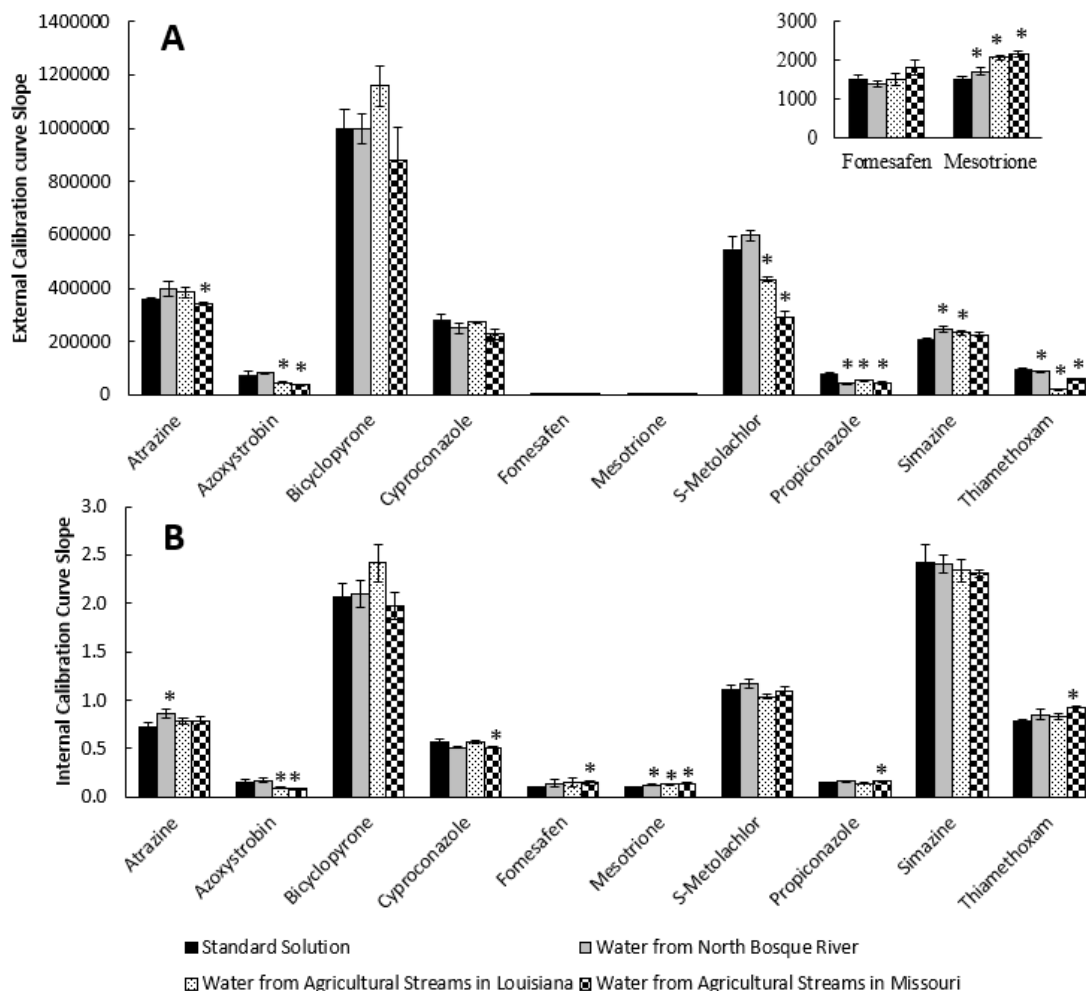


Figure 2.4. (A) Slopes resulting from solvent-based and matrix-matched, external calibration curves. (B) Slopes resulting from solvent-based and matrix-matched, internal standard calibration. Asterisks designate instances where the slope of a given matrix-matched calibration curve was found to be statistically different than the slope observed for the corresponding solvent-based calibration.

improved the agreement between calibration slopes observed for S-metolachlor, simazine, and thiamethoxam. The use of internal standards also improved the agreement between calibration slopes observed for propiconazole and (to a somewhat lesser extent) mesotrione. For the remaining analytes (atrazine, azoxystrobin, bicyclopyrone, cyproconazole and fomesafen) the use of internal standards did not substantially alter the

extent of agreement between calibration slopes relative to the external calibration condition.

Although some matrix interference was observed as shown in Figure 2.4B, it is important to recognize that the magnitude of matrix effects identified in this work are likely to have only a minimal effect on the accuracy of experimentally determined concentrations. To illustrate this point, solvent-based and matrix-matched calibration curves for mesotrione are plotted on the same graph in Figure 2.5. Horizontal lines intersecting the *y*-axis represent a hypothetical response typically observed for standards containing analyte at concentrations of 1.0 and 2.5 µg/L. Vertical lines represent the analytical concentration that would result from each of the four calibration lines. Shaded regions along the *x*-axis represent the uncertainty expected for a concentration determined from the solvent-based calibration curve. This level of uncertainty is specified by the control limits reported in Table 2.2. Note that half of the concentrations resulting from matrix-matched calibration curves fall within the expected precision range of the method and that concentrations falling outside of the range are near the margins. A similar illustrative analysis was performed for the other statistically different slopes identified in Figure 2.4B. Azoxystrobin and fomesafen were the only other analytes exhibiting a concentration from matrix-matched calibration that fell outside of the expected precision range for a solvent-based calibration curve, and even then, in no case was the concentration further from the precision margin than in the representative example shown in Figure 2.5.

Overall, a high throughput UPLC-MS/MS method was developed for the analysis of 10 pesticides in water. A linear range covering two orders of magnitude with low detection limits was achieved by direct injection of water samples. It was

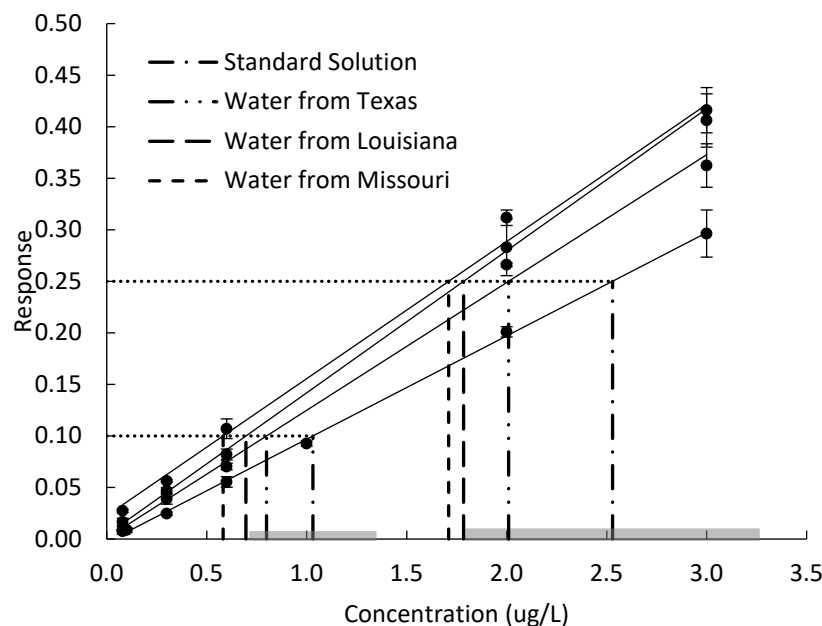


Figure 2.5. Solvent-based and matrix-matched, internal-standard calibration curves for mesotrione. The shaded grey areas along the x-axis represent the expected precision ($\pm 27\%$) of a given measurement, and vertical lines demonstrate that statistically identified matrix effects have a minimal effect on measurement accuracy. See text for details.

demonstrated that the developed method is suitable for analysis of selected pesticides in surface waters with minimal matrix effects. The protocol used to evaluate matrix effects in this study is standard practice in analytical chemistry. However, the results shown in Figure 2.5 highlight the fact that there is no hard and fast rule to determine when matrix effects are of a sufficient magnitude to warrant an alternative quantitative protocol. Based on observations reported in this work, it seems that even statistically-relevant matrix effects are unlikely to have an appreciable effect on pesticide concentrations determined using the developed methodology. However, internal standards could be used for the analysis of azoxystrobin, fomesafen and mesotrione or any other analytes as a measure to overcome any potential matrix effects.

CHAPTER THREE

Effects of Hydrodynamic Conditions and Temperature on POCIS Sampling Rates

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Abstract

The effects of changing hydrodynamic conditions and changing temperatures on Polar Organic Chemical Integrative Sampler (POCIS) sampling rates (R_s) were investigated for 12 crop protection chemicals. Exposure concentration was held constant in each laboratory experiment, and flow velocities were calculated from measured mass transfer coefficients of the water boundary layer near the surface of POCIS devices. Sampling rates at a given temperature generally increased by a factor of 2-5 between a stagnant condition and higher flow velocities (6 – 21 cm/s), but R_s for most compounds was essentially constant between the higher flow velocities. When temperature was varied between 8 and 39 °C for a given flow condition, R_s increased linearly. In general, sampling rates increased by a factor of 2-4 and 2-8 over this temperature range under flow and stagnant conditions, respectively. An Arrhenius model was used to describe the dependence of POCIS sampling rates on temperature. Adjustments of R_s for temperature did not fully explain observed differences between time weighted average concentrations of atrazine determined from POCIS and from composite water sampling in a field setting, suggesting that the effects of other competing factors still need to be evaluated.

Introduction

Monitoring of chemicals in the aquatic environment is essential for preservation of aquatic ecosystems and water quality. Manual grab or automated composite sampling have traditionally been used for the collection of water samples. However, these sampling methods only provide information corresponding to the time(s) of water collection. They are also generally costly and/or labor intensive, especially when frequent sampling is required to generate more robust data. The use of passive sampling devices as an alternative approach for monitoring dissolved chemicals has increased significantly over the past decade. Passive samplers have several advantages over grab and automated sampling methods including longer sampling duration, lower detection limits, potentially reduced cost and relatively easy deployment, transport and storage.^{69, 70}

Polar organic chemical integrative sampler (POCIS) is one of the most commonly used passive sampling devices for moderately polar organic compounds. POCIS devices have been used in a wide range of field applications including chemical screening,⁷¹ coupling with bioassay,^{72, 73} and estimation of time weighted average concentrations (TWAC) of chemicals in water.^{74, 75} However, the use of POCIS devices for evaluation of TWACs is limited in field applications. Previous studies have demonstrated a discrepancy between TWACs calculated from grab samples and from POCIS.^{35, 76} Such discrepancy is generally assumed to be caused by changing environmental conditions. Hydrodynamic conditions and temperature are important factors in field applications that may contribute to the inconsistency between TWACs. Additionally, inadequate grab sampling frequency and duration may also contribute to the discrepancy between POCIS and batch sampling results.

Previous studies have demonstrated that POCIS sampling rates increase significantly from stagnant to flow conditions.^{17, 77-79} However, there is some ambiguity related to the effect of increasing flow velocity on POCIS sampling rates. Some studies have reported that flow velocity has no effect on sampling rates,^{74, 80} while others have shown that an increase in flow velocity can increase sampling rates by up to two folds.^{81, 82} One possible factor that may contribute to such ambiguity is the lack of a standard method to characterize flow velocities in the laboratory, which makes the comparison of results among studies difficult.

Temperature has been shown to increase POCIS sampling rates of pharmaceuticals and personal care products by as much as a factor of two for a given 5 to 10 degree change in temperature within the range 5 to 25 °C.^{77, 83, 84} A more recent study has investigated the effects of temperature on the uptake of pesticides. This study proposed an Arrhenius model to describe the dependence of POCIS sampling rates on temperature.⁸⁵ However, the study only evaluated three temperature points over a relatively small temperature range (18 to 30 °C).

In the present study, a series of laboratory experiments were performed to more rigorously define potential effects of hydrodynamic conditions and temperature on POCIS sampling rates. To ensure accurate estimations of flow near the surface of POCIS devices, flow velocities were calculated from experimentally determined mass transfer coefficients of the water boundary layer. This approach represents a step forward in terms of standardizing estimations of flow rate in passive sampling experiments. Additionally, the temperature dependence of POCIS sampling rates was evaluated for five temperatures ranging from 8 to 39 °C. This temperature span brackets the range of temperatures that are

commonly encountered in field monitoring studies of crop protection chemicals. Lastly, the potential significance of using temperature-corrected sampling rates in a field setting was evaluated by comparing TWACs derived from POCIS and from daily composite water sampling.

Methods and Materials

Materials and Chemicals

All test analytes (atrazine, azoxystrobin, bicyclopyrone, cyproconazole, fomesafen, mesotrione, S-metolachlor, propiconazole, sedaxane, simazine, solatenol and thiamethoxam) were provided by Syngenta Crop Protection, LLC at > 96% purity and used as received. Atrazine-d5, MCPA-d3, metolachlor-d6, simazine-d10 and thiamethoxam-d3 were purchased from CDN isotopes (Quebec, Canada) at > 98% purity. Formic acid and HPLC grade acetonitrile (ACN) were purchased from Fisher scientific (Fair Lawn, New Jersey, USA). A Thermo Branstead Nanopure (Dubuque, Iowa, USA) Diamond UV water purification system was used to provide 18 M Ω water for preparation of samples and UPLC eluents. Empty SPE cartridges (6 mL) and polyethylene frits were purchased from VWR (Radnor, Pennsylvania, USA). Alabaster mass transfer coefficient sensors for the alabaster dissolution were purchased from PaSOC (Kimsward, The Netherlands).

Experimental Setup

Experiments were carried out in stainless steel tanks containing 20 L of deionized water. Pumps (Shurflo, CHNA343T) were used to recirculate the water in the tanks at various flow velocities. Stainless steel rods were used to secure POCIS to aluminum crossbar holders in two rows of 5 POCIS (Figs. 3.1 and Appendix, B2). A cold room or

water heaters were used to vary the temperature from 8 to 39 °C. A preliminary study was carried out to investigate the possible uptake of target analytes by the exposure system. A mixture of target analytes at 5 µg/L each in deionized water was recirculated in the exposure system over a period of 24 hours with no POCIS deployed. The experiment was carried out in triplicate and water was collected eight times over the 24 hours. Analyte concentrations remained constant over the 24-hour period with relative standard deviation ranging from 4 to 12%. These results indicate that the target analytes were stable and did not adsorb to any surfaces of the apparatus used to conduct these experiments.

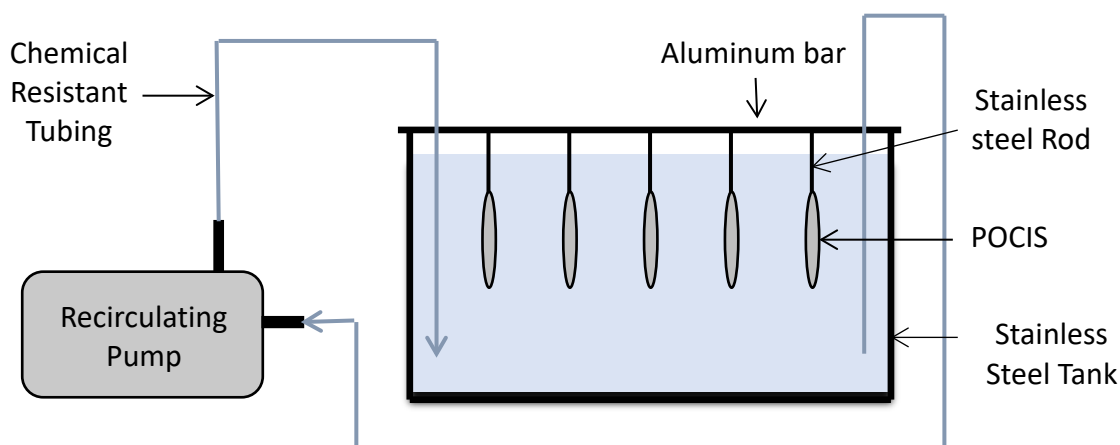


Figure 3.1. Schematic experimental setup used for the calibration of POCIS

Effects of Temperature and Hydrodynamic Conditions

All experiments were carried out by suspending POCIS devices in an aqueous solution containing a constant concentration of each analyte over a period of 21 days. One POCIS device was removed every other day, beginning on day 3 of the experiment, resulting in a total of ten time points. Water was renewed every 24 h, and water samples were collected for analysis before and after each renewal. The renewal water contained the

same pesticides and concentrations each time. Newly prepared analytes concentrations in water was $5.0 \pm 0.3 \mu\text{g/L}$ for all compounds. A depletion in analyte concentrations of less than 13% was observed for all compounds after 24 h over the 21-day exposure period. Experiments evaluating the effect of changing hydrodynamic conditions explored six different flow regimes: a stagnant condition and flow velocities of 6.2 ± 0.3 , 9.7 ± 0.7 , 15 ± 1 , 17 ± 3 and $20.5 \pm 0.7 \text{ cm/s}$. These flow velocities were experimentally determined using measured mass transfer coefficients of the water boundary layer as described in Booij et al, 2017.⁸⁶ The method for determination of flow velocities in this work is further discussed in the Results and Discussion section. Water temperature in these experiments was held constant at $33.0 \pm 0.7 ^\circ\text{C}$. This temperature was only slightly higher than the water temperature inherently generated by the pumps when operated at the highest flow velocity (i.e., $20.5 \pm 0.7 \text{ cm/s}$). Experiments evaluating the effect of changing temperature conditions explored five temperatures: $10.0 \pm 0.1 ^\circ\text{C}$, $23.0 \pm 0.8 ^\circ\text{C}$, $30.1 \pm 0.2 ^\circ\text{C}$, $34.0 \pm 0.7 ^\circ\text{C}$ and $39 \pm 1 ^\circ\text{C}$ at a constant flow velocity of $9.7 \pm 0.7 \text{ cm/s}$ and $8.0 \pm 0.1 ^\circ\text{C}$, $21.0 \pm 0.6 ^\circ\text{C}$, $30.0 \pm 0.2 ^\circ\text{C}$, $34.1 \pm 0.6 ^\circ\text{C}$ and $39 \pm 1 ^\circ\text{C}$ under stagnant conditions. Sorbent (Oasis HLB) collection from POCIS devices was carried out by disassembling each device and transferring the sorbent to an empty solid phase extraction (SPE) cartridge fitted with a polyethylene frit. Chemicals adsorbed onto the sorbent were eluted with 10 mL of acetonitrile. The eluate was evaporated to dryness under a gentle stream of nitrogen and reconstituted in 5 mL of 5:95 ACN: water (v/v) with 0.1% (v/v) formic acid. Analyte recovery was evaluated by spiking 200 mg of Oasis HLB resin with 2000 ng of each pesticide in triplicate. Average recoveries ranged from 90 to 110%, with relative standard deviations (RSDs) below 5%. Water and POCIS extract samples were analyzed by ultra-

performance liquid chromatography with electrospray ionization and tandem mass spectrometry (UPLC-ESI-MS/MS). Further details about the analysis method are reported in the Appendix B.

POCIS sampling rate for a given compound was calculated using equation (1) as follows:

$$\frac{N_s}{C_w} = R_s t \quad (1)$$

Where R_s is the sampling rate, t is the deployment period, N_s is the amount of chemical accumulated in the sorbent and C_w is the concentration of chemical in water. When the ratio of N_s over C_w is plotted versus deployment time, R_s is the slope of the resulting linear regression. The presence of a lag phase during uptake of a given compound was evaluated by examining the x-intercept of the corresponding regression line.⁸⁷ The intercepts were tested for statistical significance.

Results and Discussion

Flow Velocity Determination near the Surface of POCIS Devices

The water flow velocity in a closed system such as the one used in this experiment can be measured using flow meters or alternatively calculated from the volumetric pump output per unit time. The latter also depends on the dimensions of and the amount of water in the containment vessel (or tank). However, the flow velocity determined by either approach may poorly represent flow conditions at the surface of a passive sampler.^{69, 86} have suggested the use of an alabaster sensor plate to measure the mass transfer coefficient of the water boundary layer k_w near the surface of POCIS devices. The equations below

demonstrate how the measured mass transfer coefficient can subsequently be used to calculate the flow velocity U near the surface of POCIS devices.

The mass transfer coefficient, k_w can be related to with the friction velocity u_* by Equation 2A under short plate conditions and Equation 2B under long plate conditions.³⁴

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$$k_w = 0.81u_* \left(\frac{D_w}{v}\right)^{2/3} \left(\frac{v}{u_*L}\right)^{1/3} \quad (2A)$$

Where a short plate condition is defined as $\frac{Lu_*}{v} < 1000$

$$k_w = 0.078u_* \left(\frac{D_w}{v}\right)^{2/3} \quad (2B)$$

Where a long plate condition is defined as $\frac{Lu_*}{v} \gg 1000$

D_w is the diffusion coefficient in water, v the kinematic viscosity of water, and L the length of the plate. The friction velocity u_* is defined as:

$$u_* = \sqrt{\frac{\tau}{\rho}} \quad (3)$$

where ρ is the density of the fluid and τ is the drag force per unit surface area with the surface area equal to $2WL$; W is the width of the plate and L its length. The drag force on a flat plate F_w when the plate is wetted on both sides is defined by Equations 4A and 4B, respectively, for laminar and turbulent flow conditions:⁸⁹

$$F_w = 1.328\sqrt{\rho\eta LW^2U^3} \quad (4A)$$

$$F_w = 0.074\rho U^2WL \left(\frac{v}{UL}\right)^{1/5} \quad (4B)$$

where W is the width of the plate and L its length, ρ is the density of the fluid, η is the dynamic viscosity of the fluid, and U is the flow velocity. The relationship between friction velocity u_* and flow velocity U can be derived by combining Equations 3 and 4A under laminar flow conditions or Equations 3 and 4B under turbulent flow conditions, noting that $F_w = 2WL\tau = 2WL\rho u_*^2$. This results in Equations 5A and 5B for laminar and turbulent flow conditions, respectively.

$$u_*^2 = 0.664U^2 \sqrt{\frac{\nu}{UL}} \quad (5A)$$

$$u_*^2 = 0.037U^2 \left(\frac{\nu}{UL}\right)^{1/5} \quad (5B)$$

The flow velocity can then be calculated for either flow condition by substituting the friction velocity u_* from Equations 5A or 5B into Equations 2A or 2B and solving for flow velocity U . In the present study, experimental conditions dictated that Equations 5B and 2A were applicable (i.e., turbulent flow, short plate limit), and the resulting equation relating flow velocity to experimentally determined values of k_w is:

$$U = \frac{\nu}{L} 8.87 \left[\left(\frac{k_w L}{D_w} \right)^3 \left(\frac{D_w}{\nu} \right) \right]^{5/9} \quad (6)$$

Where $L = 0.042$ m (average length of the flow lines along the plate) and $D_w = 8.7 \times 10^{-10}$ m²/s (value for calcium sulfate at 23 °C).⁹⁰ The method for the measurement of the mass transfer coefficient used in this study is provided in Appendix B. Additionally, examples of calculation of flow velocity using Equation 6 are also illustrated in supporting data.

Two different approaches were used to determine flow velocities in the present study: (i) calculation from the volumetric pump output and the cross-sectional area of the tank; (ii) substitution of experimentally determined values of k_w into Equation 6.

Measurement of the mass transfer coefficient of the water boundary layer (k_w) at each flow setting followed the procedure described in.⁸⁶ Experimentally determined values of k_w (m/s) and calculated values for v (m²/s) at a given temperature, necessary for solving Equation 6, are reported in Table B2. The alabaster sensor used in this work had the same geometry and surface area as the POCIS device (Figure B3), and experiments performed to determine values of k_w were carried out using the same apparatus that were used to conduct POCIS experiments. Thus, it was assumed that for a given flow setting, flow velocities calculated from Equation 6 would be similar to actual flow velocities near the surface of POCIS devices.

Table 3.1. Comparison of flow velocity determined from pump output and mass transfer coefficient of the water boundary layer (Equation 6).

Pump output (Volumetric flow) (L/min)	flow velocity estimated from the pump output ^a (cm/s)	flow velocity Equation 6 ^b (cm/s)
23	1	6.2 ± 0.3
45	2	9.7 ± 0.7
68	3	15 ± 1
91	4	17 ± 3*
114	5	20.5 ± 0.7

^a The cross sectional area of water in each tank was 4 dm².

^b The margin of error represents one standard deviation for replicate measurements ($n = 3$ or 6^*).

Results in Table 3.1 demonstrate that flow velocities estimated from the volumetric pump output and cross-sectional area of the tank were lower (by as much as a factor of 6) than flow velocities calculated from Equation 6. An explanation for the observed discrepancy between flow velocities could be that water movement is not homogeneous

over the cross section of the tank. Instead, the water enters the tank in jets that set up circulation cells and cause the velocities to be larger than average.

Water flow velocities reported in literature have been determined using current meters, calculated from pump outputs or are simply described in terms of the speed of a particular agitation device. This relatively broad range of methods makes the comparison of flow conditions among studies rather difficult. Additionally, as demonstrated in this study, these methods could be underestimating or overestimating the actual flow at the surface of POCIS devices. The use of the mass transfer coefficient of the water boundary layer to estimate flow velocities at the surface of POCIS devices could potentially be used as a standard method to avoid inconsistencies associated with flow velocities in future POCIS experiments.

Effect of Hydrodynamic Conditions on POCIS Sampling Rates

The uptake profiles of twelve pesticides were investigated over a period of 21 days under various hydrodynamic conditions: a stagnant condition and flow velocities of 6.2 ± 0.3 , 9.7 ± 0.7 , 15 ± 1 , 17 ± 3 and 20.5 ± 0.7 cm/s. These flow velocities were determined using Equation 6. The amount of each pesticide accumulated in the sorbent increased approximately linearly over the 21-day exposure period in all experiments. Representative uptake curves are illustrated for S-metolachlor in Figure 3.2, and similar plots are provided for the remaining compounds in supplementary data, Figure B4. A lag phase was observed in some uptake curves and ranged from 5.8 minutes for fomesafen to 4.7 days for solatenol. Lag phases for all compounds are reported in supplemental data, Table B2. The timeframe of all lag phases identified in this work was relatively short and essentially negligible for an exposure duration of 21 days.⁹¹

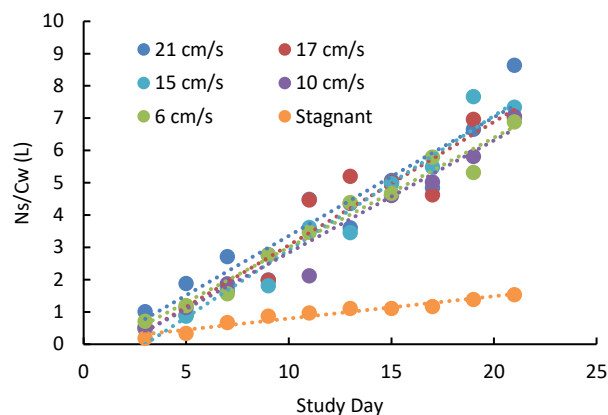


Figure 3.2. Representative uptakes at different hydrodynamic conditions for S-metolachlor. The temperature was held constant at 33 °C.

POCIS sampling rates derived from the slope of linear regressions (Equation 1) ranged from 0.01 L/day for mesotrione to 0.58 L/day for cyproconazole. Sampling rates for all compounds are reported in supplemental data, Table B2. Multiple linear regression analysis⁹² at the 95% confidence interval indicated that for eight of twelve compounds (i.e., atrazine, azoxystrobin, cyproconazole, S-metolachlor, propiconazole, sedaxane, simazine, and solatenol), the sampling rates for a given compound increased by a factor of 2 to 5 between stagnant and flow conditions. Furthermore, observed sampling rates for these compounds were essentially constant over the range of velocities between 6-21 cm/s. An increase in sampling rate between stagnant and flow conditions was also observed for mesotrione and thiamethoxam. However, statistically significant differences in sampling rates were only observed at certain velocities. Lastly, differences among sampling rates observed for bicyclopyrone and fomesafen were too sporadic to allow proper assessment of significant changes that may occur between stagnant and flow conditions or as a function of flow velocity.

These observations are consistent with results reported in several previous studies.^{17, 74, 77, 78, 80, 81, 93} It is generally assumed that under low flow conditions, the mass transfer of chemicals from water to the sorbent is governed by the water boundary layer. Under high flow conditions, water turbulence causes the water boundary layer to thin out and eventually reach a point where the increase in turbulence no longer affects sampling rates.⁶⁹ This hypothesis provides a rationalization for the increases in sampling rate (by a factor of 2 to 5) between stagnant and flow conditions that were observed for most compounds in the present study. It also explains why incremental increases in flow velocity, beyond 6 cm/s, have essentially no effect on the sampling rates observed for many compounds. However, there is still a knowledge gap in terms of characterizing potential changes in sampling rate that may occur between a stagnant condition and the point at which the thickness of the water boundary layer becomes negligible. Collectively, data from literature and from this study suggest that for flow velocities beyond 6 cm/s, any change in POCIS sampling rates as a function of velocity will be compound specific and relatively small in magnitude (a factor of 2 or less).^{81, 93} Future experiments that seek to understand what is happening between stagnant and low flow velocity conditions (≤ 6 cm/s), as well as subtle changes that may occur at higher flow velocities for select compounds, could benefit from a standard method of estimating hydrodynamic conditions, as described above, to enable easy comparisons across studies.

Effects of Temperature on POCIS Sampling Rates

The effects of temperature on POCIS sampling rates were investigated for five temperatures, ranging from 8-39 °C, under both stagnant and flow conditions. The amount of each pesticide accumulated in the sorbent increased linearly over the 21-day exposure

period in all experiments (see supplemental data, Figure B5 and B6 for flow and stagnant exposures, respectively). A lag phase was observed in some uptake curves and ranged from 57.6 minutes for simazine to 5.1 days for fomesafen under flow conditions, and from 7.2 hours for bicyclopyrone to 5 days for propiconazole under stagnant conditions. POCIS sampling rates ranged from 0.01 L/day for mesotrione to 0.36 L/day for cyproconazole under flow conditions, and from 0.005 L/day for mesotrione to 0.15 L/day for cyproconazole under stagnant conditions. Specific sampling rate values are reported for all compounds in supplemental data, Tables S3 and S4. Results demonstrate that sampling rates increased at higher temperatures under both flow and stagnant conditions, and compound specific sampling rates at a given temperature were consistently lower for stagnant exposures relative to a similar exposure under flow conditions. The effect of temperature on POCIS sampling rates was generally greater for exposures conducted under flow conditions than for similar experiments employing stagnant conditions (i.e., the sampling rate of a given compound was more sensitive to a change in temperature under flow conditions).

Several models have been developed to describe the temperature dependence of reaction rates. One of the most important and well-known models is based on the Arrhenius equation.⁹⁴ Temperature effects on R_s were modelled with an Arrhenius equation as follows:⁸⁵

$$R_s = Ae^{-E_a/RT} \quad (7)$$

Where R_s is the sampling rate (L/day), E_a the activation energy (J/mol), R the gas constant (8.314 J/mol.K), T the temperature (K) and, A the pre-exponential factor. Equation 7 can

be logarithmically transformed and rearranged to provide a linear relationship between $\ln R_s$ and $1/T$:

$$\ln(R_s) = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln(A) \quad (8)$$

where $-E_a/R$ and $\ln(A)$ are the slope and the y-intercept respectively.

Sampling rates for each pesticide were plotted logarithmically as a function of the reciprocal of temperature for experiments conducted under both flow and stagnant conditions. Representative plots for five pesticides are shown in Figure 3.3. (blue circles) for experiments involving flow, and the remaining plots are available in supplementary data (supplemental data, Figure B7). All plots were linear with R^2 values ranging from 0.94–1.00 and 0.88–0.98 for flow and stagnant experiments, respectively. These data confirm that an Arrhenius relationship is an appropriate model to describe the temperature dependence of POCIS sampling rates. Relevant Arrhenius parameters are reported in Table 3.2 for experiments conducted under flow and stagnant conditions. Activation energies ranged from 2.2 to 10.6 kJ/mol. For a given compound, the activation energy was generally lower under flow conditions than in the corresponding stagnant experiment. The magnitude of activation energies observed in this study is relatively small (*i.e.*, less than 40 kJ/mol), suggesting a physisorption process.⁹⁵⁻⁹⁷

To test whether Arrhenius relationships identified in this work were likely to be fundamental descriptors of the temperature dependence that may be expected for a given compound, sampling rates determined in previous studies were plotted alongside data from the present work. The hypothesis was that sampling rates from literature and from this work would follow the same mathematical trend. To support reliable comparisons, only studies that sampled at least four time points to determine POCIS sampling rates and employed

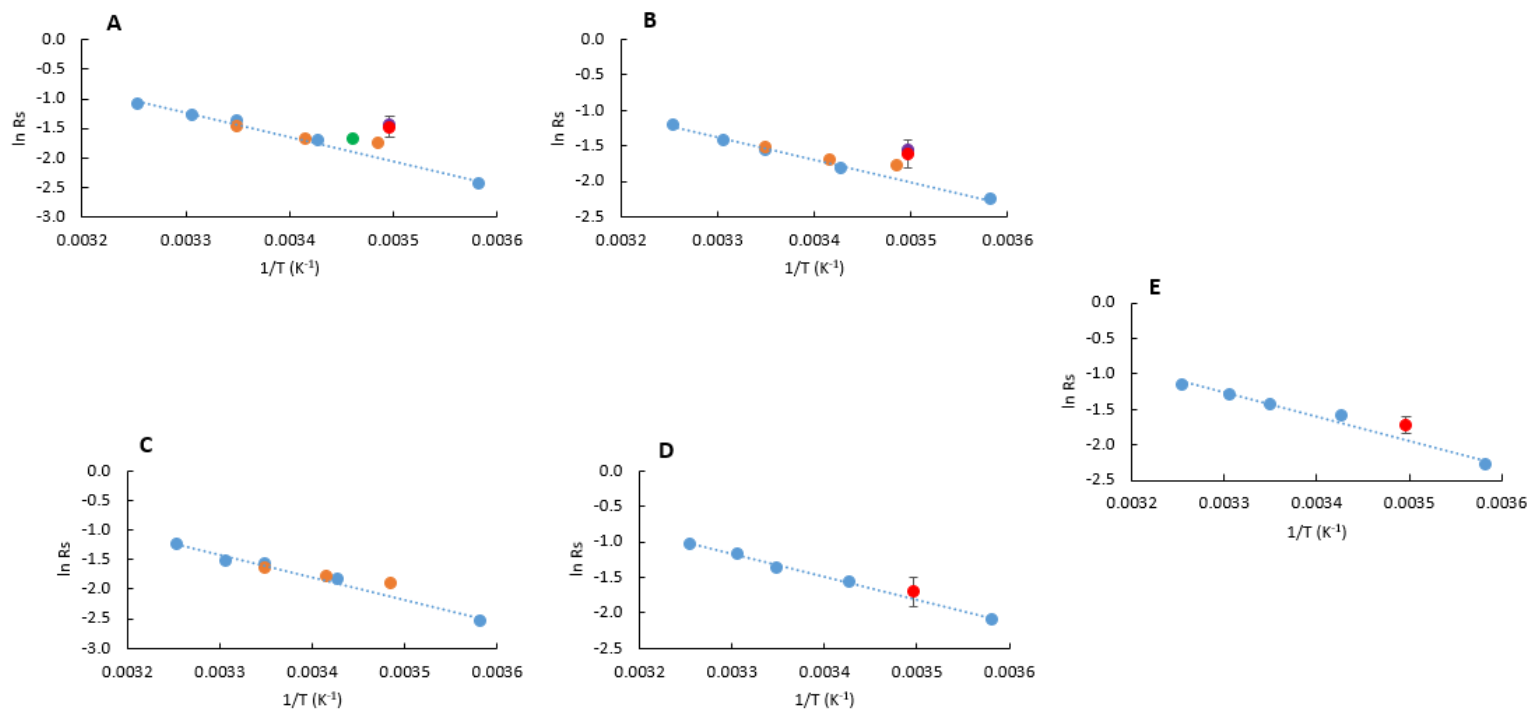


Figure 3.3. Representative Arrhenius plots (Eq. 8) for (A) atrazine, (B) simazine, (C) propiconazole, (D) metolachlor and (E) azoxystrobin. Blue circles represent sampling rates (R_s) determined in this work. Other colors represent data from literature: Yabuki et al.⁸⁵ in orange, Lissalde et al.⁹⁸ in red, Morin et al.⁹⁹ in green, and Mazzella et al.¹⁰⁰ in purple; appearing coincident with red. Error bars affiliated with the red circles represent plus and minus one standard deviation for triplicate measurements.⁹⁸

Table 3.2. Arrhenius parameters derived from plots of $\ln R_s$ versus $1/T$ under flow and stagnant conditions.

Flow velocity	9.7 cm/s					Stagnant				
Class/Compound	E_a/R (K)	$\ln A$	E_a (kJ/mol)	A (L/day)	R^2	E_a/R (K)	$\ln A$	E_a (kJ/mol)	A (L/day)	R^2
Insecticide										
Thiamethoxam	2217	5.20	2.67	1.81E+02	0.99	1825	3.46	2.20	3.17E+01	0.88
Herbicides										
Atrazine	4105	12.11	4.94	1.82E+05	0.99	3725	9.76	4.48	1.73E+04	0.89
Bicyclopyrone	2478	5.29	2.98	1.98E+02	0.94	2975	6.46	3.58	6.41E+02	0.89
Fomesafen	3764	10.57	4.53	3.91E+04	1.00	6047	16.60	7.27	1.62E+07	0.97
Mesotrione	1864	2.27	2.24	9.69E+00	0.99	3391	6.81	4.08	9.09E+02	0.98
S-Metolachlor	3235	9.34	3.89	1.14E+04	1.00	4761	13.42	5.73	6.70E+05	0.92
Simazine	3152	8.86	3.79	7.05E+03	0.99	2763	6.45	3.32	6.33E+02	0.95
Fungicides										
Azoxystrobin	3386	9.74	4.07	1.69E+04	0.98	8812	26.51	10.60	3.25E+11	0.93
Cyproconazole	3293	9.46	3.96	1.29E+04	0.99	3026	7.83	3.64	2.51E+03	0.94
Propiconazole	3844	11.08	4.62	6.47E+04	0.99	5920	17.30	7.12	3.25E+07	0.97
Sedaxane	4031	11.95	4.85	1.54E+05	0.97	7392	21.84	8.89	3.06E+09	0.95
Solatenol	3301	7.77	3.97	2.37E+03	0.98	5696	15.51	6.85	5.47E+06	0.97

a minimum 21-day exposure period were considered. These criteria were imposed to ensure that data used to define sampling rates followed a linear trend, as well as to minimize potential effects of an initial lag phase on the identified rate of uptake. Four previous studies evaluated one or more of the pesticides investigated in this work and met the experimental design criteria noted above. Each of these studies maintained flow throughout the exposure period, and it was assumed that flow velocity in all experiments had a negligible effect on POCIS sampling rates. Collectively, these studies enabled a comparison of sampling rates for five compounds.

Figure 3.3 demonstrates that POCIS sampling rates determined in previous work agreed reasonably well with the Arrhenius relationships identified in the present study. Sampling rates from the Yabuki et al.⁸⁵ study (i.e., orange circles in Figs. 3.3A-3.3C) are the only data from literature in Figure 3 that were derived from experiments designed to evaluate the effect of temperature. Sampling rates for atrazine and simazine reported by Lissalde et al.⁹⁸ (red circles in Figs. 3.3A and 3.3B) and Mazzella et al.¹⁰⁰ (purple circles essentially coincident with the red circles in Figs. 3.3A and 3.3B) lie slightly above the linear trends identified for these compounds. However, the Lissalde et al.⁹⁸ study also evaluated metolachlor and azoxystrobin in the same experiments, and sampling rates reported for these two compounds were more closely aligned with the Arrhenius relationships identified for these analytes in the present study. Additionally, the lower limits of uncertainty associated with data from Lissalde et al.⁹⁸ and Mazzella et al.¹⁰⁰ are likely within the upper limits of uncertainty affiliated with the linear trends identified in Figure 3.3. Relatively few studies of POCIS sampling rates have been conducted with enough replication to rigorously define uncertainty expectations. However, such a

statement is consistent with the range of uncertainties reported in Lissalde et al.⁹⁸ (i.e., relative standard deviations ranging from 12 to 21%). Collectively, data in Figure 3.3 support a widely applicable presentation of Arrhenius relationships that can account for, as well as predict, compound specific changes in POCIS sampling rates as a function of temperature.

Significance of Temperature-Corrected Sampling Rates in a Field Setting

POCIS devices have been extensively used in field studies. However, a discrepancy is often observed between time weighted average concentrations (TWACs) calculated from POCIS data and from grab water samples.^{69, 70} This inconsistency is due to variable environmental conditions, which are not accounted for in laboratory calibration experiments. One way to overcome this issue is to carry out *in situ* calibrations.^{101, 102} However, an *in situ* calibration would be required for each study, which is not practical. Another approach to correct for the change in R_s with environmental conditions involves the use of performance reference compounds (PRCs),^{82, 103, 104} but there are still significant hurdles for the use of PRCs to determine *in situ* POCIS sampling rates.^{105, 106} The Arrhenius parameters reported in Table 3.2 can be used to estimate R_s at various temperatures, which may also improve agreement between TWACs derived from POCIS and from grab or composite water samples.

To evaluate the potential importance of applying a temperature correction to chemical sampling rates, a retrospective analysis of atrazine field data was performed. Forty-three POCIS devices were deployed for a period of 21 days each at nine sampling locations in major corn and sorghum producing areas of the United States during the growing season of 2016. ISCO auto samplers (Teledyne ISCO 6712) placed near the

POCIS deployment locations were used to collect daily composite water samples. Atrazine concentration was measured in the daily composites, and the TWACs of atrazine were calculated for the 21-day deployment period. Arrhenius parameters reported for atrazine in Table 3.2 were used to calculate temperature-corrected sampling rates under flow conditions, which were in turn used to calculate TWACs from parallel POCIS measurements. The average water temperatures, temperature corrected sampling rates, and TWACs calculated from ISCO (C_w ISCO) and POCIS (C_w POCIS) are reported for all sites in supplemental data, Table B5.

A plot of the C_w POCIS/ C_w ISCO ratio versus C_w ISCO is shown in Figure 3.4 for temperature corrected sampling rates. If temperature was the only important factor leading to discrepancies between these two sampling approaches, one would expect data to follow a horizontal line with an average C_w POCIS/ C_w ISCO ratio equal to 1. When sampling rates were corrected for temperature, the average C_w POCIS/ C_w ISCO ratio was equal to 1.05 (dashed line in Figure 3.4). The laboratory data presented earlier and the proximity of the average ratio to unity suggest that adjusting POCIS sampling rates for temperature is a reasonable thing to do when calculating and comparing TWACs. However, the data points in Figure 4 are clearly scattered about the horizontal line, demonstrating that other factors are likely involved in explaining observed differences between TWACs determined using POCIS and composite sampling methods. Previous studies have investigated the effects of fouling,¹⁰⁷ water quality,⁸³ dissolved organic matter,¹⁰⁸ and non-organic matter⁷⁸ on POCIS sampling rates. These studies have improved qualitative understanding of potential effects these environmental factors may have on POCIS sampling rates, but further work is needed to determine quantitative relationships. Lastly, data in Figure 4 suggest a possible

negative bias for TWACs determined from POCIS data at low concentrations (e.g., at C_w ISCO concentrations below 1 $\mu\text{g/L}$). An explanation for this observation is not apparent, but it is important to recognize that these concentrations do not challenge LC-MS/MS detection limits for atrazine. Experiments that more fully characterize the relationship between C_w POCIS and C_w ISCO at low concentrations are beyond the scope of the present study, but future work should seek to examine whether the apparent concentration effect in Figure 3.4 is a general trend or more simply an artifact of these specific data.

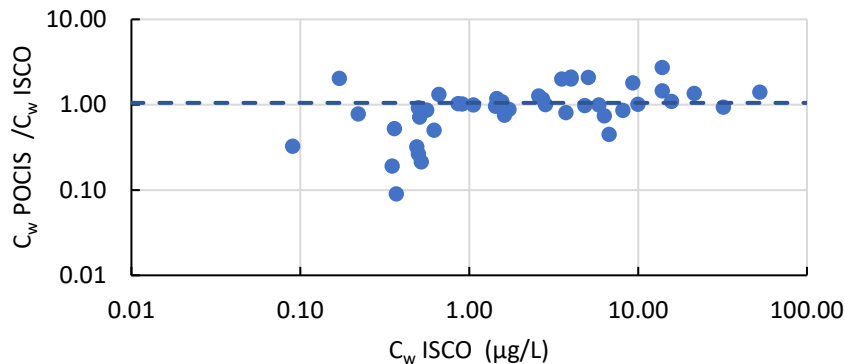


Figure 3.4. Data demonstrating the level of agreement observed between TWACs of atrazine determined from POCIS measurements and daily composite water sampling in a field setting. Arrhenius parameters reported for atrazine in Table 3.2 were used to calculate C_w POCIS. The dashed line denotes the average C_w POCIS/ C_w ISCO ratio.

CHAPTER FOUR

Effects of POCIS Exposure to Sediment on Pesticide Sampling Rates

Abstract

Effects of chemical uptake onto polar organic chemical integrative samplers (POCIS) exposed to total suspended solid (TSS) sediment concentration of 0 and 3600 ppm were investigated for 12 pesticides at constant concentration, temperature, and flow velocity. The effect on POCIS uptake was negligible for compounds with PES-water partition coefficients ($\log K_{\text{PESW}}$) more than 3 when exposed to sediment. However, significant effects were observed for three of the 12 compounds tested, where there was a change in POCIS sampling rates by a factor of up to 4-fold increase between exposure at 0 and 3600 ppm. Effects of sediment on pesticides distribution between polyethersulfone (PES) membrane and Oasis HLB sorbent were also investigated and provided further understanding of mass transfer processes across PES. Pesticide fractions accumulated on the PES membrane were generally lower for most compounds and ranged from 0 to 33%. However, four compounds with higher affinity to PES had fraction accumulated on PES membrane ranging from 64 to 96%. Incorporation of chemicals accumulated within PES membranes into the sampling rate calculation lead to an increase of up to 18-fold in sampling rate for compounds with higher hydrophobicity and affinity to the PES membrane.

Introduction

Integrative passive samplers such as polar organic chemical integrative sampler (POCIS) and semipermeable membrane devices (SPMD) have been increasingly used for monitoring pesticides, pharmaceuticals and personal care products in agricultural and urban streams.^{28, 109-114} However, changes in environmental factors such as temperature, flow velocity, and turbidity can limit the utility of these devices in field applications that seek to determine the time weighted average concentration (TWAC) of chemicals.⁶⁹ Two POCIS configurations are commercially available: “pesticides-POCIS” and “pharmaceuticals-POCIS.” The “pharmaceutical-POCIS” configuration is more commonly used because it works well on a broader range of compounds. “Pharmaceutical-POCIS” are composed of Oasis HLB sorbent sandwiched between two porous polyethersulfone (PES) membranes that are tightly held in place with two stainless steel rings. The sorbent is considered as the receiving phase and is typically the only component of the device subject to analysis. The two PES membranes physically hold the sorbent in place and regulate the movement of chemicals from the surrounding water to the sorbent.

Diffusion of chemicals through PES membranes can occur via water filled-pores or via the PES matrix.^{32, 91, 115-117} Environmental factors such as the presence of microorganisms can potentially foul, or otherwise alter, the structure of PES membranes. This may affect the diffusion of chemicals across the membranes and subsequently affect the uptake rate of chemicals by the sorbent. Two laboratory studies have investigated the effects of PES membrane fouling on the uptake properties of POCIS.^{83, 107} Harman et al. investigated the effects of membrane fouling by algae and various other microorganisms for 27 alkylphenol compounds.¹⁰⁷ PES membranes were allowed to foul in an ecological pool

for 39 days prior to POCIS assembly, and an increase in POCIS sampling rates, ranging from 25 to 55%, was observed for most compounds. Baily et al. monitored POCIS uptake of six pharmaceuticals from tap water and from wastewater.⁸³ A decrease in POCIS sampling rates, ranging from 28 to 44%, was observed for most analytes in wastewater experiments and attributed to fouling of the PES membranes. These two studies suggest that membrane fouling can have significant effects on the uptake of chemicals by POCIS and that the effects are compound dependent.

The presence of sediment may also influence the uptake of chemicals by passive samplers. Total suspended solid (TSS) concentrations in some small agricultural streams can be as high as 18,000 ppm during heavy runoff events, with median concentration ranging from 500 to 2000 ppm,¹¹⁸ and heavy sediment deposits have been observed on the surface of POCIS devices deployed in those streams. To our knowledge, no previous studies have evaluated potential effects of sediment on POCIS sampling rates. In the present study, POCIS sampling rates were determined for 12 pesticides, representing a range of physicochemical properties and chemical structures, using water that contained an average TSS concentration of 3600 ppm and water that contained no sediment (as a control). The amount of each pesticide adsorbed onto Oasis HLB sorbent and PES membranes was monitored independently to determine if the presence of sediment altered the amount of pesticide adsorbed onto either material. These data were interpreted in the context of a common mass transport model for movement of chemicals across the PES membrane.

Materials and Methods

Materials and Chemicals

Target analytes (atrazine, azoxystrobin, bicyclopyrone, cyproconazole, fomesafen, mesotrione, S-metolachlor, propiconazole, sedaxane, simazine, solatenol and thiamethoxam) were provided by Syngenta Crop Protection, LLC. Internal standards (atrazine-d5, MCPA-d3, metolachlor-d6, simazine-d10 and thiamethoxam-d3) were purchased from CDN isotopes (Quebec, Canada). Formic acid and HPLC grade acetonitrile (ACN) were purchased from Fisher scientific (Fair Lawn, New Jersey, USA). Water used for samples preparation and UPLC eluents was collected from a Thermo Branstead Nanopure (Dubuque, Iowa, USA) Diamond UV water purification system.

Laboratory Uptake Experiments

Experimental apparatus, samples preparation and LC-MS/MS method for samples analysis have been previously described in Toteu Djomte et al.¹¹⁹ Briefly, POCIS were exposed to water with added sediment (n=3) and water with no added sediment (n=3) for a period of 10 days. The work flow and experimental set up are illustrated in Figure 4.1. Pumps (Mag Drive PP Centrifugal Pump, IWAKI Co., LTD) were used to recirculate water (flow velocity = 6 cm/s); temperature was constant at 24 ± 1 °C for both exposure types. Control and water with added sediment was renewed every 24 hours. Water samples were collected before and after each renewal and POCIS were retrieved every other day. Newly prepared analyte concentrations in water were 5.1 ± 0.2 µg/L for all compounds. A depletion in analyte concentration of less than 12% was observed for all compounds after 24 hours over the 10-day exposure period.

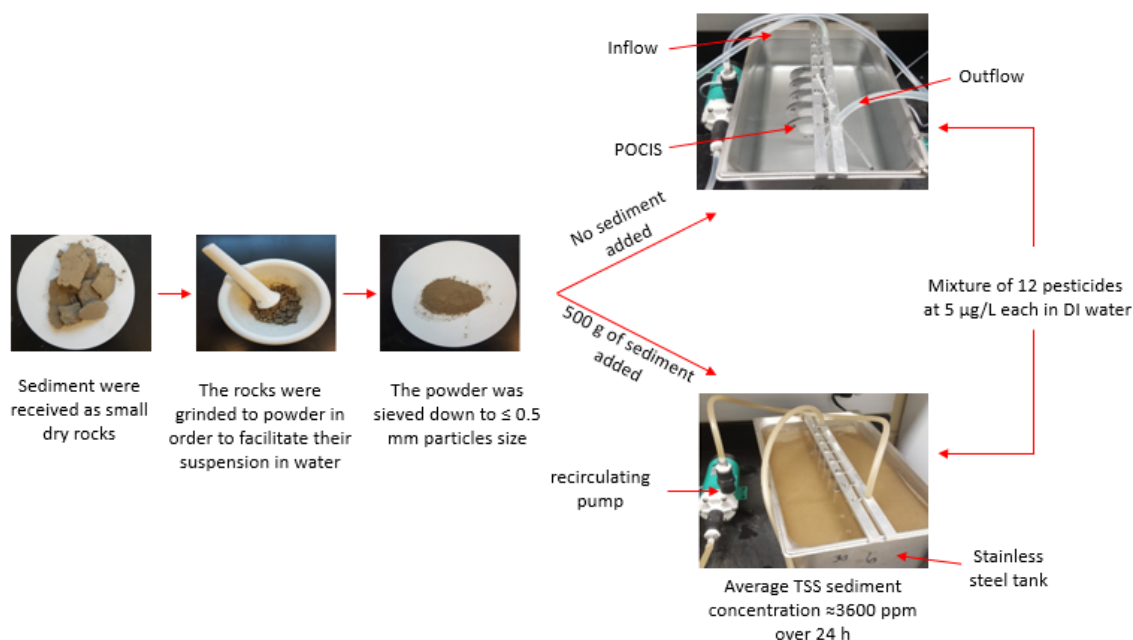


Figure 4.1. Work flow and experimental set up used to investigate sediment effects on POCIS sampling rates.

The sediment used in the present work was collected from a small agricultural stream in Iowa in the spring of 2017. X-ray diffraction analysis demonstrated that the sediment mineralogy was composed of quartz, feldspar, calcite, smectite, illite and kaolinite. Additional chemical and physical sediment characteristics are reported in Table 4.1. TSS sediment concentration in water was measured four times a daily by sampling 1 mL of water from each tank and measuring the dry weight of suspended sediment particles. An independent study was carried out to evaluate analyte adsorption onto the sediment by mixing 500 mg of sediment with 50 mL of pesticides mixture at $5 \mu\text{g/L}$ each in water in an amber vial. The vial was shaken for 72 hours in an incubator with temperature set at 22°C . Five water samples of $200 \mu\text{L}$ each were collected over the 72 hours time period and analytes concentration in water was monitored by LC-MS/MS. No detectable change in

water concentration was observed for all analytes (data are reported in Table C1). Thus, analyte adsorption onto this particular sediment was negligible for all analytes over a period of 72 hours probably due to low organic matter (1.7%) found in the sediment.

Table 4.1. Sediment characterization summary.

Characteristics	Description
Color	Grey
Grain size	Sand - 46 %
	Silt - 30 %
	Clay - 24 %
USDA Textural Class	Loam
Bulk Density (gm/cc)	1.13
Cation Exchange Capacity (meq/100g)	17.5
Organic Matter (%)	1.7
pH (in 1:1 soil:water ratio)	7.8
Olsen Phosphorus (ppm)	23
Total Nitrogen (%)	0.08
Soluble Salts (mmhos/cm)	0.28
Cation Composition	Calcium - 77%
	Magnesium - 12%
	Sodium - 0.4%
	Potassium - 1.5%
	Hydrogen - 9.2%

PES Membrane Extraction

PES membranes from POCIS devices were gently washed with nanopure water and transferred into 50 mL amber vials containing 20 mL of ACN. Vials were shaken for 30 minutes and the extract from each vial was transferred to another 50 mL amber vial. The same procedure was repeated and a total of 40 mL extract was produced from each set of membranes. Analyte recovery from PES membranes was evaluated by spiking two PES membranes with 2000 ng of each pesticide in triplicate. Average recoveries ranged from

92 to 111%, with relative standard deviations (RSDs) below 8%. All PES membrane from POCIS exposed to control water were extracted (n = 15 POCIS devices). However, PES membrane from only 10 POCIS devices were extracted for POCIS exposure sediment added water. PES membrane from the remaining 5 POCIS devices were used for PES characterization.

PES Membrane Characterization

PES membranes from five POCIS devices, each randomly selected on retrieval day, were analysed with a scanning electron microscope (SEM; Versa 3D, FEI Company, Hillsboro, OR, USA). Signal was collected with an Everhart-Thornley Detector (ETD) at high vacuum mode with an accelerating voltage of 30 kV. Each membrane set was gently rinsed with nanopure water and dried in an oven at 70 °C for 1 hour. Small square pieces were then cut from each membrane and coated with gold (10nm) with a sputter coater ACE600 (Leica).

Sorption Kinetic Experiments

Sorption kinetics of the 12 pesticides on Oasis HLB and PES membranes were monitored in parallel experiments by contacting 20 mg of Oasis HLB or PES membrane with 30 mL of the pesticides mixture at 3 µg/L each in water in amber vials. Vials were shaken for 200 hours in an incubator with temperature set at 22 °C. Up to ten water samples of 200 µL each were collected over the 200-hour time period and analyzed by LC-MS/MS.

Results and Discussion

Decrease of TSS Concentration over Time

POCIS devices were exposed to control water and water containing 500 g of sediment over a period of 10 days. However, daily monitoring of TSS concentration throughout the 10-day exposure period indicated that there was an exponential decrease of TSS over a 24-hour period (Fig. 4.2). TSS concentration in each tank (n=3) was typically monitored four times during the 24-hour period between each water renewal, and RSDs for a given tank and time point ranged between 16 and 35%. Daily average TSS concentration was 3600 ± 600 ppm with $74 \pm 11\%$ depletion over the 24-hour period, indicating that this level of depletion was highly reproducible over the course of these experiments. The observed decline in TSS concentration could be explained by three processes: (i) deposition of sediment particles at the bottom of the tank over time, (ii) flocculation of sediment particles, also leading to a deposition at the bottom of the tank over time, and/or (iii) adhesion of sediment particles to POCIS devices and the lining of the apparatus.

Deposition of sediment particles over time has been used to understand sediment transport and accumulation in marine environments.¹²⁰ The rate at which sediment particles are deposited in water is determined by particle size, shape and density. The effect of these variables on settling velocity have been studied extensively. Many models have been derived to predict and understand settling velocity of a wide range of sediment classes.¹²¹⁻¹²⁶ The rate at which particles settle in water increases with density, size and Corey shape factor (CFS), which is the ratio of the cross-sectional area of a sphere to the maximum cross-sectional area of an ellipsoid (i.e. smaller CFS values represent flatter particles).¹²² Since individual particles of a given sediment type can vary greatly in terms of density,

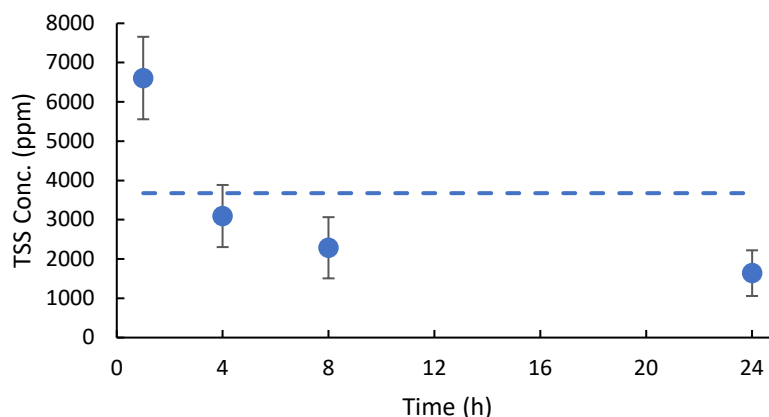


Figure 4.2. Total suspended solid (TSS) sediment concentration in water over 24 hours. Each data point represents average measurements from the 3 exposure tanks and measurement on each time point was carried out up to 10 times. Dashed line represents average TSS concentration over the 24-hour period. Error bars represent one standard deviation ($n = 30, 24, 24$ and 30 for time points 1, 4, 8 and 24 h, respectively).

size and/or CFS, the particles will settle at different rates. Deposition was likely the primary process responsible for the rapid decrease in TSS concentration observed during the period $t \leq 4$ hours in Figure 4.2.

Flocculation may also contribute to the rapid decrease in TSS concentration. Flocculation is the formation of larger particles from the aggregation of smaller particles through physical, chemical, and biological means.^{127, 128} Flocculation may have caused an alteration of the suspended sediment particles by increasing the density, size and CFS over time, which as described above will lead to sediment deposition. The propensity of sediment particles to flocculate decreases with decreasing concentration.¹²⁸ Thus, the relative contribution of this process to the observed decrease in TSS is expected to decrease over time.

Adhesion of sediment to POCIS devices and the lining of the apparatus is likely to have been the primary factor governing the slower decrease of TSS concentration between

4 and 24 hours. POCIS devices were retrieved every other day over the course of each 10-day experiment, and a gradual accumulation of sediment was observed on the surface, as shown in Figure 4.3. Sediment adhesion to the inner lining of the apparatus (i.e., vertical tank surfaces and pump tubing) was also observed, though not to the same degree since water was renewed daily and the tanks were cleaned to remove any residual sediment particles prior to each renewal.

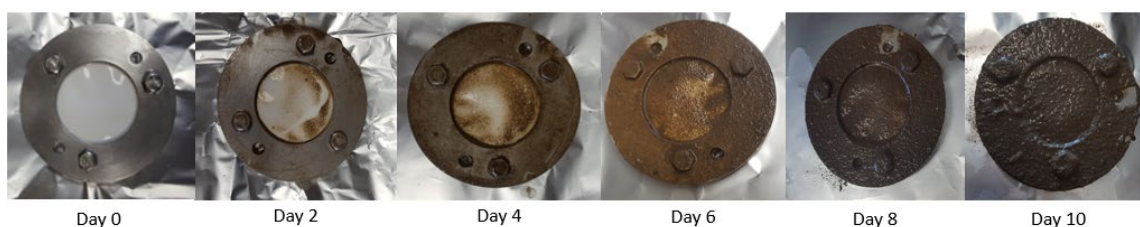


Figure 4.3. Sediment on PES membranes and stainless-steel ring of the POCIS device over the 10-day exposure period. POCIS were exposed to TSS sediment concentration of 3600 ppm.

SEM images were used to evaluate the accumulation of sediment on PES membranes at a microscopic level (Fig. 4.4). Images in Figure 4A and 4B demonstrate that PES membranes are made of a network of irregular pores, and visual assessment indicates that there were no obvious differences between PES membranes in the native dry state and PES membranes after 10 days of exposure to control water. In contrast, the image in Figure 4.4C demonstrates that the membrane was obstructed with layers of sediment that were accumulated on top of the PES membrane. Sediment also appears to be obstructing some pores, but neither the depth of sediment penetration nor the extent of pore blockage was readily discernable from SEM images.

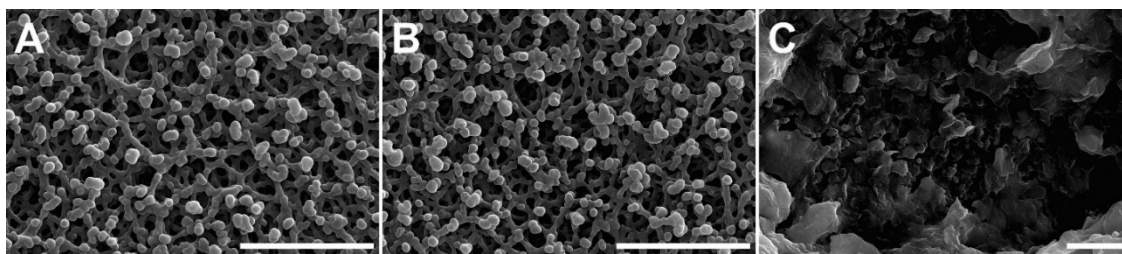


Figure 4.4. Scanning electron microscope (SEM) images comparing (A) native dry polyether sulfone (PES) membrane, (B) PES membranes from POCIS exposed in control water and (C) PES membranes from POCIS exposed in water with added sediment (3600 ppm daily average) at the end of 10 days of exposure. The scale bar on each image represents 5 μm .

Effects of Sediment on POCIS Uptake of Pesticides

The uptake of chemicals by POCIS has been described to follow a three-compartment, first-order kinetic model, with chemicals first diffusing through water to the PES membrane where they may be sorbed, then diffusing through the PES membrane to the Oasis HLB sorbent where they are accumulated.^{91, 115} Diffusion of chemicals through PES membranes may occur via the matrix, the water-filled pores, or both. It is generally assumed that compounds with high affinity for PES diffuse primarily through the matrix and that compounds with relatively low affinity diffuse primarily through the pores. For compounds diffusing through the pores, a decrease in pore size is expected to promote a decrease in POCIS sampling rate.^{32, 91, 115-117}

The visual accumulation of sediment shown in Figures 4.3 and 4.4C raises the rather obvious question of whether sediment influences POCIS sampling rates. To the extent that sediment obstructs or constricts the porous network of PES membranes, one would expect sampling rates to decrease, especially for molecules that have low affinity for PES. Similarly, if sediment obstructs a molecule's access to the surface of the PES membranes, it could decrease the sampling rate for molecules that diffuse primarily

through the matrix. If a molecule has relatively high affinity for the sediment, one might assume that sediment accumulation could effectively “trap” (or strongly sorb) the molecule and prevent its transport across the membrane. However, independent batch sorption experiments confirmed that none of the target analytes in this study had any measurable affinity for the sediment used in this work (Table C1). Thus, it is reasonable to hypothesize that observed changes in sampling rate between control experiments and experiments with added sediment are likely due to alteration of mass transport processes through (or across) the PES membranes. POCIS sampling rates and PES-water partition coefficients ($\log K_{\text{PESW}}$) are reported in Table 4.2. Uptake plots for each compound are provided in Figure C1. POCIS sampling rates ranged from 0.022 to 0.53 L/day, and the relative standard deviation of a given sampling rate (% RSD, $n = 3$) ranged from 3% to 27%. This level of uncertainty is within the range typically reported for laboratory determinations of POCIS sampling rates.^{98, 111, 115} Lag phases ranging from 5 to 43 hours were observed in some uptake curves (Table C2). This duration corresponds to <20% of the total exposure time in any given experiment. Thus, it is reasonable to assume that sampling rates were not appreciably influenced by the presence of a lag phase. PES-water partition coefficients were calculated as described in Vermeirssen et al.,⁹¹ and $\log K_{\text{PESW}}$ values determined for atrazine, S-metolachlor and simazine were similar to previous reports.^{91, 129, 130} Overall, $\log K_{\text{PESW}}$ values ranged from 1.60 to 4.71, and excluding azoxystrobin and thiamethoxam, there was a general increase of $\log K_{\text{PESW}}$ with increasing hydrophobicity ($\log K_{\text{ow}}$) of the pesticide.

Sampling rates (R_s) in Table 4.2 demonstrate that sediment accumulation had a negligible effect on the transport of most compounds across PES membranes. No effect

Table 4.2. Target compounds listed with their log K_{ow} , log K_{PESW} , log K_{HLBW} , sampling rates, lag phase and fraction adsorbed to HLB values POCIS exposure to water with and without sediment.

Compound	Log K_{ow}	Log K_{PESW}	Log K_{HLBW}	R_s (L/day)		$R_{HLB+PES}$ (L/day)	
				No sediment	Sediment	No sediment	Sediment
Insecticide							
Thiamethoxam	-0.13	2.17	4.61	0.12 ± 0.01	0.11 ± 0.01	0.12	0.11
Herbicides							
Atrazine	2.75	3.31	4.88	0.20 ± 0.02	0.18 ± 0.01	0.23	0.21
Bicyclopyrone	1.58	1.60	4.39	0.05 ± 0.01	0.13 ± 0.03	0.05	0.13
Fomesafen	2.9	2.66	5.01	0.12 ± 0.02	0.53 ± 0.08	0.12	0.54
Mesotrione	1.49	2.39	4.68	0.022 ± 0.001	0.010 ± 0.003	0.022	0.010
S-Metolachlor	3.13	3.05	4.59	0.22 ± 0.02	0.21 ± 0.01	0.24	0.22
Simazine	2.18	3.28	4.98	0.17 ± 0.03	0.18 ± 0.02	0.24	0.24
Fungicides							
Azoxystrobin	2.5	4.71	4.55	0.22 ± 0.01	0.22 ± 0.03	0.61	0.54
Cyproconazole	2.9	3.04	4.25	0.19 ± 0.01	0.16 ± 0.01	0.21	0.20
Propiconazole	3.72	4.05	3.22	0.18 ± 0.02	0.14 ± 0.02	0.33	0.23
Sedaxane	3.3	3.91	4.05	0.23 ± 0.03	0.25 ± 0.01	0.51	0.48
Solatenol	4.3	4.52	4.90	0.04 ± 0.01	0.03 ± 0.01	0.76	0.28

Reported values are average \pm one standard deviation for n = 3

was observed for compounds with $\log K_{\text{PESW}} \geq 3$, but statistical differences in R_s were observed for 3 of 12 compounds, relative to the control. An approximate 2-fold decrease in R_s was observed for mesotrione in experiments with added sediment. However, the sampling rate for this compound was relatively low, with and without sediment present, and the absolute change in average sampling rate between these two experiments was equal to or less than the absolute change observed for other compounds that did not exhibit statistically relevant differences. Thus, it is difficult to say if the decrease observed for mesotrione is meaningful in a practical sense or is more simply an artifact of these specific data. In contrast, increases in R_s observed for bicyclopyrone and fomesafen with added sediment were not only statistically relevant, but also of sufficient magnitude to have practical significance.

To further investigate potential effects of accumulated sediment, the amount of each chemical accumulated on PES membranes was examined. Figure 4.5 compares the amounts of analyte accumulated on PES after 10-days of exposure for experiments with and without added sediment, and the complete uptake plots (showing an identical comparison on days 2, 4, 6, 8 and 10) are provided in Figure C3. sediment and no sediment are illustrated with analytes arranged in order of increasing affinity to PES. Results demonstrate that POCIS exposure to sediment did not affect PES membrane uptake for most pesticides. As expected, there was significant increase in PES accumulation of fomesafen (by about 3-fold). However, there was a decrease of bicyclopyrone accumulated in the membrane. No quantifiable amount of bicyclopyrone and mesotrione was detected in PES membranes from POCIS exposed sediment in comparison to relatively very little for POCIS exposure to no sediment. On the other hand, there was an unexpected significant

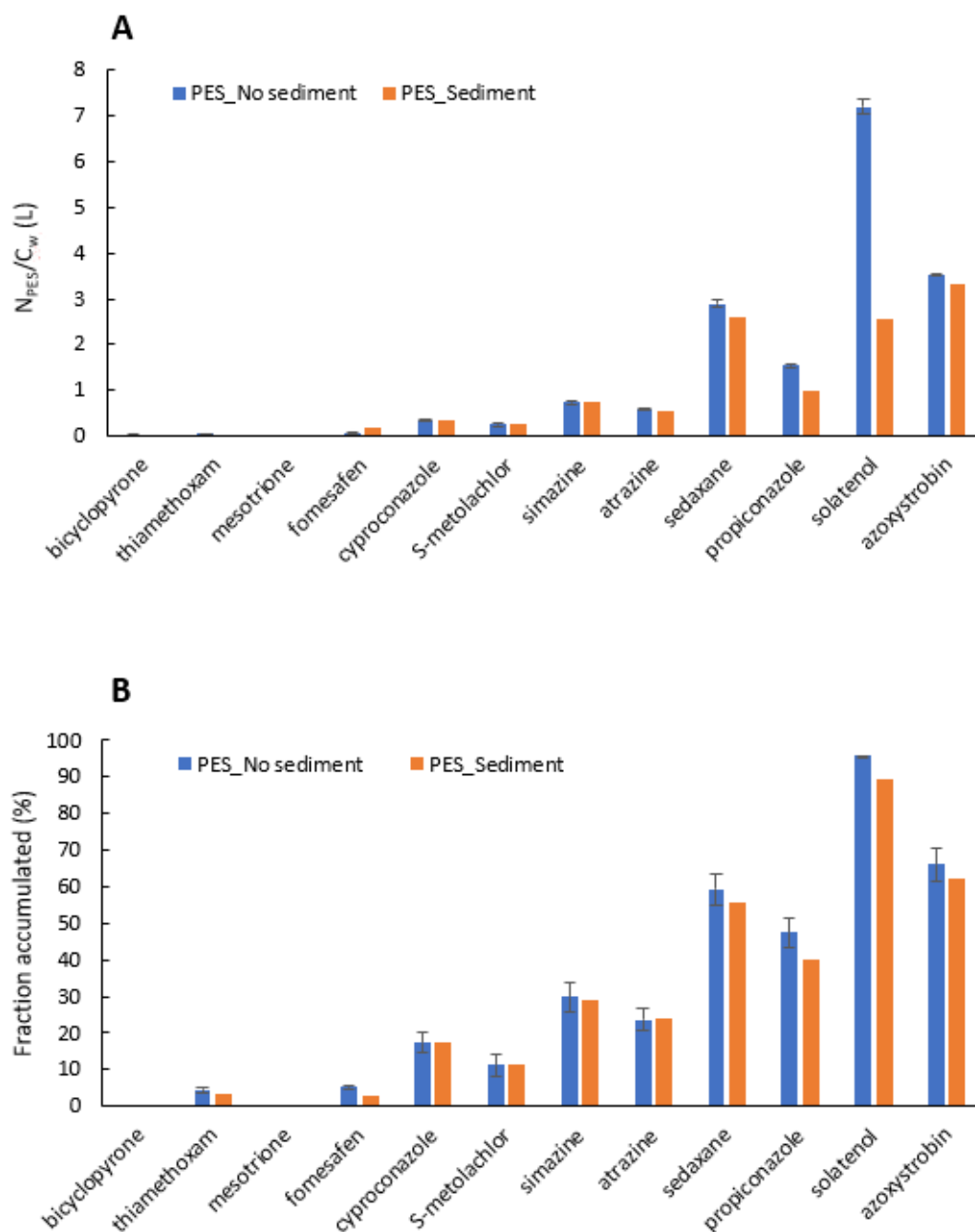


Figure 4.5. Graphs illustrating (A) the amount of analytes accumulated in PES for POCIS exposed to sediment and no sediment (3600 ppm and 0 ppm TSS concentration, respectively), and (B) the fraction of analyte accumulated in PES relative to total amount accumulated in both PES and Oasis HLB. Error bars represent one standard deviation from replicate tanks ($n = 3$). PES extraction for POCIS exposed to sediment were only carried out for two tanks because PES membranes from the third tank were used for SEM imaging.

decrease in PES uptake of solatenol and propiconazole (by 2.5 and 1.5-fold, respectively) when POCIS exposure changed from no sediment to sediment.

Solatenol and propiconazole with a $\log K_{PESW}$ of 4.52 and 4.05, respectively have a relative high affinity to PES. Therefore, they may diffuse through the membrane primarily via the PES matrix. Hence the decrease in PES uptake for POCIS exposed to sediment may be due to sediment obstruction of the PES matrix, which may have slowed down their diffusion across the membrane. However, the decrease in both solatenol and propiconazole diffusion across the membrane was not significantly reflected on their uptake rates on the sorbent. Solatenol accumulation on Oasis HLB is a relatively slow process (R_s of 0.04 L/day). Even though the mass transfer across the membrane was slowed down, enough solatenol molecules may have still diffuse to keep the uptake rate on the sorbent unchanged. On the other hand, the relatively low decrease of propiconazole diffusion across the membrane may not have been enough to affect the accumulation on Oasis HLB.

Fomesafen with a $\log K_{PESW}$ of 2.66 has relatively low affinity to PES and may diffuse through the membrane primarily via PES porous structure. The observed increase in fomesafen PES uptake for POCIS exposed to sediment may suggest that sediment obstruction of PES matrix may have enhanced fomesafen mass transport via PES porous structure. This increase in fomesafen uptake on the membrane was also reflected on fomesafen accumulation on Oasis HLB, where an increase in uptake rate was observed for POCIS exposed to sediment.

Bicyclopyrone with a $\log K_{PESW}$ of 1.60, also has relatively low affinity to PES and may diffuse primarily via PES porous structure. However, unlike fomesafen, a decrease in

PES uptake was observed for bicyclopyrone. Obvious explanations to these observations are not apparent. Transport through PES appear to be more complex. Additional experiments with expanded molecular diversity of target analytes and higher degree of replication would be beneficial to better comprehend the different mechanisms involved. POCIS exposure to sediment did not affect uptake rates for most target analytes. However, these results are only valid for POCIS exposure to sediment with similar characteristics as the one used in the present study. Other sediment type, such as sediment with higher organic matter content may have different effects on POCIS uptake rates.

Increased POCIS Sensitivity for Compounds with Relatively High Hydrophobicity and High Affinity to PES

Evaluation of PES membrane versus Oasis HLB sorbent pesticides uptake in Figure 4.5 demonstrated that PES membrane uptake of pesticides was in most cases lower than sorbent uptake except for azoxystrobin, propiconazole, sedaxane and solatenol, where it was either similar or greater than Oasis HLB sorbent uptake. The fraction of chemicals accumulated to PES were low for most compounds and ranged from 0 to 33%. PES accumulation of propiconazole, azoxystrobin, and sedaxane were intermediate with the fraction of PES accumulation ranging from 53 to 64%. PES accumulation of solatenol was the highest with fraction accumulated in the membrane of 96 %. There was a general increase in PES accumulation with increasing hydrophobicity and PES affinity. Previous studies which have also investigated accumulation in PES and Oasis HLB have made similar observations.^{91, 115, 129}

Silvani et al.¹¹⁵ investigated POCIS uptake of alkylphenols and suggested the incorporation of both PES and Oasis HLB amount of chemicals accumulated into sampling

rates calculation for alkylphenols with high hydrophobicity ($\log K_{ow} \geq 4$) that are primarily accumulated in PES. This was suggested in order to increase POCIS sensitivity and more effectively monitored chemicals concentration in water for those compounds. Similar approach was followed in this study, with the amount of chemicals adsorbed to PES incorporated into sampling rates calculation using in Equation 1:

$$\frac{N_{HLB+PES}}{C_w} = R_{HLB+PES}t \quad (1)$$

Where $R_{HLB+PES}$ is the sampling rate determined from both oasis HLB and PES, $N_{HLB+PES}$ is the total amount of chemicals accumulated by Oasis HLB sorbent and PES, t is the deployment and C_w is the chemicals concentration in water.

Sampling rates ($R_{HLB+PES}$) calculated from Equation 1 are reported in Table 4.2 for all compounds and exposure types. Results demonstrated that sampling rates calculated from both Oasis HLB and PES were generally similar to sampling rates calculated from only Oasis HLB for compounds with relatively low hydrophobicity and affinity to PES ($\log K_{ow} \leq 3$ and $\log K_{PESW} \leq 3$). The most impact was observed for solatenol, which has relatively high hydrophobicity and affinity to PES ($\log K_{ow}$ of 4.30 and $\log K_{PESW}$ of 4.52), where an 18-fold increase in sampling rate was observed between $R_{HLB+PES}$ and R_s . Thus, the incorporation of the amount of chemicals accumulated to PES into POCIS sampling rates calculation may well indeed significantly increase POCIS sensitivity for compounds with relatively high hydrophobicity and PES affinity such as solatenol.

An increase (about 2 folds) in sampling rates was observed for sampling rates calculated from both the amount of chemicals accumulated in PES and Oasis HLB for sedaxane and propiconazole, which are both slightly less hydrophobicity ($\log K_{ow}$ of 3.3 and 3.72, respectively) and have less affinity to PES than solatenol ($\log K_{PESW}$ of 3.91 and

4.05). Interestingly, a similar increase (about 3 folds) in the same sampling rate was also observed for azoxystrobin, which has higher affinity to PES than solatenol ($\log K_{\text{PESW}}$ of 4.71), but much lower hydrophobicity ($\log K_{\text{ow}}$ of 2.5). An obvious explanation for this observation is not apparent. Nonetheless, unlike the other target analytes with similar hydrophobicity, azoxystrobin has three aromatic rings (see Figure C1). The higher number of aromatic rings may lead to stronger π - π interactions with the phenyl groups on PES, causing azoxystrobin to have high affinity to PES. Even though a significant increase in sampling rates was observed for azoxystrobin, propiconazole and sedaxane when the amount accumulates in both PES and Oasis HLB was considered for sampling rates calculation, such increase may not necessarily translate into a meaningful change in POCIS sensitivity for those compounds. Thus, the increase of POCIS sensitivity with $R_{\text{HLB+PES}}$ appears to be more meaningful for compounds with not only relatively high hydrophobicity ($\log K_{\text{ow}} \geq 4$) as suggested by Silvani et al.¹¹⁵ but also with relatively high affinity to PES ($\log K_{\text{PESW}} \geq 4$).

The use of both PES and Oasis HLB extracts may be even more so relevant for field monitoring studies using analytical methods that are not equipped for trace analysis. However, changes in environmental factors such as flow rate, temperature, pH or sediment as demonstrated in this study, may have different effects on the PES compare to those observed for the Oasis HLB sorbent. Therefore, caution should be taken when incorporating PES chemicals accumulation into POCIS sampling rates calculation. Alternatively, the use of passive sampling devices such as SPMD could be explored for monitoring chemicals with relatively high hydrophobicity stronger affinity to the PES membrane. Oasis HLB extracts from POCIS exposure to surface and ground water have

been used for screening and in combination with bioassays for bioanalytical assessment of chemicals in water.^{71-73, 131, 132} This specific type of application typically required relatively high concentration of chemicals in order to be efficient. The use of both PES and Oasis HLB may significantly increase chemicals concentration, especially the ones with relatively high hydrophobicity and affinity to PES, that would not have been detected otherwise due to the fact that they primarily accumulated in PES. Therefore, the extraction of both PES and Oasis HLB in POCIS experiments may be incorporated for studies that aim to investigate compounds with relatively high hydrophobicity and affinity to PES. However, fundamental processes of PES uptake should be better characterized in order to efficiently use this proposed method, especially when used for the determination of TWAC.

CHAPTER FIVE

Effects of Concentration Exposure on POCIS Sampling Rates

Abstract

The effects of concentration exposure on Polar Organic Chemical Integrative Sampler (POCIS) sampling rate and POCIS ability to operate in an integrative regime were investigated for 12 pesticides. In 41 independent 21-day experiments, POCIS devices were exposed to pesticides constant concentrations ranging from 3 to 60 $\mu\text{g/L}$ and multiple pulse concentrations with maximum peaks ranging from 5 to 150 $\mu\text{g/L}$. Temperature and flow velocity were held constant for each experiment at 23 ± 2 $^{\circ}\text{C}$ and 10 cm/s, respectively. No significant effect was observed on POCIS ability to operate in an integrative regime over 21-day exposures to constant concentrations ranging from 3 to 60 $\mu\text{g/L}$ and pulse concentrations with peak height ranging from 5 to 50 $\mu\text{g/L}$. However, POCIS integrative capabilities was shortened to 12 days for POCIS exposure to pulses concentration with a peak concentration of 100 and 150 $\mu\text{g/L}$. On the other hand, no significant difference was observed in POCIS sampling rate for exposure to constant concentration ranging from 3 to 60 $\mu\text{g/L}$, as well as pulses concentration with low peak height (5 and 20 $\mu\text{g/L}$). However, the increase in POCIS sampling rate by a factor of up to 2-fold was observed between pulses concentration with high peak concentrations (50 to 150 $\mu\text{g/L}$) and pulses concentration with low peak concentration. A similar increase in POCIS sampling rate was also observed between pulses concentration with high peak concentration and constant concentration with corresponding time-weighted average concentration. Preliminary assessment of the observed differences in POCIS sorbent coverage surface area between

pulses concentration with high peak height and the other concentration exposures (constant concentration and pulses with low peak height) did not explained the observed increase in sampling rate, suggesting that further investigation is still needed to understand and characterize factors affecting POCIS sampling rate.

Introduction

Methods for monitoring pesticides in agricultural and urban streams have recently shifted from using conventional discrete grab water sampling to integrative passive samplers, such as polar organic chemical integrative sampler (POCIS) devices.^{28, 109-112} POCIS devices can provide several advantages over traditional discrete grab water sampling, including longer sampling period and the capability to capture short spike and low chronic exposures. POCIS devices are typically made of Oasis HLB resin uniformly distributed and sandwiched between two PES membranes, which are held together by two stainless steel rings. Chemical accumulation in POCIS devices typically follows a first-order kinetic model, where accumulation is first integrative, then curvilinear, and finally reaches equilibrium.^{31, 32} Determination of accurate time-weighted average concentration (TWAC) using POCIS in field applications is highly dependent on the device operating in the integrative regime and the use of accurate sampling rate, which are both compound dependent and may deviate with changing environmental conditions including hydrodynamic conditions, temperature and concentration.^{35, 36, 69, 133}

The occurrence of pesticides in surface water has been be associated with runoff from agricultural and urban areas, wastewater discharges, atmospheric deposition, spills, and ground water inflow.¹¹ These different routes of exposure can cause temporal variability in pesticide concentrations over several orders of magnitude.¹³⁴ Such drastic

change in environmental conditions may affect the integrative property of POCIS and the ability of POCIS to determine accurate TWAC of pesticides in agricultural streams. Moreover, laboratory-derived POCIS sampling rates are typically determined under low constant concentration exposure. Hence, these laboratory-derived POCIS sampling rates may not account for those high fluctuations in chemical concentration observed in field studies.

Few studies have evaluated the ability of POCIS to accurately provide TWAC of chemicals in water with temporal variation of concentrations.^{35, 36, 135-138} Mazzella et al.³⁵ investigated the effect of concentration exposures of herbicides on the integrative properties of POCIS over a period of nine days. POCIS were exposed to constant concentrations ranging from 2.6 to 3.6 $\mu\text{g/L}$ and to a 3-day pulse concentration with peak concentrations ranging from 15 to 24 $\mu\text{g/L}$. They observed a full integration of herbicide concentrations under both constant and pulse concentration exposures. Belden et al.¹³⁷ investigated the effects of munition constituents and pesticide exposure type on POCIS sampling rates over a period of 28 days. Sampling rates were determined for single and multiple pulses corresponding to a TWAC of 0.43 $\mu\text{g/L}$ and a constant concentration exposure of 1 $\mu\text{g/L}$. They observed linear uptake over the 14 days exposure time and no significant difference in POCIS sampling rates between pulses and constant concentration exposures for target compounds. More recently, Bernard et al.¹³⁸ investigated the ability of POCIS to integrate short pesticides peaks. POCIS were exposed to a constant background concentration of pesticides at 1 $\mu\text{g/L}$ and then 5 $\mu\text{g/L}$ for seven days each. Additionally, three pulse concentrations with peak height of 10, 40, and 60 $\mu\text{g/L}$ lasting 24h, 6h, and 1h, respectively, were simulated on day one, five, and nine. They observed linear POCIS

uptake over the 14 days and a relatively good integration of the very short concentration peaks. These studies have furthered our current understanding of concentration exposure effects on POCIS uptake. However, they only explored constant and pulses concentration exposures with relatively low concentration and/or short exposure duration. Previous reports indicate that estimated environmental pesticide concentrations can have a TWAC of up to 60 µg/L, with a peak height of 150 µg/L.¹³⁹⁻¹⁴²

The ability of POCIS to accurately determine atrazine's TWAC in comparison to daily composite grab water sampling was assessed in a mesocosm study for high, multiple concentration pulses (*i.e.*, 3 pulses for 96 hours duration each at 50, 100 and 150 µg/L), distributed evenly over 30 days.¹⁴³ A laboratory-derived sampling rate published in the literature was used for TWAC calculations from POCIS. Results demonstrated that atrazine's TWAC calculated from POCIS was in good agreement with the ones calculated from daily composite water sampling for the first 10 days of the three pulses concentration levels. However, the same comparison for 20-day and 30-day period demonstrated that there were significant inconsistencies between TWAC for pulses concentrations of 100 and 150 µg/L, while there were still good agreements for POCIS exposed to pulses concentration with peak concentration of 50 µg/L. This study indicated that concentration exposure may affect POCIS accumulation of atrazine. However, the change in other environmental parameters (*i.e.*, biofouling, temperature) over the 30-day period, with demonstrated ability to interfere with POCIS accumulation,^{83, 85, 107, 119} made it difficult to independently evaluate the effects of concentration exposure on POCIS accumulation of atrazine.

In the present work, a series of independent laboratory experiments were performed to investigate the effects of concentration exposures on POCIS sampling rates of 12 organic pesticides with a wide range of physico-chemical properties and structures. To ensure realistic environmental concentration scenarios, five pulse concentration exposure experiments with peak concentrations ranging from 5 to 150 µg/L and seven constant concentration exposure experiments with concentration ranging from 3 to 60 µg/L were performed.

Materials and Methods

Materials and Chemicals

Target analytes (atrazine, azoxystrobin, bicyclopyrone, cyproconazole, fomesafen, mesotrione, S-metolachlor, propiconazole, sedaxane, simazine, solatenol and thiamethoxam) were provided by Syngenta Crop Protection, LLC at > 96% purity and used as received. Internal standards (atrazine-d5, MCPA-d3, metolachlor-d6, simazine-d10 and thiamethoxam-d3) were purchased from CDN isotopes (Quebec, Canada) at > 98% purity. Formic acid and HPLC grade acetonitrile (ACN) were purchased from Fisher Scientific (Fair Lawn, New Jersey, USA). Water used for samples preparation and UPLC eluents was collected from a Thermo Branstead Nanopure (Dubuque, Iowa, USA) Diamond UV water purification system.

Laboratory Uptake Experiments

POCIS were exposed to pulse and constant concentrations of pesticides mixture (atrazine, azoxystrobin, bicyclopyrone, cyproconazole, fomesafen, mesotrione, S-metolachlor, propiconazole, sedaxane, simazine, solatenol and thiamethoxam) in DI water over a period of 21 days. Concentration exposure profiles are shown in Figure 5.1. Pulse exposures were conducted with three equivalent 4-day concentration pulses over a 21-day period. Five independent experiments investigated pulse exposure with peak concentrations of 5, 20 $\mu\text{g/L}$ for all compounds, and 50, 100, and 150 $\mu\text{g/L}$ for atrazine only. Seven independent experiments examined constant concentration exposure, with concentrations of 3 and 11 $\mu\text{g/L}$ for all compounds and 10, 20, 30, 40 and 60 $\mu\text{g/L}$ for atrazine only.

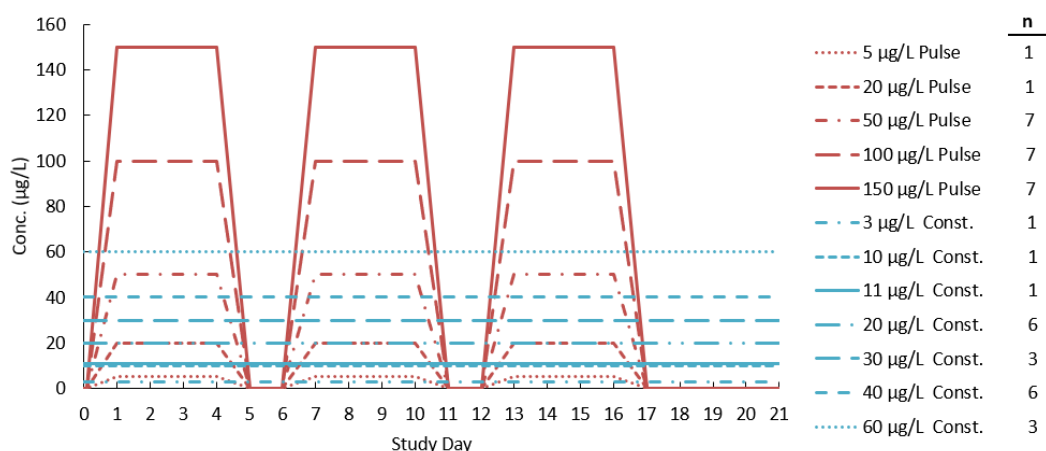


Figure 5.1. Concentration profiles of laboratory POCIS experiments. Atrazine concentration ranged from 5 to 150 $\mu\text{g/L}$ and 3 to 60 $\mu\text{g/L}$ for pulse and constant exposure, respectively. Lower concentrations (5 and 20 $\mu\text{g/L}$ for pulse peak concentration, 3 and 11 $\mu\text{g/L}$ for constant concentration) were targeted for azoxystrobin, bicyclopyrone, cyproconazole, fomesafen, mesotrione, S-metolachlor, propiconazole, sedaxane, simazine, solatenol and thiamethoxam. The number of replicate experiments performed for a given concentration profile is designated by n.

Temperature and flow velocity were held constant in these experiments at 23 ± 2 °C and 10 cm/s, respectively. Water was renewed every 24 hours, and water samples were collected before and after each renewal and POCIS were retrieved every other day. Newly prepared analyte concentrations in water were 3.0 ± 0.8 , 10 ± 1 , 11 ± 2 , 20 ± 2 , 31 ± 2 , 40 ± 2 , and 60 ± 3 µg/L for constant concentration exposures. Newly prepared analyte concentrations in water during pulse events were 5 ± 1 µg/L, 20 ± 3 µg/L, 52 ± 5 µg/L, 102 ± 9 µg/L, and 153 ± 15 µg/L. A depletion in analyte concentration of less than 20% was observed for all compounds and both concentration exposure types after 24 hours over the 21-day exposure period. Experimental apparatus, procedure for POCIS extraction and sample analysis were previously described in Toteu Djomte et al.¹³³

Results and Discussion

Determination of pesticides TWACs in the environment with POCIS highly relies on the device operating in the integrative regime as well as accurate determination of POCIS sampling rates, which may both be affected by environmental conditions such as concentration exposure.^{69, 143} Laboratory POCIS calibration experiments for the determination of sampling rates that are reported in the literature have been typically carried out at low constant and pulse concentration exposure (≤ 5 and 24 µg/L, respectively).^{35, 69} However, reports indicate that higher concentration exposures of pesticides have been observed in the environment (TWACs and peak concentrations of up to 60 and 150 µg/L, respectively).¹⁴⁰⁻¹⁴² A previous mesocosm study where POCIS were exposed to multiple high concentration pulses over 30 days suggested that POCIS exposure to high concentration may affect POCIS integrative phase and/or uptake rates.¹⁴³ To evaluate the effects of concentration exposure on POCIS sampling rates, POCIS devices

were exposed to a range of constant and multiple pulses concentrations in series of independent laboratory experiments as illustrated in Figure 5.1.

POCIS devices were first exposed to constant concentrations of pesticides mixture at 3 and 11 $\mu\text{g/L}$ over a period of 21 days. Higher concentrations ranging from 20 to 60 $\mu\text{g/L}$ were targeted for atrazine to ensure its realistic higher environmental concentration relative to the other target analytes. Representative uptake curves are illustrated in Figure 5.2A, 5.2B and 5.2C for atrazine at constant concentration of 11, 30 and 60 $\mu\text{g/L}$, respectively. Similar plots are provided in Figure D1 and D2 for the remaining constant concentration exposure experiments. Sampling rates are reported in Table 5.1 for all compounds with constant concentrations of 3 and 11 $\mu\text{g/L}$ and in Table 5.2 for atrazine with constant concentrations ranging from 3 to 60 $\mu\text{g/L}$.

Uptake curves for each pesticide were fit to a linear regression model and residual analysis was carried out to evaluate the fit of the data to the model. Figures 5.3A and 5.3C illustrate residual plots of POCIS uptake curves for atrazine constant concentration of 3 and 60 $\mu\text{g/L}$. These plots show that data points in each residual plot are randomly scattered around the horizontal dashed line ($y = 0$). Similar residual plots are provided in Figure D4 to D15 for the remaining compounds at constant concentrations exposure. These results demonstrated that linear regression was a good fit. Thus, POCIS uptake remained within the integrative phase over the 21-day for constant concentration exposure with concentrations ranging from 3 to 11 $\mu\text{g/L}$ for all target pesticides and from 3 to 60 $\mu\text{g/L}$ for atrazine.

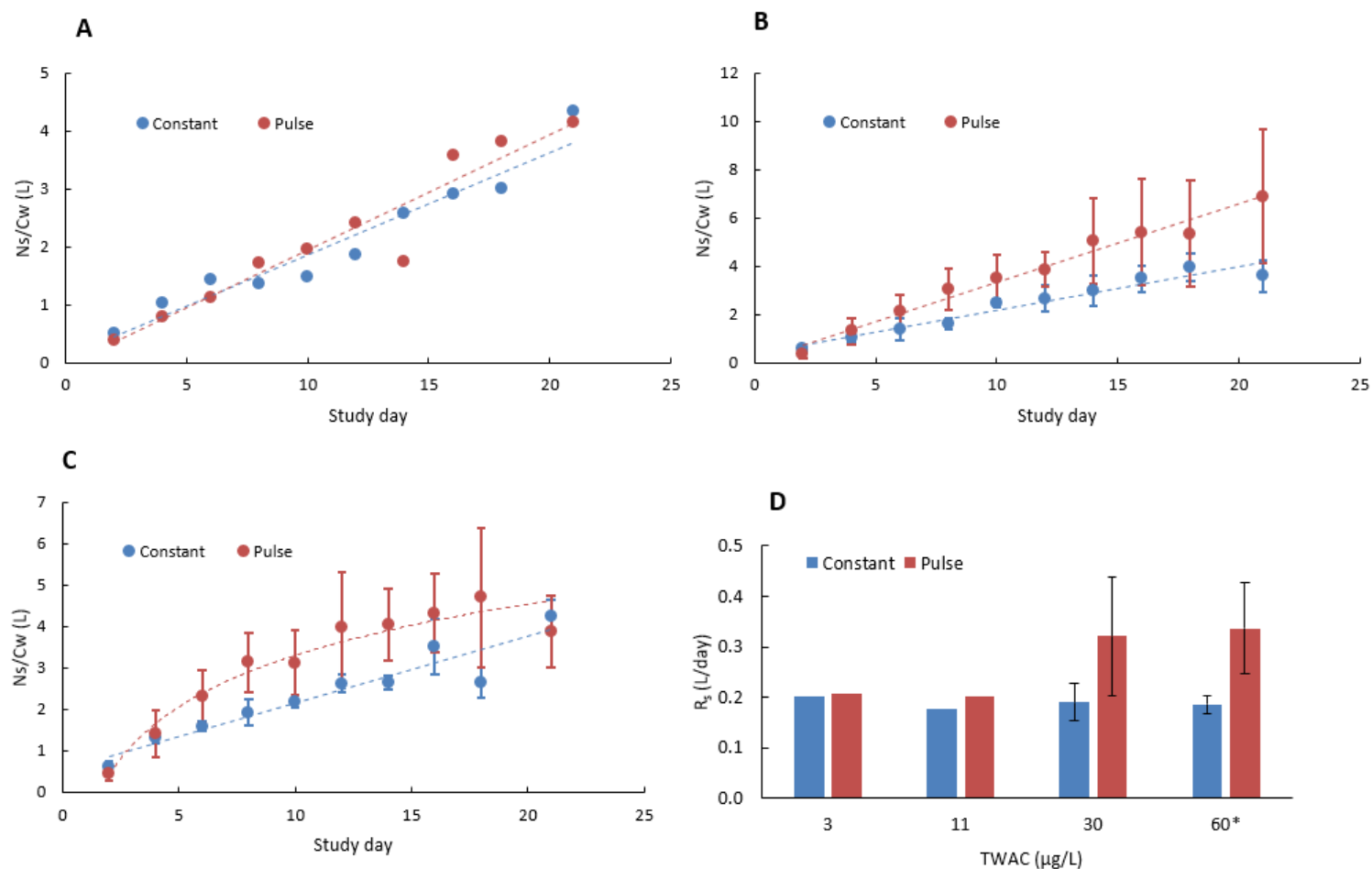


Figure 5.2. Atrazine POCIS uptake for (A) constant and pulse concentration with TWAC of 11 $\mu\text{g/L}$, (B) constant and pulse concentration with TWAC of 30 $\mu\text{g/L}$, and (C) constant and pulse concentration with TWAC of 60 $\mu\text{g/L}$. (D) Illustrates sampling rates comparison between constant and pulse concentration exposures, where (*) indicates that sampling was determined from a 12-day exposure time period. The error bars represent one standard deviation for n number of replicates.

Table 5.1. Target analytes sampling rates for constant and pulse concentration exposures.

Compound	Rs_Constant (L/day)		Rs_Pulse (L/day)	
	3 µg/L	11 µg/L	5 µg/L	20 µg/L
Thiamethoxam	0.12	0.11	0.11	0.12
Mesotrione	0.02	0.02	0.02	0.02
Bicyclopyrone	0.05	0.05	0.04	0.04
Simazine	0.18	0.19	0.20	0.21
Azoxystrobin	0.20	0.22	0.17	0.19
Atrazine	0.20	0.18	0.21	0.20
Cyproconazole	0.21	0.20	0.22	0.22
Fomesafen	0.14	0.15	0.13	0.13
S-Metolachlor	0.21	0.21	0.22	0.20
Sedaxane	0.21	0.21	0.22	0.23
Propiconazole	0.19	0.20	0.19	0.19
Solatenol	0.03	0.03	0.03	0.04

Table 5.2. Atrazine sampling rates for constant and pulse concentration exposures.

Concentration (µg/L)	Rs_Constant (L/day)	Rs_Pulse (L/day)
3	0.20	
5		0.21
11	0.18	
10	0.19	
20	0.16 ± 0.04 ^a	0.20
30	0.19 ± 0.04 ^b	
40	0.22 ± 0.07 ^c	
50		0.3 ± 0.1 ^e
60	0.16 ± 0.02 ^d	
100		0.34 ^h ± 0.09 ^f
150		0.28 ^h ± 0.06 ^g

^{a, c, e, f, g} one standard deviation for n = 7

^{b, d} one standard deviation for n = 3

^h sampling rate calculated from 12-day exposure time

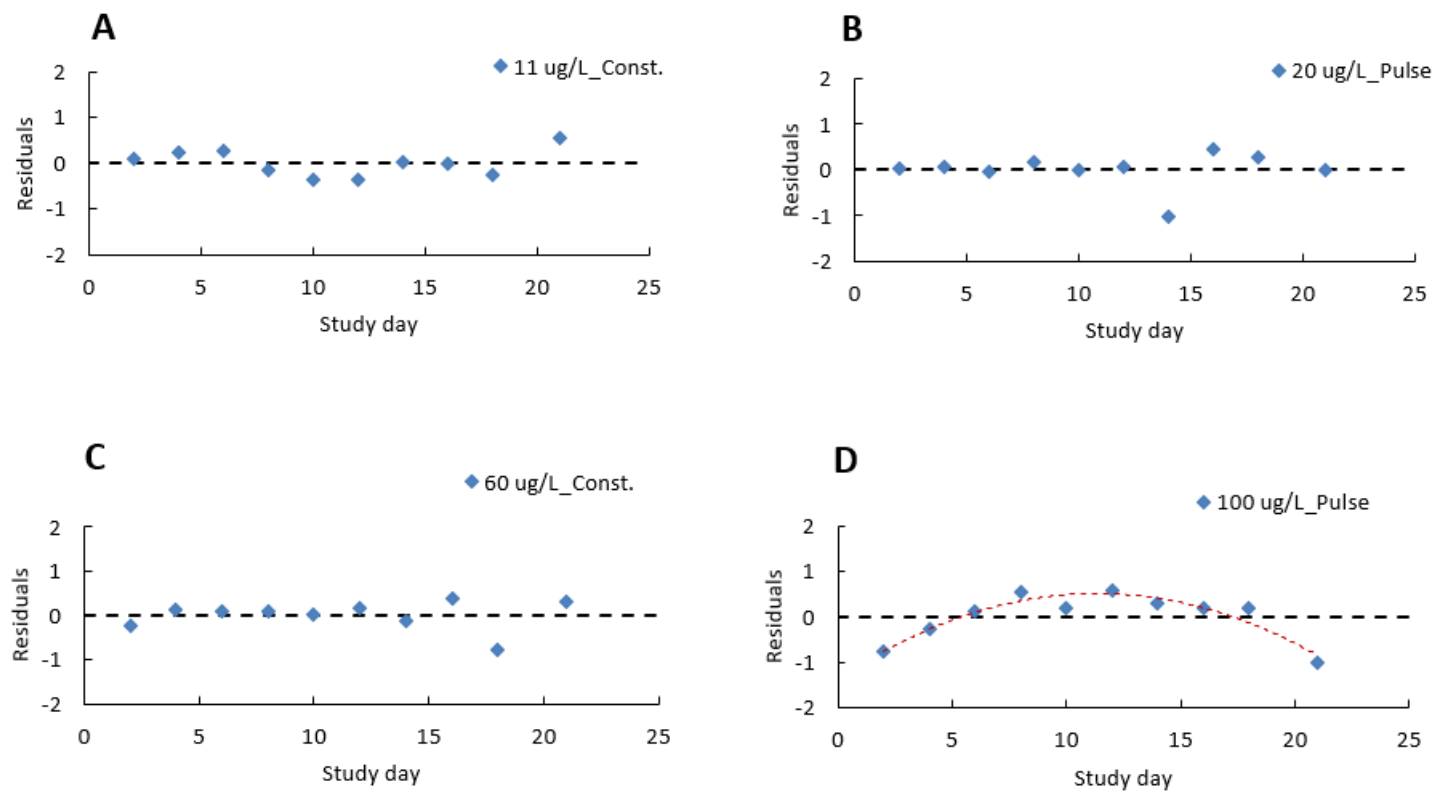


Figure 5.3. Residual plots of atrazine uptake curves for constant concentration exposure at (A) 11 $\mu\text{g/L}$ and (C) 60 $\mu\text{g/L}$; multiple pulses concentration exposure with peak height at (B) 20 $\mu\text{g/L}$ and (D) 100 $\mu\text{g/L}$, with TWAC of 3 and 63 $\mu\text{g/L}$, respectively. The error bars represent one standard deviation for $n = 3$ and 7 for (C) and (D), respectively.

Multiple linear regression analysis⁹² demonstrated that for all target analytes, there was no significant difference ($p \geq 0.05$) between sampling rates for constant concentration of 3 and 11 $\mu\text{g/L}$. Similarly, there were no significant differences between atrazine sampling rates for constant concentrations ranging from 3 to 60 $\mu\text{g/L}$. Therefore, POCIS exposure to relatively high constant concentrations did not affect POCIS integrative properties nor did it affect sampling rates for this group of target analytes.

Second, POCIS devices were exposed to multiple pulses concentration with peak height ranging from 5 to 150 $\mu\text{g/L}$ over a period of 21 day as illustrated in Figure 5.1. Peak concentrations of 5 and 20 $\mu\text{g/L}$, with corresponding TWAC of 3 and 5 $\mu\text{g/L}$, respectively, were evaluated for all target analytes. Atrazine concentration exposure was expanded to included peak concentrations of 50, 100 and 150 $\mu\text{g/L}$ with TWACs of 31, 63 and 96 $\mu\text{g/L}$, respectively. Representative uptake curves are illustrated in Figure 5.2A, 5.2B and 5.2C for atrazine with pulse concentrations at peak heights of 20, 50 and 100 $\mu\text{g/L}$, respectively. Similar plots are provided in Figure D1 and D3 for the remaining pulse concentration exposure experiments. Sampling rates are reported in Table 5.1 for all target analytes with peak concentrations height of 5 and 20 $\mu\text{g/L}$ and in Table 5.2 for atrazine with peak concentrations height ranging from 5 to 150 $\mu\text{g/L}$.

A linear regression model fit and residual analysis were also used to evaluate uptake curves for each pesticide. Representative residual plots are illustrated in Figure 5.3B and 5.3D for atrazine pulses concentration with peak height of 20 and 100 $\mu\text{g/L}$. Similar plots for the remaining compounds are provided in Figure D4 to D15. Results demonstrated that linear regression was a good fit for POCIS uptake of pulses concentration with peak height of 5 and 20 $\mu\text{g/L}$ over 21-day exposure time for all target analytes. Linear regression model

was also a good fit for atrazine pulse concentrations with peak height of 50 $\mu\text{g/L}$ over 21-day exposure time period. Thus, POCIS uptake remained within the integrative phase for multiple pulse concentrations exposure of 5 and 20 $\mu\text{g/L}$ for all compounds and 50 $\mu\text{g/L}$ for atrazine. Interestingly, the linear regression model was not a good fit for atrazine pulse concentrations with peak height of 100 and 150 $\mu\text{g/L}$. As illustrated in Figure 5.2D for the pulse exposure with 100 $\mu\text{g/L}$ peak height, data points on the residual plots were not randomly scattered around the horizontal dashed black line $y = 0$. Instead, they were scattered around a parabolic curve (dashed red in Figure 5.2D). The linear regression fit of the uptake curves for these two high pulse concentrations exposures was significantly improved when the residual analysis was only carried out for the first 12 days of the exposure time window.

Multiple linear regression analysis was carried out for the linear portion of each uptake curve (*i.e.*, 21 days for pulses with peak heights of 5 to 50 $\mu\text{g/L}$ and 12 days for pulses with peak heights of 100 and 150 $\mu\text{g/L}$) in order to evaluate the effects of increasing multiple pulses concentration peak heights on POCIS sampling rates. Results demonstrated that there was no significant difference in POCIS sampling rate when peak height for pulse exposures increased from 5 to 20 $\mu\text{g/L}$. Additionally, there was no significant difference in POCIS sampling rate between atrazine pulse concentration with peak heights of 50, 100 and 150 $\mu\text{g/L}$. However, there was a statistically significant increase (1.6-fold) in atrazine POCIS sampling rate between the lower (5 and 20 $\mu\text{g/L}$) and the higher (50, 100 and 150 $\mu\text{g/L}$) pulse concentrations.

Effect of concentration exposure type (*i.e.*, constant versus pulse concentration exposure) was investigated. POCIS uptake of each pesticide for exposure to pulse

concentrations was compared to that of constant concentration exposure with similar TWAC and illustrated in Figure 5.2D for atrazine. No difference was observed in POCIS uptake between the two exposure types for all pesticides with TWAC of 3 and 11 µg/L. However, there was a significant 1.7-fold increase in atrazine POCIS sampling rate when exposure type was changed from constant to pulse concentration for TWAC of 30 µg/L. Similarly, there was a significant 1.8-fold increase in sampling rate calculated from a 12-day exposure time frame for constant concentration of 60 µg/L and pulse concentration with peak height of 100 µg/L. These results suggest that increase in multiple pulses concentration peak height to a certain threshold increases POCIS sampling rate. Further increase in peak height beyond that threshold causes POCIS uptake to precociously change from an integrative to a curvilinear or an equilibrium accumulation regime. Morin et al.¹⁴⁴ reported that POCIS accumulation of atrazine has a half-life of 30 days for POCIS exposure to 3 µg/L constant atrazine concentration and experimental conditions similar to the one in this study, *i.e.*, under flow condition and a temperature of 20 °C. As a result, POCIS uptake of atrazine under those conditions should remain within the integrative regime minimally for a period of 30 days. Thus, the observed shortening of the integrative regime to 12 days for high atrazine pulse concentration exposure suggests that POCIS maximum adsorption capacity for atrazine was reached.

Sorption isotherm between atrazine and Oasis HLB was performed in order to investigate the mechanism of adsorption as well as to determine the maximum adsorption capacity. Details about Sorption isotherm experiment are provided in supplementary data. Langmuir and Freundlich sorption isotherm models were used to interpret the data and a good fit was observed with the Freundlich model ($R^2 = 0.91$). Atrazine sorption isotherm

plot is illustrated in Figure D16. The slope of the Freundlich isotherm plot ($1/n$) was equal to 0.66, indicating a physisorption, with decreasing adsorbent-adsorbate interaction with increasing surface concentration over time.¹⁴⁵⁻¹⁴⁷ Freundlich sorption isotherm model only provides a relative adsorption capacity. Therefore, it was not possible to determine Oasis HLB maximum adsorption capacity for atrazine. Nonetheless, it is reasonable to suggest that POCIS exposure to high atrazine concentrations (*i.e.*, $\geq 100 \mu\text{g/L}$) would cause Oasis HLB maximum adsorption capacity to be reached beyond 12-day exposure time period. Thus, the use of POCIS devices for atrazine TWAC monitoring in agricultural streams with concentration as high as $100 \mu\text{g/L}$ should be limited to 12 days. Increase in POCIS sorbent mass may increase the sorbent capacity load. Further work is needed to understand and characterize the effect of sorbent mass on POCIS capacity load.

Inconsistent Oasis HLB resin redistribution and settling between PES membrane has been observed in most of the conducted POCIS experiments our research group. Examples of Oasis HLB redistribution between PES membrane are illustrated in Figure 5.4. Similar observations of Oasis HLB redistribution have also been reported in the literature. But, no apparent factor has been associated with this observed change in Oasis HLB surface area coverage within the PES membranes so far.^{91, 103, 148} Fauvelle et al.¹⁴⁸ has investigated the effects of Oasis HLB mass and surface area coverage within the PES membranes. An increase in POCIS sampling rates by a factor of up to 1.83-fold was observed and attributed to the increase in Oasis HLB surface area coverage within the PES membranes. POCIS exposure to atrazine pulses concentration with peak heights of 50, 100, and $150 \mu\text{g/L}$ was carried out in three sets of duplicate experiments for each concentration. Interestingly, no Oasis HLB redistribution and settling was observed during the first set, while inconsistent

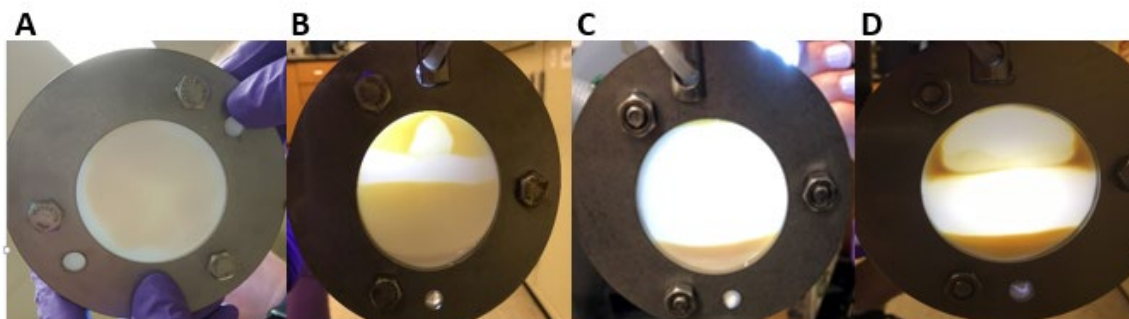


Figure 5.4. Images highlighting the distribution of the Oasis HLB resin between the PES membranes of POCIS devices: (A) before deployment and (B) three days after deployment, (C) 10 days after deployment and (D) 21 days after deployment.

redistribution and settling of Oasis HLB was observed during the other two sets. Additionally, sampling rates calculated from that first set of experiments were higher than the ones from the other two sets and contributed the most to the significant increase in sampling rates relative to lower pulses concentration and constant concentration exposures as illustrated in Figure D17. These results suggest that the higher sampling rates values in the first set of high pulses concentration exposures was due to the larger surface area coverage of Oasis HLB between PES membranes for that set, relative to the other constant and pulses concentration exposures. The redistribution and settling of sorbent between the PES membranes may reduce the effective surface area available for analyte adsorption, which can potentially influence POCIS sampling rates, *i.e.*, increase in sampling rate with increase sorbent surface area coverage between PES membranes. Future work should further investigate the impact variability in POCIS device structure on POCIS sampling rate and POCIS ability to accurately measure TWAC.

The main objectives of this work were to investigate the effects of concentration exposure types (constant concentrations and multiple pulse concentrations exposures) on POCIS integrative properties and POCIS sampling rate. Results suggest that POCIS ability

to integrate is affected by chemical load rather than exposure type. POCIS exposed to atrazine concentrations equal or below 60 $\mu\text{g/L}$ remain integrative for 21 days. However, for POCIS exposure to atrazine concentrations equal or above 100 $\mu\text{g/L}$, the sorbent chemical load reaches maximum capacity. Similar studies exploring a combination of exposure time and concentration height (including concentrations ranging from 60 to 100 $\mu\text{g/L}$) for a wider panel of compound would further the current understanding of the effects of high concentration exposures on POCIS integrative properties.

The current study demonstrated that POCIS sampling rate was not affected by concentration exposure ranging from 3 to 60 $\mu\text{g/L}$ for constant concentration and from 5 to 20 $\mu\text{g/L}$ for pulses concentration exposures. Interestingly, sampling rate appeared to increase for higher pulses concentrations (50, 100 and 150 $\mu\text{g/L}$). Explanation for this increase in sampling rate was not apparent. Further work is needed to better understand and characterize the effect of higher pulses concentration exposures on POCIS sampling rate.

CHAPTER SIX

Conclusion

POCIS is one of the emerging passive sampling devices used for the monitoring of pesticides in the aquatic environment. POCIS provides significant advantages including convenience and relatively low cost over traditional methods. However, the use of POCIS for accurate determination of TWACs in field settings is still questionable because of the effects of environmental conditions on POCIS uptake. The objective of this dissertation was to provide advanced fundamental understanding of the effects of changing environmental conditions on POCIS uptake, in order to bridge the gap between data derived in the laboratory and in field settings and improve accuracy in the determination of TWAC in field settings using POCIS. Environmental conditions evaluated in this work included hydrodynamic conditions, temperature, suspended sediment and concentration exposure. The study focused on 12 pesticides (atrazine, azoxystrobin, bicyclopyrone, cyproconazole, fomesafen, mesotrione, S-metolachlor, propiconazole, sedaxane, simazine, solatenol, and thiamethoxam), representing the different type of pesticides used in the US as well as chemicals with a broad range of physicochemical properties. A UPLC-MS/MS method was developed for water and POCIS extracts analyses and reported in Chapter two.

A good understanding about the effects of varying hydrodynamic conditions (stagnant and flow velocities ranging from 6 to 21 cm/s) on POCIS sampling rates was developed in Chapter three. POCIS sampling rates generally increased between a stagnant condition and a flow velocity of 6 cm/s, but essentially remained constant for flow

velocities ranging from 6 to 21 cm/s. Additionally, for the first time, an independent method for determining flow velocity at the surface of POCIS was developed, enabling better characterization of laboratory and field hydrodynamic conditions at the surface of POCIS, as well as facilitating data comparisons among studies. Following this, a better understanding of the effects of temperature (8 to 39°C) on POCIS sampling rates was developed in Chapter three. For a given flow condition there was a linear increase in POCIS sampling rates with increasing temperature. Mathematical relationships between POCIS sampling rate and temperature derived from an Arrhenius model were used to correct laboratory derived POCIS sampling rates for temperature in field applications. However, the temperature corrections do not fully explain the scatter observed when comparing time weighted average concentrations (TWACs) of atrazine based on grab and passive sampling (i.e., POCIS) methods.

The effects of total suspended sediment concentration (average 3600 ppm) on POCIS sampling rates were evaluated in Chapter four. Sediment had a negligible effect on POCIS sampling rates for most compounds with the exception of bicyclopyrone and fomesafen, where meaningful changes in sampling rates were observed. The effects of sediment on pesticides distribution between PES membrane and Oasis HLB sorbent were also explored and provided an improved understanding of mass transfer processes across PES membranes. Data demonstrated that PES membranes, which are typically not extracted for POCIS analysis in field studies, can be used to broaden POCIS use for hydrophobic compounds, as well as increase POCIS sensitivity for compounds with relatively high hydrophobicity and high affinity for PES. This increase in POCIS sensitivity is especially beneficial for analytical methods with high detection limits. However,

incorporation of PES membrane extractions for TWAC field applications should not be performed without good understanding of the effects of environmental conditions such temperature and flow velocity on PES uptake.

The effects of concentration exposure on POCIS integrative properties and POCIS sampling rates were investigated in Chapter five. Data demonstrated that POCIS uptake remains integrative for POCIS exposure for concentrations ranging from 3 to 60 $\mu\text{g/L}$. However, data suggested that at high concentration exposure (i.e., $\geq 100 \mu\text{g/L}$ for atrazine), POCIS load reaches maximum capacity precociously, which ultimately reduces the POCIS integrative phase. POCIS integrative phase was reduced to 12 days for POCIS exposure to atrazine concentration $\geq 100 \mu\text{g/L}$. Data also demonstrated that POCIS sampling rate is not affected by constant concentration ranging from 3 to 60 $\mu\text{g/L}$ and for pulse concentration with peak heights of 5 and 20 $\mu\text{g/L}$ with TWAC corresponding to 3 and 11 $\mu\text{g/L}$, respectively. Interestingly, sampling rate appeared to increase for higher pulses concentration (i.e., 50, 100 and 150 $\mu\text{g/L}$ for atrazine). Observations from prior POCIS experiments suggested that the increase in sampling rate was possibly due to inconsistencies within Oasis HLB surface area coverage. However, preliminary assessment of Oasis HLB distribution suggested that there was no correlation between POCIS sampling rate and Oasis HLB distribution between PES membranes.

The work accomplished in this dissertation has significantly improved the fundamental understanding of POCIS uptake and the effects of changes in environmental conditions on POCIS uptake. First, laboratory sampling rates for 12 pesticides were determined, some of which (i.e., bicyclopyrone, cyproconazole, fomesafen, sedaxane, solatenol, and thiamethoxam) for the first time. Mathematical models were derived to

calculate temperature-corrected sampling rate for each of the 12 pesticides in field settings. Second, an independent method for the determination of flow velocity near the surface of POCIS device was developed and this method was used to narrow the flow velocity range that has an impact on POCIS uptake. Third, understanding of transport processes of chemicals across PES membrane was improved. Finally, the concept of POCIS reaching maximum adsorption capacity in realistic field exposure concentration settings was introduced for the first time, and the concentration exposure range that may challenge POCIS integrative capability was provided.

Future Work

Effects of Sorbent Mass, Sorbent Surface Area Coverage and Exposed PES Surface Area on POCIS Sampling Rates

Observations from this work and previous work in the literature suggest that changes in POCIS structure may have an impact on POCIS uptake.²² A POCIS device is typically made of 200 mg Oasis HLB sorbent (60 μm particles size) sandwiched between two PES membranes (90 mm diameter, 0.1 μm pore size and 132 μm thickness). The PES membranes are held together by two stainless steel rings with 5.4 cm inner diameter and 46 cm^2 PES membrane exposed surface area. In concept, the POCIS device configuration should provide a maximum sorbent surface area coverage (i.e. area where the sorbent is in contact with the PES membranes) of 46 cm^2 , provided the sorbent uniformly covers the entire inner surface of the PES membranes. In practice, this is difficult to achieve and reproduce. Additionally, the observed inconsistent redistribution and settling of Oasis HLB sorbent between the PES membranes after POCIS deployment may further reduce the

sorbent surface area coverage, which may reduce the effective surface area available for analyte adsorption and potentially influence POCIS sampling rates.

As described earlier in Chapter one, POCIS sampling rate is proportional to the overall mass transfer coefficient (k_0) and the surface area (A) of the sampler. However, it is not clear whether the exposed PES membrane surface area or the sorbent surface area coverage between the PES membrane or both are the influential parameters in the equation. Investigations of the influence and relative importance of sorbent surface area coverage, and exposed PES surface area on POCIS sampling rates are needed.

Fauvelle et al.²² is currently the only study that has quantitatively addressed potential effects of sorbent mass, sorbent surface area coverage, and exposed PES surface area on POCIS sampling rates. In one set of experiments, the authors increased the mass of sorbent from 200 mg to 600 mg, while maintaining the exposed PES surface area (or “exposure window”) at 46 cm². The increase in sorbent mass resulted in an approximately 2-fold increase of POCIS sampling rates for several chemicals, including atrazine. The increase in sorbent mass also increased the effective surface area of sorbent coverage after settling from 11 to 17 cm². In a second set of experiments, the authors evaluated a similar increase in sorbent mass from 200 mg to 400 mg, using a μ POCIS device configuration. The exposed PES surface area for the μ POCIS design was 3 cm². In this case, there was minimal settling of sorbent, and the increase in sorbent mass did not produce substantial increases in μ POCIS sampling rates. A significant decrease of sampling rates was observed in the μ POCIS experiment with 200 mg sorbent, relative to sampling rates observed for the analogous experiment employing the more traditional POCIS design. This decrease was presumably due to the smaller “exposure window.” These data collectively suggest: (a)

variation of sorbent mass does not fundamentally (or independently) influence POCIS sampling rates; (b) for a given “exposure window,” sorbent surface area coverage is the primary factor influencing sampling rate; and (c) POCIS sampling rates scale proportionally with exposed PES surface area. However, the number of experiments performed in the Fauvelle et al. study was insufficient to mathematically define any important trend(s) among variables.

Further investigation of sorbent settling effects is needed, and experiments described in this section have been designed to more fully characterize the independent influence and relative importance of sorbent mass, sorbent surface area coverage, and exposed PES surface area on POCIS sampling rates. These investigations will further our understanding of changes in POCIS sampling rate associated with structural and/or physical changes in the sampling device that, in some cases, cannot be controlled in the field (e.g. sorbent settling). Additionally, results will provide insight on how one might account (or correct) for these changes when using POCIS devices. This work may also inform how one might, in the longer term, minimize any confirmed effects of structural/physical changes through future improvements in sampling device design and/or construction.

Experiments using modified POCIS configurations to evaluate the effects of sorbent mass sorbent surface area coverage and PES exposed surface area on POCIS sampling rates are proposed herein. The working hypothesis is that a positive correlation exists between POCIS sampling rates and sorbent surface area coverage. Sorbent settling will be monitored by collecting images of POCIS devices before and after retrieval and estimating sorbent surface area coverage through electronic integration of the visual

sorbent-membrane contact area. This will not only provide more statistical strength to the identification of any correlations that may exist between sorbent settling and observed trends in pesticides accumulation, but it will also enable the identification of any ancillary factors that may contribute to differential sorbent settling among similar experiments.

The experimental approach to test the hypothesis will rely on series of experiments that independently vary the mass of Oasis HLB sorbent, the sorbent Surface area coverage and the exposed PES surface area. Modifications to a typical POCIS configuration that would vary exposed PES surface area are illustrated in Figure 6.1. The mass of sorbent can also be varied in each configuration. POCIS configuration C will be evaluated at two sorbent loadings (e.g., 400 mg and 800 mg) to confirm the result in Fauvelle et al.²², suggesting that sorbent mass has a minimal effect on POCIS sampling rates when the “exposure window” and sorbent surface area coverage are constant. POCIS configuration A will be evaluated at five sorbent loadings (e.g., 200, 400, 600, 800, 1000 mg). Assuming the expected result is observed with POCIS configuration C, configuration A experiments should be sufficient to support a mathematical model defining the relationship between sorbent surface area coverage and sampling rate. This model could potentially be used to correct for variable sorbent settling in future lab and field experiments.

A study that mathematically defines the correlation between sampling rate and exposed PES surface area has not been reported. To address this knowledge gap, POCIS configuration A and three variants of POCIS configuration B will be evaluated with a constant amount of sorbent (200 mg). In these experiments, one variant will be identical to the configuration shown in Figure 6.1B., another will include a stainless-steel sheet on both sides (i.e., front and back) of the sampling device and a third will employ a stainless-steel

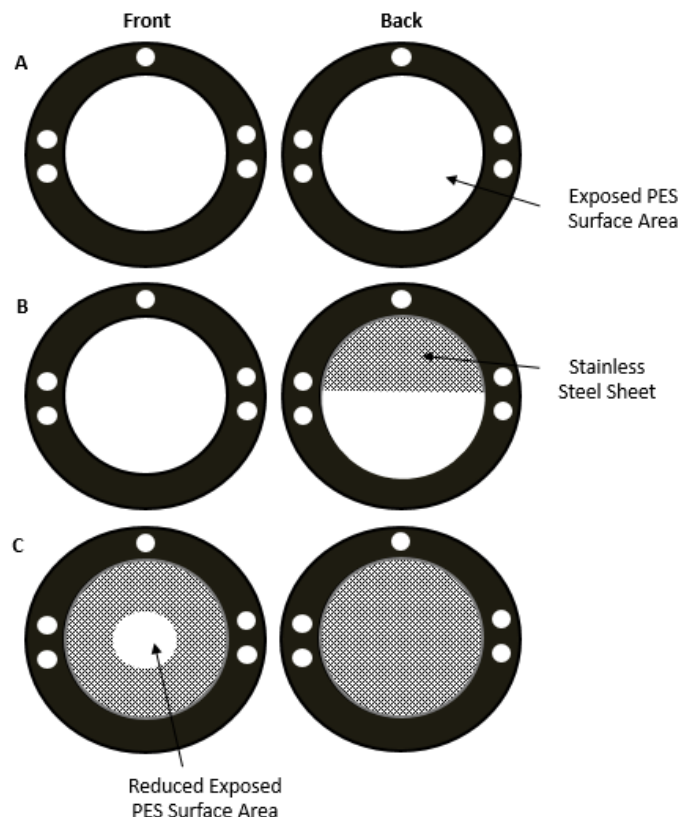


Figure 6.1. Schematic demonstrating modified POCIS configurations that vary the exposed surface of PES membranes (i.e., the “exposure window”): (A) conventional POCIS configuration with exposed PES surface area of 46 cm², (B) modified POCIS configuration with exposed PES surface area of 34 cm², (C) modified POCIS configuration with exposed PES surface area of 6 cm².

sheet that masks off a smaller fraction of exposed PES surface area than the masked area shown in Figure 6.1B. To promote constant sorbent surface area coverage for the duration of contaminant exposures, it may be necessary to pre-expose POCIS devices to water that is free of contaminants for a period ≥ 10 days; to allow time for sorbent settling to occur.

All experiments described in this section will rely on POCIS exposure to a single, constant concentration (such as 5 µg/L) for a period of 21 days. Work in Chapter 5 indicated that maximum POCIS adsorption capacity may be reached for POCIS exposure to high concentration (*i.e.*, ≥ 100 µg/L). Experiments with POCIS configuration A using

various sorbent loadings mass will be used to investigate the effect of POCIS sorbent mass on POCIS adsorption capacity. POCIS in these experiments could be exposed to low and high constant concentration (such as 5 and 200 µg/L, respectively). Temperature and flow velocity in all experiment will be held constant at 24 °C and 9 cm/s, respectively. Water will be renewed daily and POCIS devices will be removed from tanks every other day. Each experiment will be performed in triplicate to support statistical evaluations.

Can POCIS Help Understand Exposure?

Assessment of environmental exposure to a given pollutant in the aquatic system is the measurement of the magnitude, frequency and duration with which aquatic organisms interact with the biologically-available fraction of that particular pollutant. The bio-available fraction of a chemical in the aquatic system is the fraction of that chemical in water that is accessible for uptake by aquatic organisms, and include freely dissolved chemicals and chemicals bound to natural organic matter (NOM).^{149, 150} Sorption of compounds to NOM is controlled by chemical hydrophobicity (which is characterized by K_{ow} for neutral compounds), as well as chemical ionicity, with increased binding to NOM for ionized species relative to the neutral form for a given chemical.¹⁵⁰⁻¹⁵³ Thus measurements of exposure to a chemical in the aquatic system should provide a good understanding of the concentration of freely dissolved pollutants, as well as pollutants bound to NOM.

Unlike grab water sampling methods that sample chemicals that are both freely dissolve and bound to NOM, POCIS is only design to sample the freely dissolved fraction of polar organic pollutants ($\log K_{ow} < 4$). Even though polar organic pollutants bound to particulates with a lesser extent than non-polar organic pollutants, other factors such as

chemical ionicity and pH can considerably increase the proportion of polar organic chemical that binds to particulates. POCIS uptake is greatest when the amount of the neutral species in solution is maximized relative to the ionized species.^{108, 154} So, the inability of POCIS to sample NOM may be a limitation for POCIS's ability to accurately measure a pollutant's bioavailable concentration, especially for acidic and basic compounds that are predominantly ionized at environmentally relevant pH. Furthermore, although hydrophobic compound are generally defined as compound with $\log K_{ow} > 4$,^{19, 69} some studies classify compounds with $\log K_{ow}$ between 2.5 and 4.3 as slightly hydrophilic with medium sorption potential onto NOM.^{20, 155, 156}

Work on POCIS so far including the one carried out in this dissertation mainly focuses on the ability of POCIS to determine the TWAC of freely dissolved pollutants in surface water.^{30, 35, 36, 74, 75, 80} Future work should also assess the effects of chemicals sorption to NOM on POCIS ability to measure bioavailable concentration of pollutants. This will enable to evaluate the usefulness of POCIS to help understand exposure, which is a key component in risk assessment. POCIS use could then move a step forward toward a standard sampling technique for the monitoring of pollutants in water.

Experiments aiming to assess the ability of POCIS to measure bioavailable concentration of pollutants in water with a combination of a range of NOM concentration and pH are proposed herein. The working hypothesis is that polar organic pollutants sampled by POCIS also sorb to NOM. Additionally, the sorption of the pollutants to NOM significantly reduces their freely dissolved concentration. The experimental approach to test the hypothesis will rely on a series of laboratory experiments that investigate the sorption of polar organic chemicals (with a wide range of physico-chemical properties) on

a range of NOM (including DOM, colloids and particulates) under various conditions including pH, temperature and flow velocity. The laboratory experiments will be conducted to investigate the ability of POCIS to measure the bioavailable concentration of the selected chemicals under a combination of NOM concentration and pH. Temperature and flow velocity will be held constant. The diagram in Figure 7.2 summarizes the different steps of sample preparation, analysis and data interpretation. Finally, a similar study will be carried out in a monitoring site in order to evaluate the ability of POCIS to measure bioavailable concentrations of pollutants under real environmental scenario.

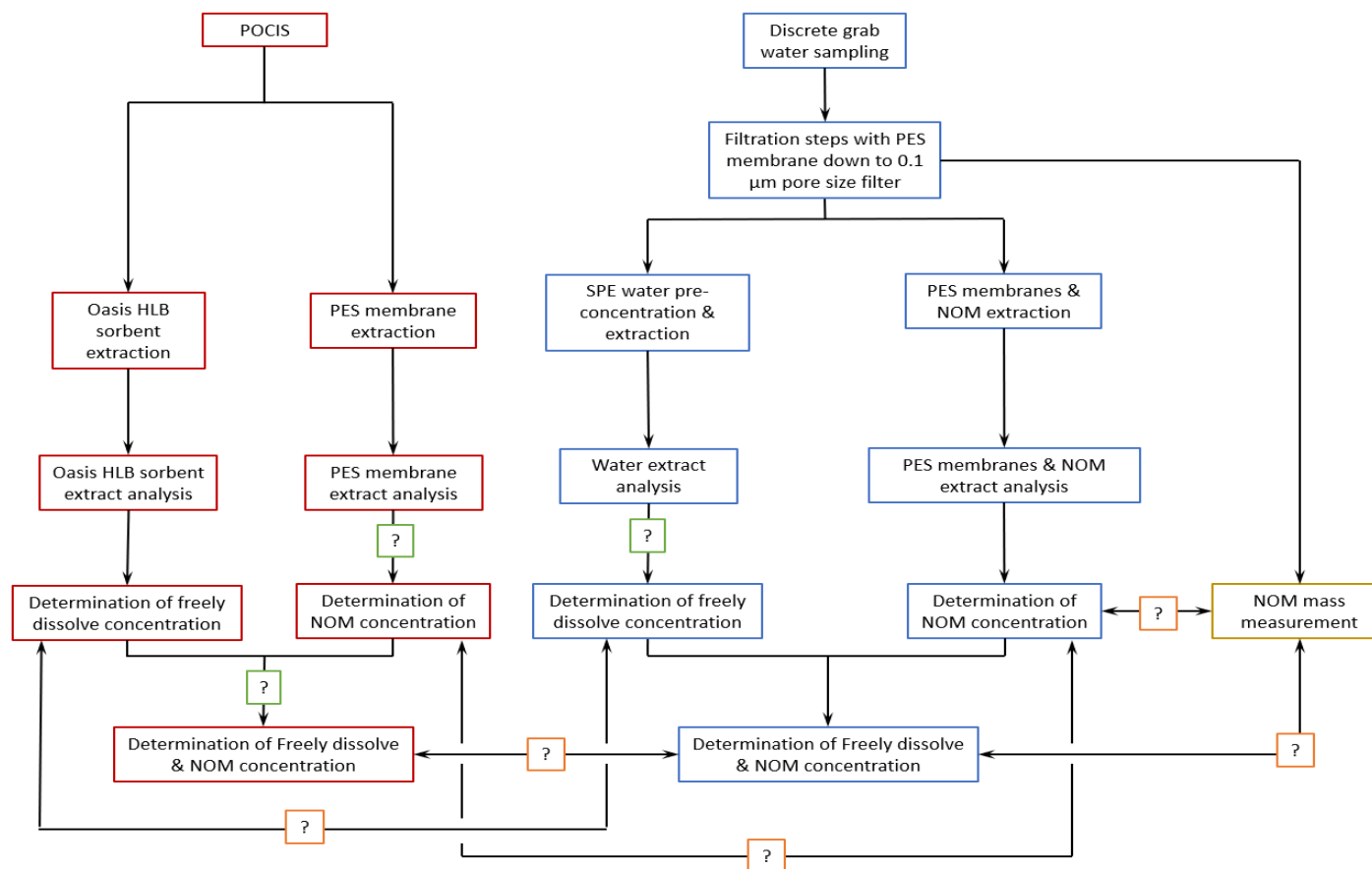


Figure 6.2. Workflow for sample preparation and analysis for the assessment of the ability of POCIS to measure bioavailable concentration of chemicals for POCIS exposure to NOM. The question marks in green boxes represent the investigation of the feasibility between the two connections in the direction of the arrow, while the question marks in orange boxes represent the investigation of the relationship between the two connections.

APPENDICES

APPENDIX A

Supplement Information for “Development of a Multiresidue UPLC-MS/MS Method for Direct Injection Analysis of 10 Pesticides in Water using Internal Standards”

Table A1. Binary steps gradient for chromatographic separation. 0.1% (v/v) aqueous formic acid (A solvent) and acetonitrile with 0.1% (v/v) formic acid (B solvent) at a flow rate of 0.7 mL/min.

Time (min)	%A	%B
0.0	95	5
0.5	95	5
1.0	60	40
1.4	60	40
1.41	46	54
2.0	46	54
2.15	5	95
2.5	5	95
3.0	95	5
5.5	95	5

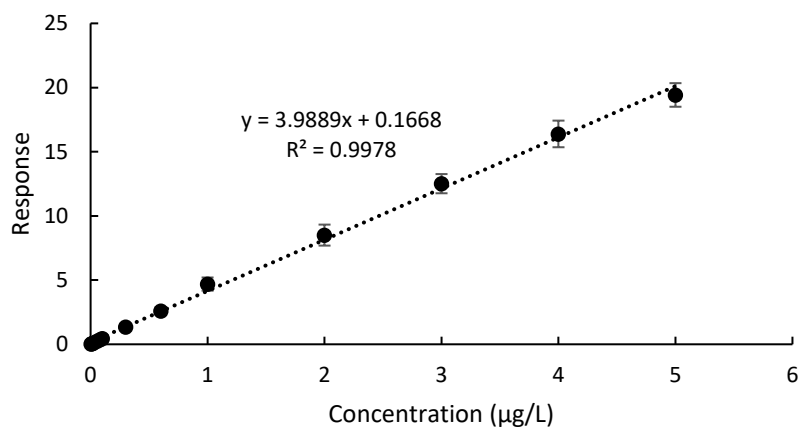


Figure A1. Internal standard calibration curve for thiamethoxam. Circles represent mean response and error bars represent ± 1 standard deviation for replicate calibrations ($n = 8$).

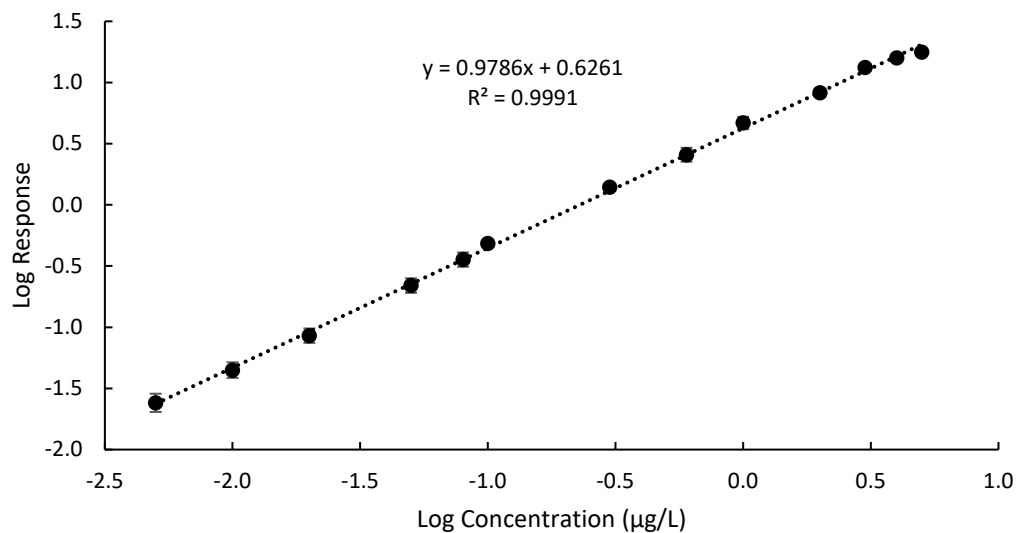


Figure A2. Logarithmic representation of calibration data shown in Figure A1. Circles represent mean response and error bars represent ± 1 standard deviation for replicate calibrations ($n = 8$).

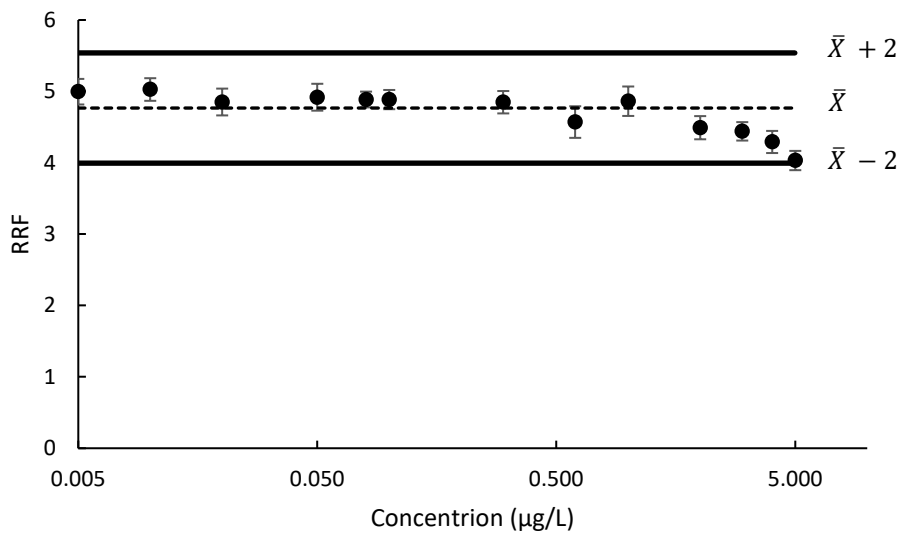


Figure A3. Representative plot of relative response factor (RRF) versus concentration for thiamethoxam. Circles represent mean RRF and error bars represent ± 1 standard deviation for replicate calibrations ($n = 8$). The dashed and the solid lines represent \bar{X} and $\bar{X} \pm 2s$ respectively, where \bar{X} is the mean RRF and s the standard deviation. Note that data for higher concentrations are clearly trending downward. In this particular instance, the highest concentration level (5 µg/L) was excluded from the reported linear range.

Table A2. Calculated Student's t-values used for statistical comparison of slopes resulting from external calibrations. Calculated Student's t-values were compared with a tabulated t-value of 2.776 for 4 degrees of freedom at 95% confidence interval.

compound	Water from North Bosque River	Water from Louisiana Stream	Water from Missouri Stream
Atrazine	2.090	2.043	4.550
Azoxystrobin	1.325	3.237	4.334
Bicyclopyrone	0.069	2.646	1.470
Cyproconazole	2.061	0.702	3.160
Fomesafen	2.269	0.244	2.518
Mesotrione	2.922	12.412	11.442
S-Metolachlor	1.711	4.099	8.376
Propiconazole	67.043	17.795	14.814
Simazine	4.864	4.484	2.707
Thiamethoxam	6.042	41.991	21.308

Table A3. Calculated Student's t-values used for statistical comparison of slopes resulting from internal standard calibrations. Calculated Student's t-values were compared with a tabulated t-value of 2.776 for 4 degrees of freedom at 95% confidence interval.

compound	Water from North Bosque River	Water from Louisiana Stream	Water from Missouri Stream
Atrazine	4.206	2.142	2.291
Azoxystrobin	1.121	2.899	3.644
Bicyclopyrone	0.313	2.497	0.733
Cyproconazole	3.412	0.002	3.429
Fomesafen	1.682	1.899	3.118
Mesotrione	4.758	8.666	7.935
S-Metolachlor	1.574	2.390	0.610
Propiconazole	1.688	0.784	3.542
Simazine	0.099	0.618	0.979
Thiamethoxam	2.301	2.660	6.580

APPENDIX B

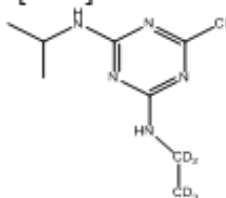
Supplement Information for “Effects of Hydrodynamic Conditions and Temperature on POCIS Sampling Rates”

UPLC-MS/MS Analysis

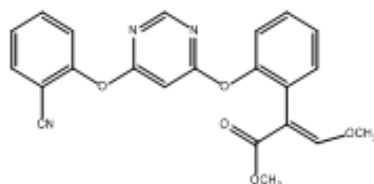
Samples were analyzed directly by UPLC with electrospray ionization and tandem mass spectrometry (UPLC-ESI-MS/MS). Chromatographic separations were performed by an Acquity UPLC system (Waters Corp.) with an Acquity UPLC BEH C18 column (2.1 x 50 mm x 1.7 μ m) connected to a VanGuard pre-column (Acquity UPLC BEH C18 2.1 x 5 mm x 1.7 μ m). Mobile phase eluent consisted of a mixture of 0.1% (v/v) aqueous formic acid (A solvent) and acetonitrile with 0.1% (v/v) formic acid (B solvent) at a flow rate of 0.7 mL/min. The binary step gradient developed for optimal separation of analytes was as follows: 0–0.5 min, 5% B; 0.5–1, 40% B; 1–1.4 min 40% B; 1.4–1.41 min 54% B; 1.41–2 min, 54% B; 2–2.15 min, 95% B; 2.15–2.5 min, 95% B; 2.5–3 min, 5% B; 3–5.5 min, 5% B. Detection of analytes was via a Xevo TQ-S mass analyzer with an ESI source used in both positive and negative mode. The mass analyzer was operated in multiple reactions monitoring (MRM) mode throughout the analysis. Mass spectrometry parameters held constant during analysis were as follows: capillary voltage = 2.00 kV; source offset = 50 V; desolvation temperature = 600 °C; desolvation gas flow = 900 L/h; Cone gas flow = 150 L/Hr; nebulizer gas flow = 7 bar; collision gas flow = argon @ 0.15 mL/min. Selected parent and product ions of target analytes are reported in Table B1. Prior to analysis, a 900- μ L aliquot of water sample or POCIS extract sample was combined with 100 μ L of an

internal standard mixture containing atrazine-d5, metolachlor-d6, simazine-d10 and thiamethoxam-d3 at a final concentration of 0.5 µg/L each. 10 µL of the resulting solution was injected onto the column. Linear calibrations for target analytes were constructed using 9 standards with concentrations extending from 0.02-5 µg/L.

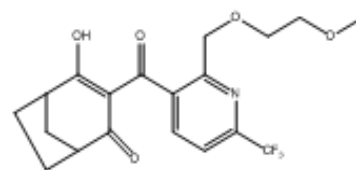
Atrazine
 $[M+H]^+ 216 > 174, 96$
Atrazine-d5
 $[M+H]^+ 221 > 179$



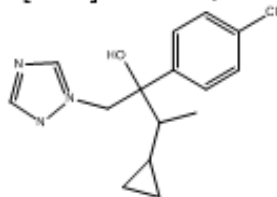
Azoxystrobin
 $[M+H]^+ 404 > 329, 372$



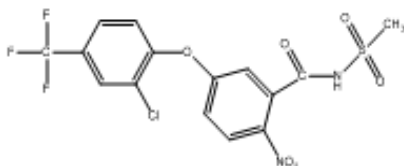
Bicyclopyrone
 $[M+H]^+ 400 > 324, 228$



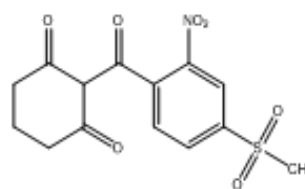
Cyproconazole
 $[M+H]^+ 292 > 70, 125$



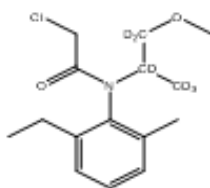
Fomesafen
 $[M-H]^- 437 > 195, 222$



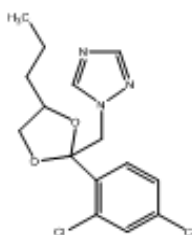
Mesotrione
 $[M-H]^- 338 > 290, 212$



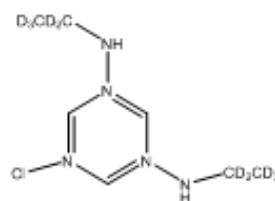
S-metolachlor
 $[M+H]^+ 284 > 252, 176$
Metolachlor-d6
 $[M+H]^+ 290 > 258$



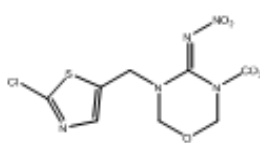
Propiconazole
 $[M+H]^+ 342 > 159, 69$



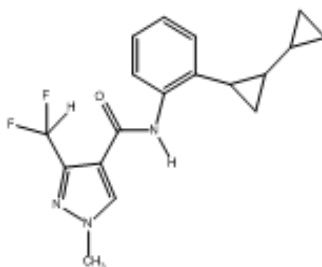
Simazine
 $[M+H]^+ 202 > 124, 132$
Simazine-d10
 $[M+H]^+ 212 > 134$



Thiamethoxam
 $[M+H]^+ 292 > 211, 181$
Thiamethoxam-d3
 $[M+H]^+ 295 > 214$



Sedaxane
 $[M+H]^+ 332 > 159$



Solatenol
 $[M-H]^- 396 > 368$

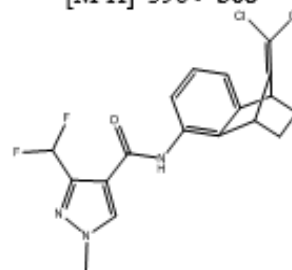


Figure B1. Common name, optimized MS/MS transitions ($[M \pm H]^{+/-}$ -precursor ion > quantification ion, qualifier ion, where $[M + H]^+$ and $[M - H]^-$ represent protonated and deprotonated molecular ion respectively) and chemical structure of monitored analytes. Deuterium positions are shown on analytes for isotopically-labeled internal standards

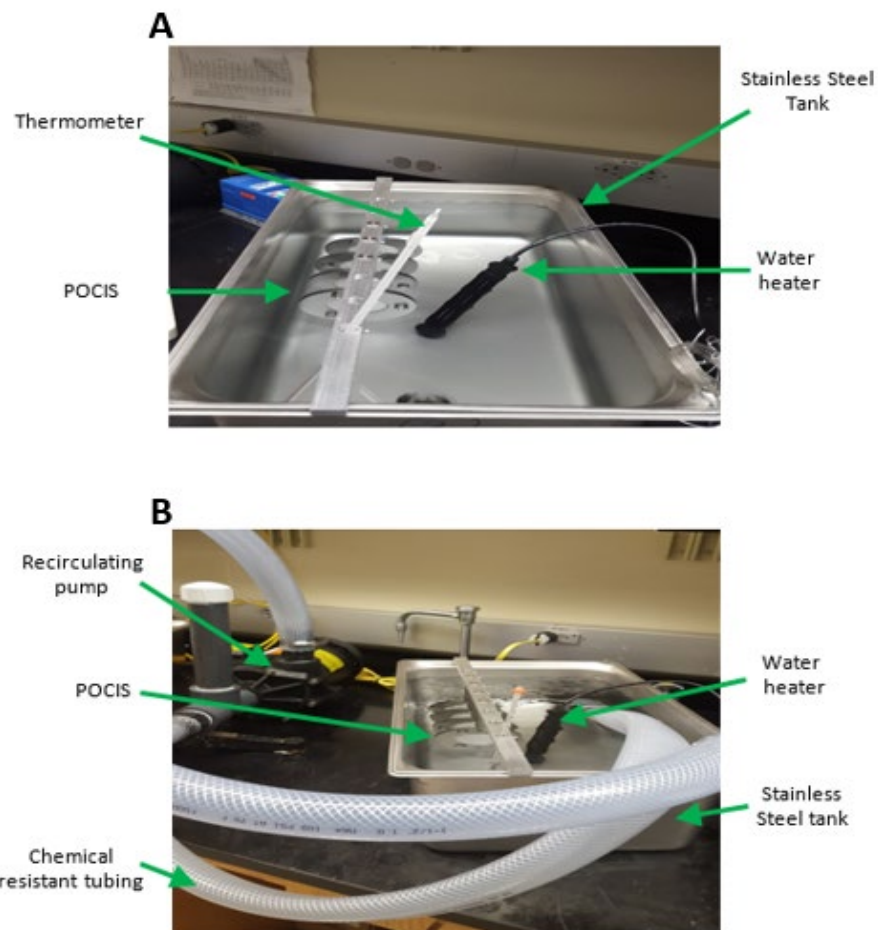


Figure B2. Pictures of experimental set up under stagnant (A) and flow (B) conditions.

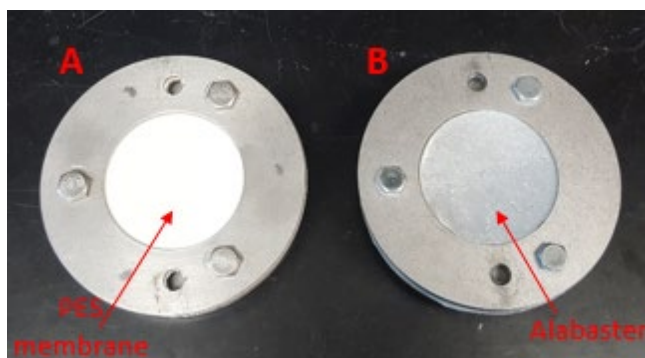


Figure B3. Photograph demonstrating identical geometry and surface area of POCIS (A) and alabaster sensor plate (B).

Estimating Flow Velocities from Alabaster Dissolution Rates

Alabaster is a natural deposit of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The mass loss (Δm) of an alabaster plate in that is exposed to a water mass with volume V is governed by Booij et al.⁸⁶

$$\Delta m = VC_w^* \left[1 - \exp\left(-\frac{k_w A t}{V}\right) \right]$$

where C_w^* is the alabaster solubility in the exposure medium, A is the surface area, k_w is the mass transfer coefficient of the water boundary layer and t is time. The k_w can therefore be calculated from

$$k_w = -\frac{V}{At} \ln\left(1 - \frac{\Delta m}{VC_w^*}\right)$$

The model that is used for estimating C_w^* of pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is described in detail by O'Brien et al.¹⁵⁷ These authors also provide calculation examples for applying their C_w^* model. The following characteristics of the exposure water are required for the exposure medium:

- background ionic strength
- background concentrations of calcium and sulfate
- temperature
- density

In the present study, experiments were carried out in deionized water and the rate of mass loss (Δm) was determined without refreshing the water between replicates. Thus, the initial ionic strength and background concentrations of calcium and sulfate were zero. A representative calculation of flow rate is detailed below for the highest flow setting. In the first replicate the mass loss was 0.2034 g in 20 min. The temperature was 25 °C. The water volume was 20.0 L. The solubility of pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was calculated as

0.0149 mol per kg water, following the method outlined by O'Brien et al.¹⁵⁷ The ratio of measured solubility of alabaster relative to calculated solubility of pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is 1.028.⁸⁶ Thus, alabaster solubility equaled $0.0149 \times 1.028 = 0.0153$ mol per kg water. Water density was obtained from Jones and Harris (1992):¹⁵⁸ 0.997 kg L^{-1} , yielding an alabaster solubility of $0.0153 \text{ mol L}^{-1} = 2.64 \text{ g L}^{-1}$.

$$k_w = -\frac{20.0 \text{ L}}{0.458 \text{ dm}^2 \times 20 \text{ min}} \ln \left(1 - \frac{0.2034 \text{ g}}{20.0 \text{ L} \times 2.64 \text{ g L}^{-1}} \right) = 0.00846 \text{ dm min}^{-1}$$

$$= 14.1 \mu\text{m s}^{-1}$$

In the second replicate the mass loss was 0.2469 g in 25 min, determined at a water temperature of 26°C . The initial concentrations of calcium and sulfate were obtained from the mass loss of the first replicate: $0.2034 \text{ g} \div (172.17 \text{ g mol}^{-1}) \div (20.0 \text{ L}) = 0.00006 \text{ mol L}^{-1}$. The initial ionic strength was therefore $0.00024 \text{ mol L}^{-1}$. The solubility of alabaster for this replicate was again 2.64 g L^{-1} , and $k_w = 13.7 \mu\text{m s}^{-1}$.

In the third replicate the mass loss was 0.2028 g in 20 min, determined at a water temperature of 26°C . This initial concentrations of calcium and sulfate were obtained from the mass loss of the first and second replicate: $(0.2034 \text{ g} + 0.2469 \text{ g}) \div (172.17 \text{ g mol}^{-1}) \div (20.0 \text{ L}) = 0.00013 \text{ mol L}^{-1}$. The initial ionic strength was therefore $0.00052 \text{ mol L}^{-1}$. The solubility of alabaster for this replicate was 2.62 g L^{-1} , and $k_w = 14.1 \mu\text{m s}^{-1}$.

Effective flow velocities were estimated from equation 6 of the main text

$$U = 8.87 \frac{\nu}{L} \left[\left(\frac{k_w L}{D_w} \right)^3 \left(\frac{D_w}{\nu} \right) \right]^{5/9}$$

The average k_w ($13.9 \mu\text{m s}^{-1}$), a diffusion coefficient of $8.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$,⁹⁰ and a kinematic viscosity of $0.87 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ were adopted. The effective length of the flow lines along the alabaster surface was taken to be 4.2 cm (one-sided area divided by the diameter). The dimensionless group $k_w L / D_w$ equals 671, and $v / D_w = 1000$.

The estimated flow velocity equals

$$U = 8.87 \frac{0.87 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}}{0.042 \text{ m}} [673^3 \times 0.001]^{5/9} = 0.205 \text{ m s}^{-1} = 20.5 \text{ cm s}^{-1}$$

Table B1. Mass transfer coefficient (k_w) and kinematic viscosity of water (v) used to calculate flow velocity.

Pumping Rate (L/min)	Temp (°C)	k_w (m/s)	v (m ² /s)
23	22.0	6.4E-06	9.6E-07
	23.0	6.78E-06	9.3E-07
	24.0	6.81E-06	9.1E-07
45	23.0	9.13E-06	9.3E-07
	25.5	8.71E-06	8.8E-07
	25.0	8.56E-06	8.9E-07
	25.0	1.17E-05	8.9E-07
68	25.0	1.09E-05	8.9E-07
	25.0	1.19E-05	8.9E-07
	23.0	1.13E-05	9.3E-07
	23.0	1.08E-05	9.3E-07
	23.0	1.15E-05	9.3E-07
91	24.0	1.32E-05	9.1E-07
	24.0	1.22E-05	9.1E-07
	22.0	1.43E-05	9.6E-07
	25.0	1.41E-05	8.9E-07
114	26.0	1.37E-05	8.7E-07
	26.0	1.41E-05	8.7E-07

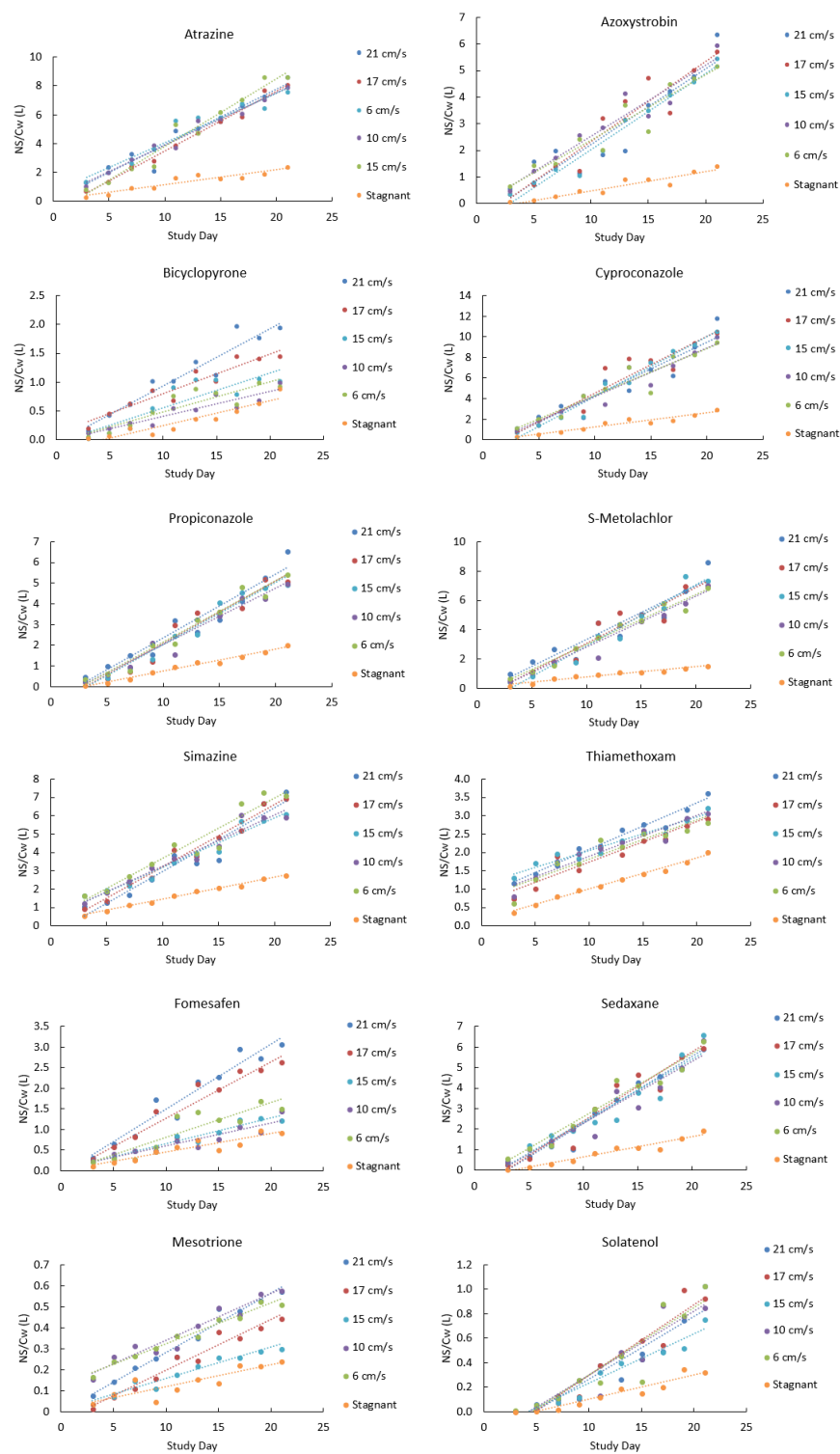


Figure B4. POCIS uptake under stagnant and flow (6, 10, 15, 17, and 21 cm/s) conditions

Table B2. POCIS sampling rates and lag phases under various hydrodynamic conditions.
Temperature was held constant at 33 °C

Compound	Stagnant		6.2 (cm/s)		9.7 (cm/s)		15.0 (cm/s)		17.0 (cm/s)		20.5 (cm/s)	
	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)
Atrazine	0.11	-	0.47	-	0.36	-	0.34	1.9	0.41	-	0.39	-
Azoxystrobin	0.07	3.3	0.29	0.4	0.27	0.5	0.25	-	0.30	2.3	0.28	2.2
Bicyclopyrone	0.043	-	0.05	0.6	0.043	0.6	0.06	0.8	0.069	-	0.10	0.8
Cyproconazole	0.14	1.0	0.58	0.5	0.47	1.2	0.46	-	0.55	1.7	0.52	1.7
Fomesafen	0.04	0.004	0.06	0.4	0.05	-	0.08	-	0.14	0.6	0.16	0.6
Mesotrione	0.010	-	0.015	-	0.022	-	0.019	-	0.024	2.0	0.028	0.1
S-Metolachlor	0.069	-	0.42	1.2	0.35	1.9	0.34	-	0.38	2.0	0.37	0.9
Propiconazole	0.11	-	0.30	-	0.27	-	0.30	-	0.30	-	0.31	2.4
Sedaxane	0.098	-	0.31	1.5	0.30	2.4	0.31	2.3	0.34	-	0.33	-
Simazine	0.122	-	0.27	-	0.28	-	0.33	-	0.34	0.6	0.35	1.5
Solatenol	0.020	-	0.040	4.7	0.052	-	0.055	-	0.057	-	0.051	-
Thiamethoxam	0.08	-	0.10	-	0.11	-	0.11	-	0.11	-	0.13	-

The number of significant digits reported for a given value was dictated by the standard deviation of the slope for a given least squares regression.

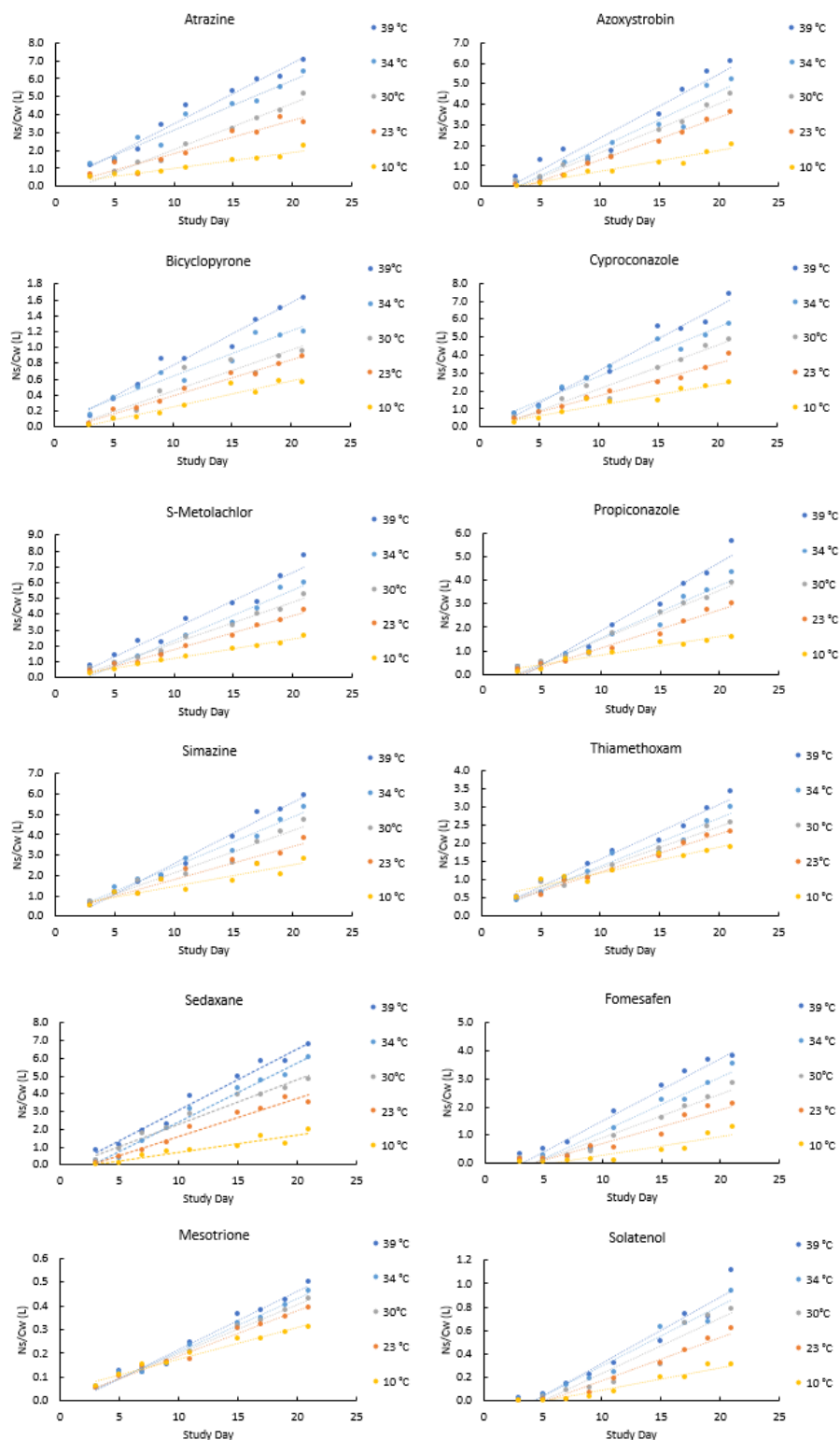


Figure B5 continued. POCIS uptake at temperature of 10, 23, 30, 34 and 39 °C. Flow rate was maintained constant at 9.7 cm/s.

Table B3. Sampling rate values and lag phases under flow condition (9.7 cm/s) for different temperatures.

Compound	10 °C		23 °C		30 °C		34 °C		39 °C	
	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)
Atrazine	0.088	-	0.18	0.2	0.25	-	0.28	-	0.34	-
Azoxystrobin	0.10	2.9	0.206	-	0.24	-	0.27	-	0.32	2.5
Bicyclopyrone	0.033	2.4	0.045	1.3	0.052	1.4	0.058	0.9	0.079	0.3
Cyproconazole	0.12	-	0.18	0.7	0.25	1.4	0.27	-	0.36	1.4
Fomesafen	0.07	5.1	0.12	-	0.16	-	0.19	-	0.22	-
Mesotrione	0.013	-	0.019	-	0.021	0.3	0.022	0.7	0.025	1.1
S-Metolachlor	0.124	0.5	0.21	-	0.26	-	0.31	-	0.36	1.3
Propiconazole	0.08	-	0.16	-	0.21	-	0.22	-	0.29	-
Sedaxane	0.09	2.6	0.22	-	0.25	0.8	0.33	-	0.35	1.1
Simazine	0.11	-	0.16	-	0.21	0.1	0.24	0.04	0.30	-
Solatenol	0.019	-	0.037	-	0.047	-	0.051	-	0.056	-
Thiamethoxam	0.07	-	0.10	-	0.12	-	0.13	-	0.15	-

The number of significant digits reported for a given value was dictated by the standard deviation of the slope for a given least squares regression.

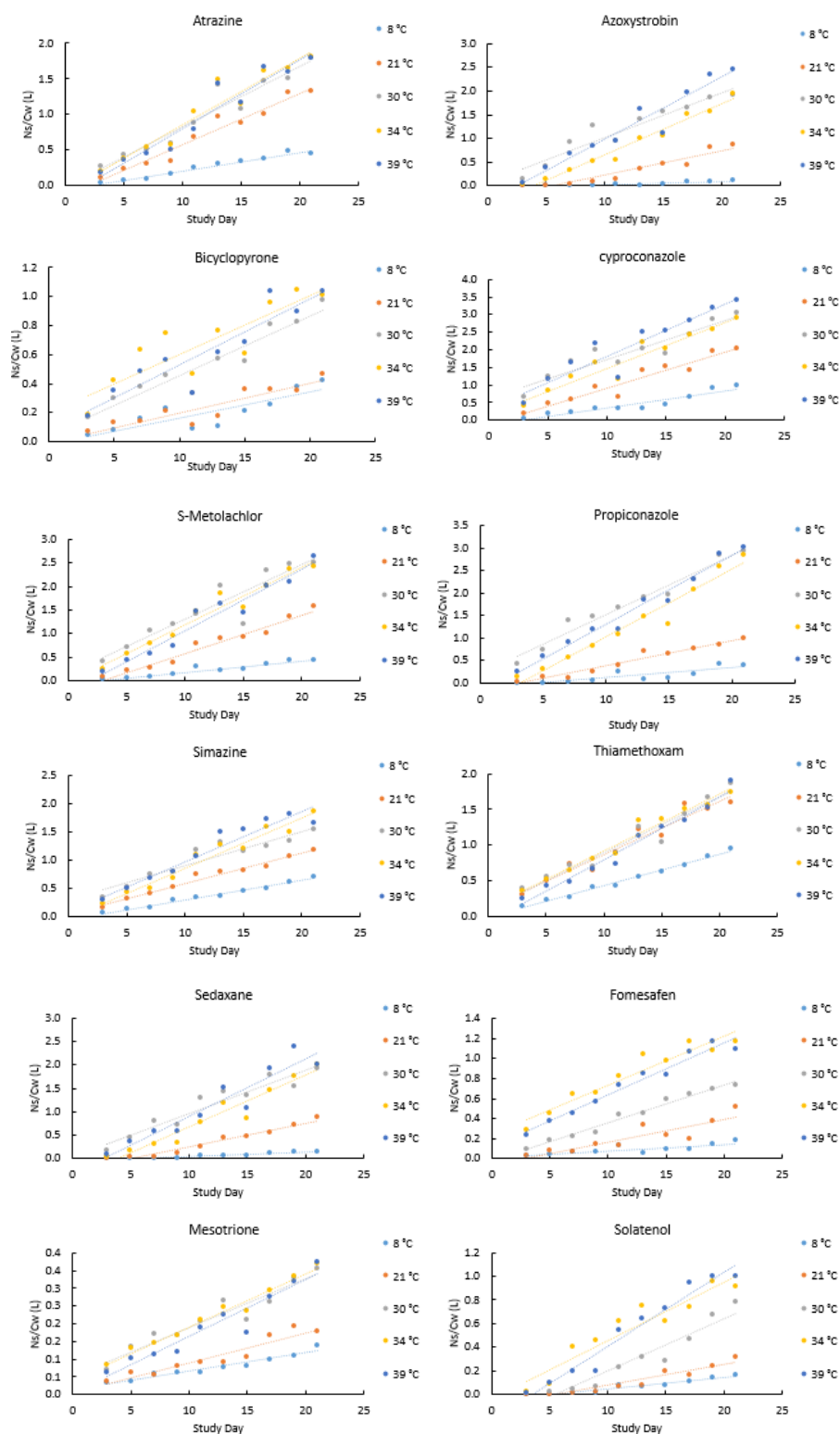


Figure B6 continued. POCIS uptake under stagnant condition at temperature of 8, 21, 30, 34 and 39 °C.

Table B4. Sampling rates values and lag phases under stagnant condition for different temperatures.

Compound	8 °C		21 °C		30 °C		34 °C		39 °C	
	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)	R_s (L/day)	Lag phase (day)
Atrazine	0.026	-	0.072	2.0	0.085	0.3	0.093	0.8	0.10	1.6
Azoxystrobin	0.006	-	0.051	-	0.09	-	0.107	-	0.13	2.5
Bicyclopyrone	0.018	0.8	0.021	0.3	0.041	-	0.040	-	0.045	-
Cyproconazole	0.048	2.9	0.10	1.1	0.11	-	0.13	-	0.15	-
Fomesafen	0.007	-	0.023	2.6	0.038	0.6	0.049	-	0.052	-
Mesotrione	0.005	-	0.009	-	0.014	-	0.015	-	0.016	-
S-Metolachlor	0.025	2.8	0.081	-	0.12	-	0.123	0.4	0.13	1.8
Propiconazole	0.022	5.0	0.056	-	0.132	-	0.151	-	0.153	1.5
Sedaxane	0.010	-	0.050	-	0.09	-	0.11	-	0.12	2.6
Simazine	0.034	1.2	0.054	-	0.061	-	0.089	0.3	0.089	-
Solatenol	0.009	-	0.017	-	0.044	-	0.049	0.7	0.063	-
Thiamethoxam	0.044	0.8	0.075	-	0.079	-	0.079	-	0.088	1.0

The number of significant digits reported for a given value was dictated by the standard deviation of the slope for a given least squares regression.

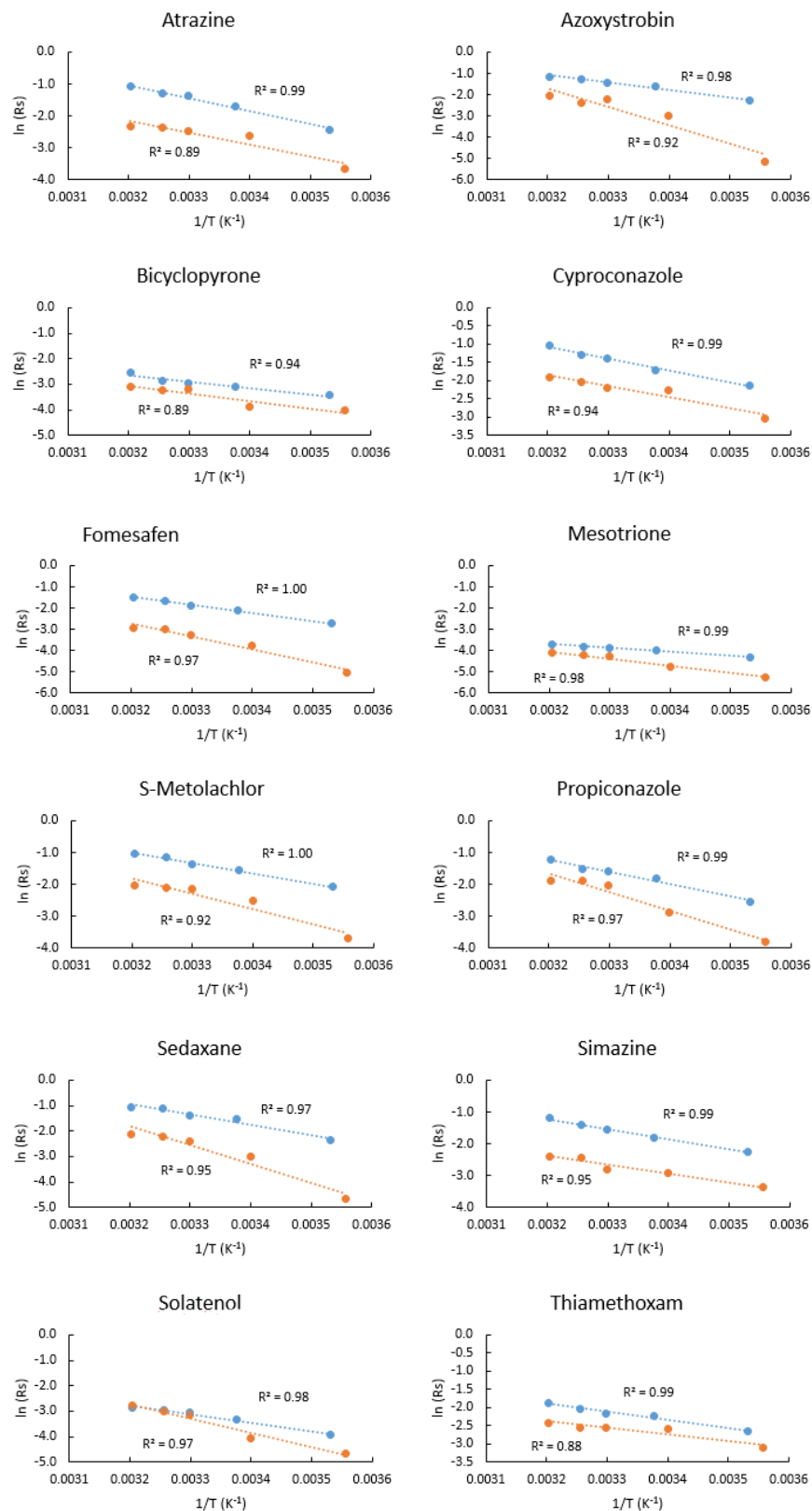


Figure B7 continued. Arrhenius plots under stagnant and flow conditions for temperature ranging between 8 to 39 °C (281.2 to 312.2 K).

Table B5. Average water temperature, temperature corrected sampling rates and time weighted average concentration calculated from ISCO and POCIS.

Site ID	Temperature \pm s ($^{\circ}$ C)	R_s (mL/day)	C_w ISCO (μ g/L)	C_w POCIS (μ g/L)
1.1	15 \pm 2	118	4.01	7.98
1.2	17 \pm 3	133	5.87	5.81
1.3	24 \pm 2	178	1.43	1.37
1.4	24 \pm 2	179	2.72	3.15
1.5	24.8 \pm 0.9	189	1.62	1.22
2.1	14 \pm 2	114	5.07	10.59
2.2	16 \pm 2	122	21.49	29.14
2.3	21 \pm 2	160	1.56	1.69
2.4	23 \pm 2	173	0.62	0.31
2.5	24.2 \pm 0.8	183	0.37	0.03
3.1	22 \pm 2	166	13.91	37.78
3.2	24 \pm 2	178	8.12	6.95
3.3	27 \pm 2	211	0.91	0.93
3.4	28 \pm 1	223	0.22	0.17
4.1	15 \pm 2	121	3.53	7.05
4.2	17 \pm 3	129	15.77	17.23
4.3	23 \pm 2	175	3.74	3.00
4.4	24 \pm 2	178	1.72	1.52
4.5	25 \pm 1	187	0.52	0.11
5.1	16 \pm 1	127	13.92	20.21
5.2	17 \pm 2	132	32.03	29.86
5.3	22 \pm 2	165	2.58	3.25
5.4	23 \pm 2	172	1.06	1.05
5.5	24 \pm 1	183	0.49	0.16
6.1	16 \pm 2	125	4.01	8.41
6.2	18 \pm 2	138	9.97	10.02
6.3	24 \pm 1	178	2.83	2.83
6.4	23 \pm 2	176	0.86	0.88
6.5	25 \pm 1	191	0.50	0.13
7.1	17 \pm 2	131	52.60	73.75
7.2	18 \pm 3	135	9.30	16.76
7.3	24 \pm 2	183	1.46	1.72
7.4	24 \pm 3	182	0.66	0.87
7.5	26 \pm 1	196	0.56	0.48
8.1	18 \pm 2	134	0.51	0.36
8.2	23 \pm 1	175	0.50	0.46
8.3	23 \pm 2	170	0.17	0.35
8.4	23 \pm 1	176	0.09	0.03
9.1	14 \pm 3	114	4.84	4.73
9.2	18 \pm 2	139	0.36	0.19
9.3	21 \pm 2	161	6.73	3.01
9.4	21 \pm 2	158	0.35	0.07
9.5	25 \pm 1	186	6.32	4.66

Supplement Information for “The Effects of POCIS Exposure to Sediment on Pesticides
Sampling Rates”

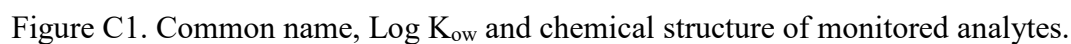


Table C1. Evaluation of sediment adsorption of target compounds. Water concentration at various time points

Compound	0 h ($\mu\text{g/L}$)	3.5 h ($\mu\text{g/L}$)	7 h ($\mu\text{g/L}$)	24 h ($\mu\text{g/L}$)	72 h ($\mu\text{g/L}$)	Mean ($\mu\text{g/L}$)
Thiamethoxam	4.88	4.61	4.77	4.80	4.62	4.7 ± 0.1
Mesotrione	4.89	5.20	5.58	5.46	5.15	5.3 ± 0.3
Bicyclopyrone	5.46	5.24	5.25	5.17	5.55	5.3 ± 0.2
Simazine	4.91	4.52	4.23	4.80	4.95	4.7 ± 0.3
Azoxystrobin	4.57	4.51	4.39	4.54	4.52	4.51 ± 0.07
Atrazine	5.33	5.01	5.24	5.17	5.20	5.2 ± 0.1
Cyproconazole	4.92	4.75	4.85	4.80	4.92	4.85 ± 0.07
Fomesafen	5.15	5.17	5.54	5.25	5.41	5.3 ± 0.2
S-Metolachlor	4.53	4.61	4.54	4.44	4.70	4.6 ± 0.1
Sedaxane	4.77	4.59	4.50	4.61	4.50	4.6 ± 0.1
Propiconazole	5.01	4.96	4.98	4.99	4.80	4.95 ± 0.08
Solatenol	4.67	4.65	4.69	4.78	4.89	4.7 ± 0.1

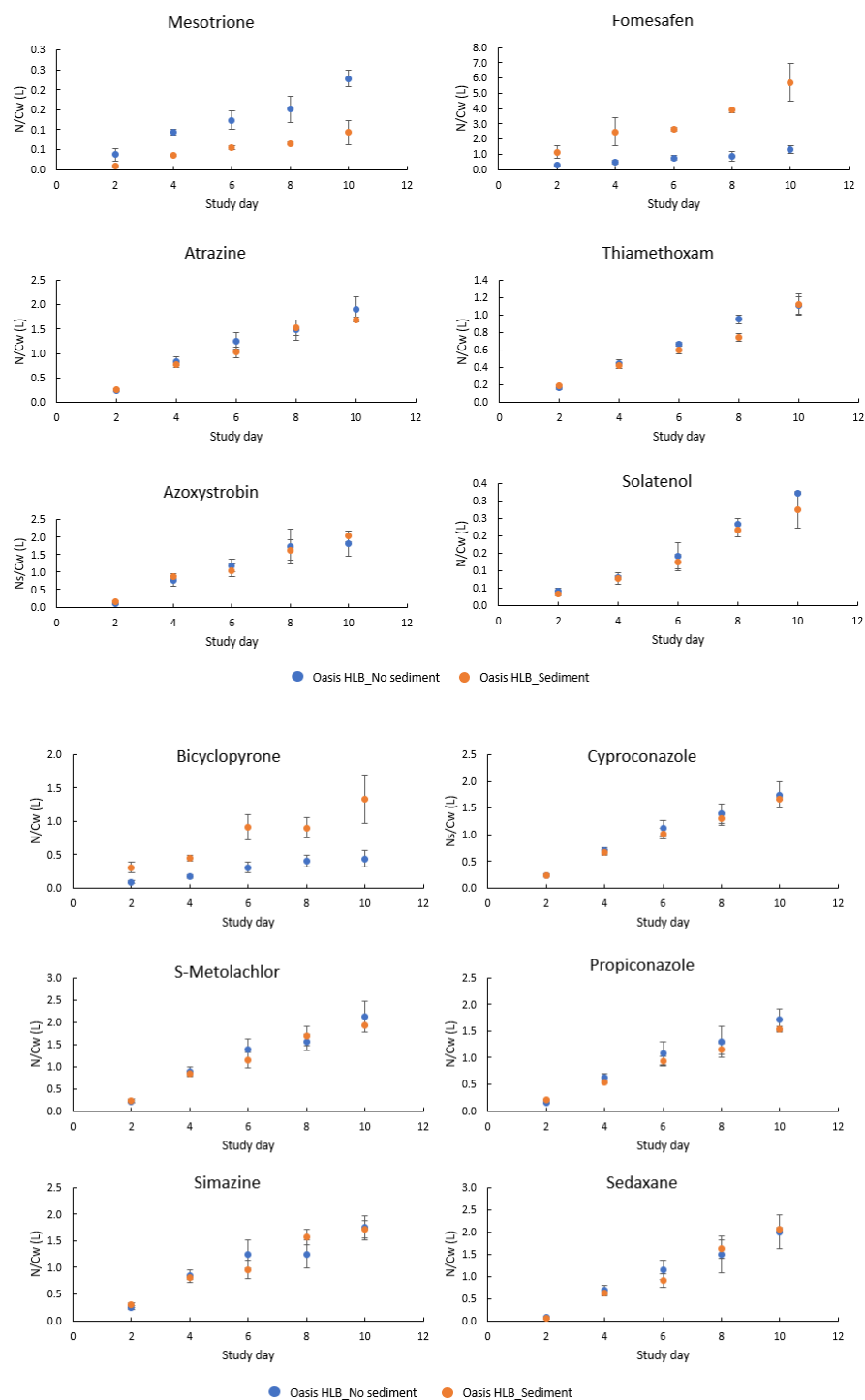


Figure C2. Oasis HLB sorbent uptakes for control water (blue) and water with 3600 ppm TSS sediment concentration (orange). The error bars represent one standard deviation from replicate tanks (n = 3).

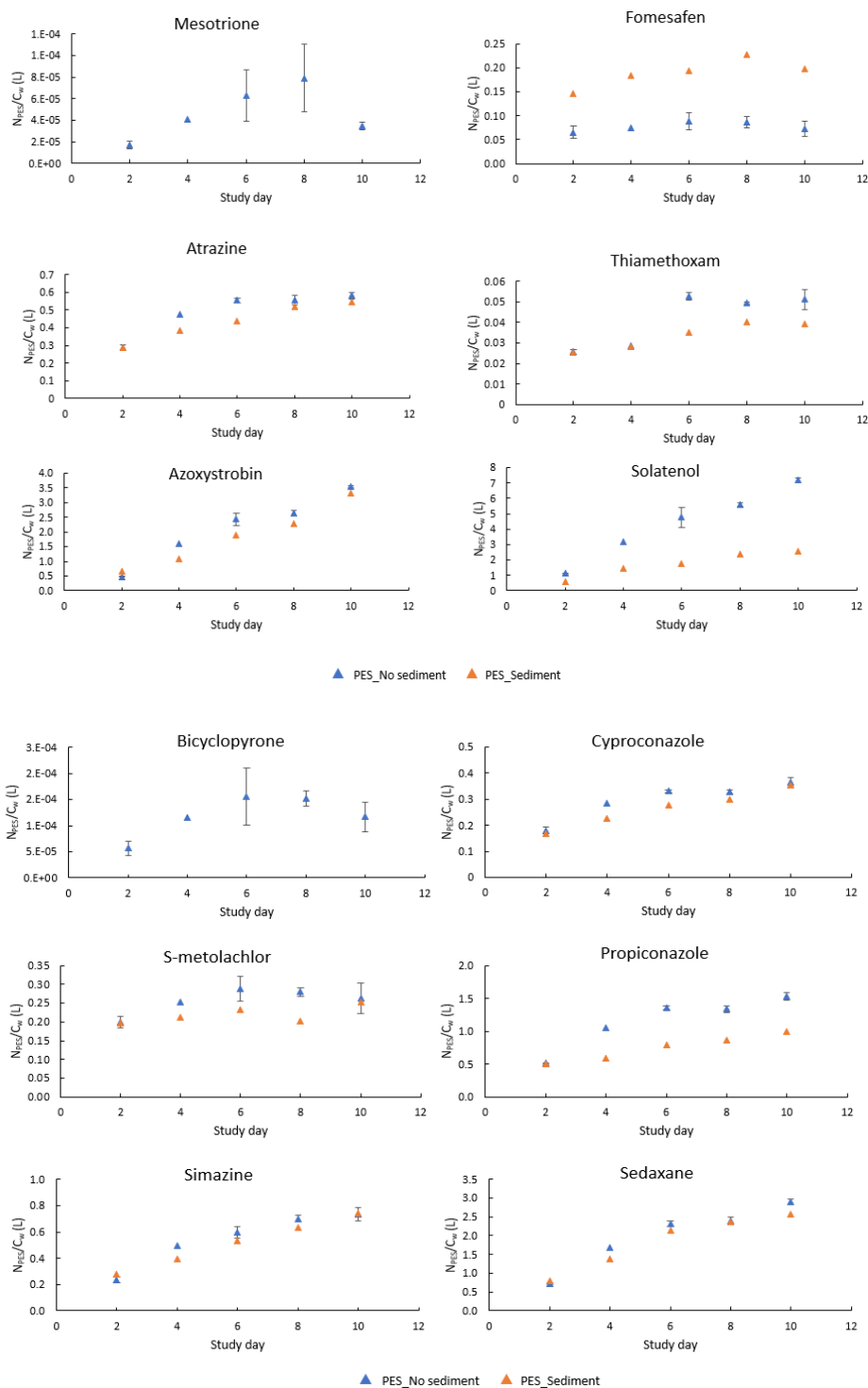


Figure C3. PES uptakes for control water (blue) and water with 3600 ppm TSS sediment concentration (orange). The error bars represent one standard deviation from replicate tanks (n = 3).

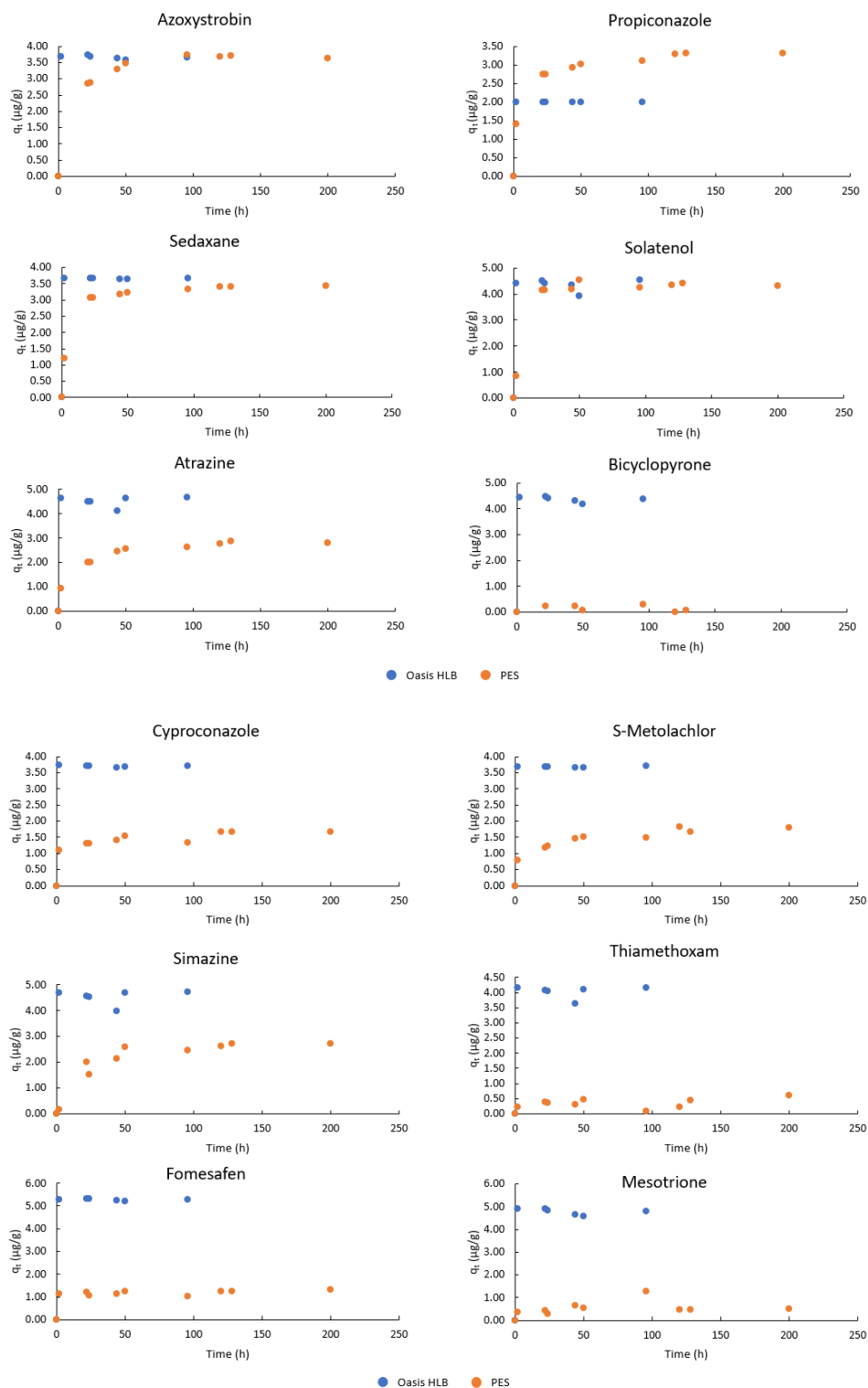


Figure C4. Oasis HLB (blue) and PES membrane (orange) Kinetic isotherm plots in water. Temperature was held constant at 24 °C.

APPENDIX D

Supplement Information for “Effects of Concentration Exposure on POCIS Sampling Rates”

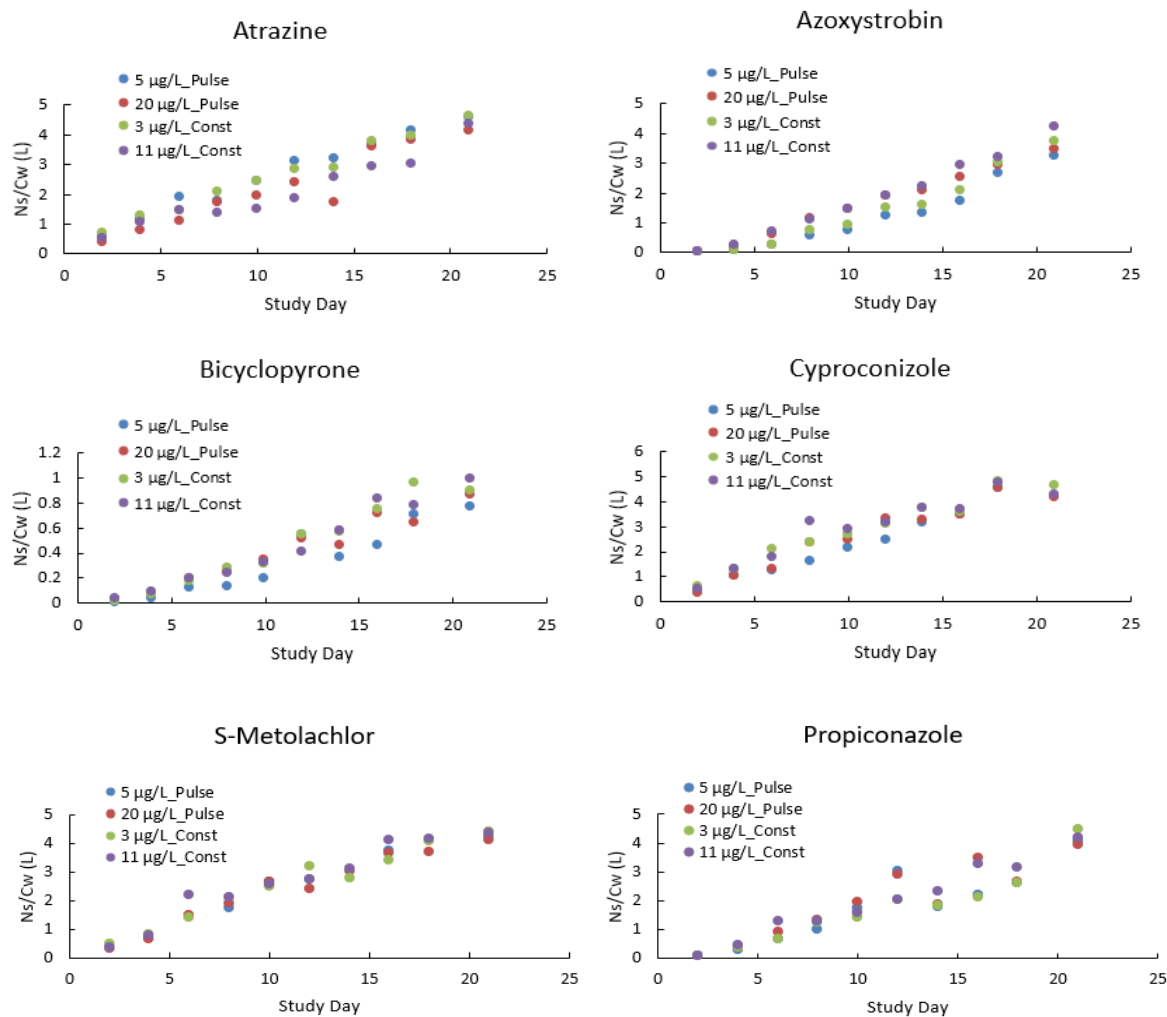


Figure D1. POCIS uptake for multiple pulses concentration with peak height of 5 and 20 µg/L, and corresponding time-weighted average constant concentration of 3 and 11 µg/L. The temperature and the flow velocity were held constant at 23 ± 2 °C and 10 cm/s, respectively.

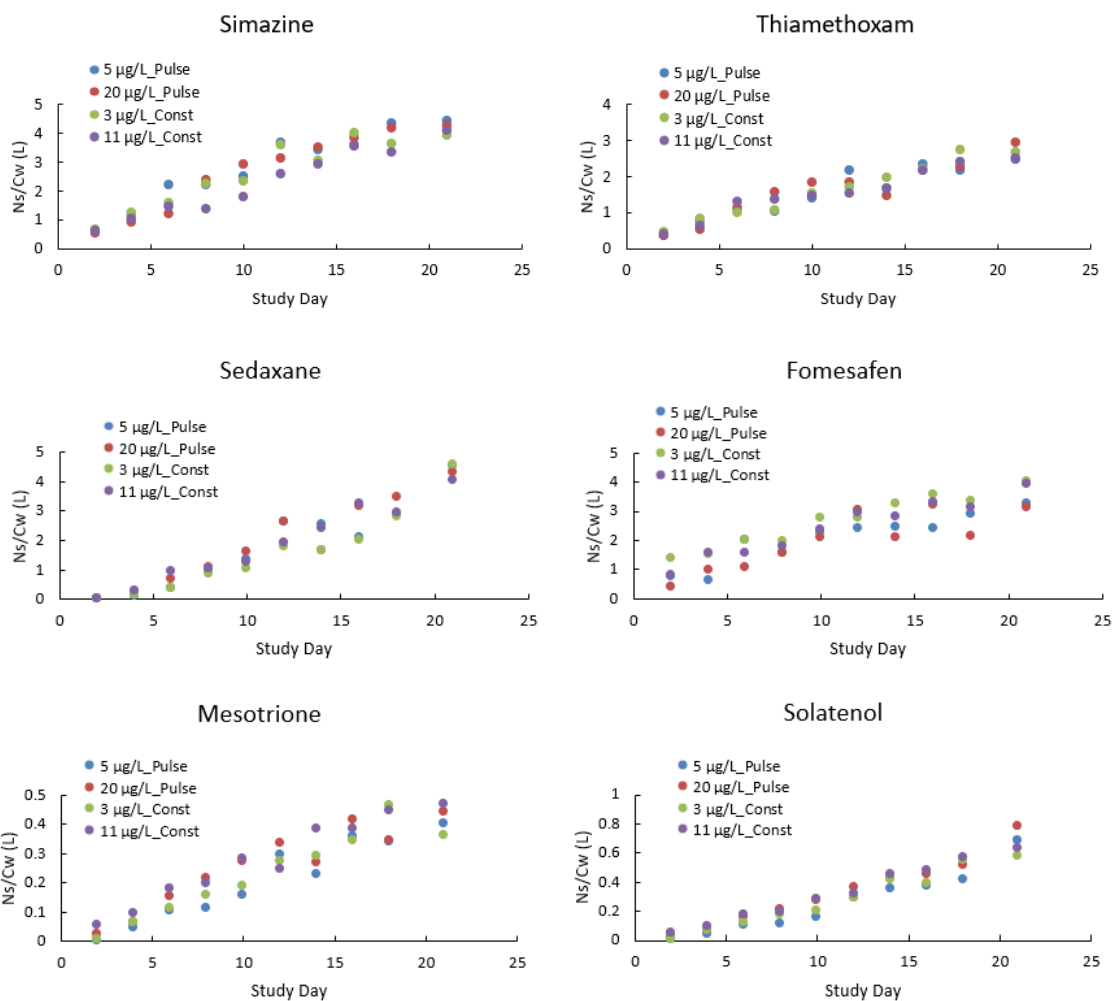


Figure D1continued. POCIS uptake for multiple pulses concentration with peak height of 5 and 20 µg/L, and corresponding time weighted average constant concentration of 3 and 11 µg/L. The temperature and the flow velocity were held constant at 23 ± 2 °C and 10 cm/s, respectively.

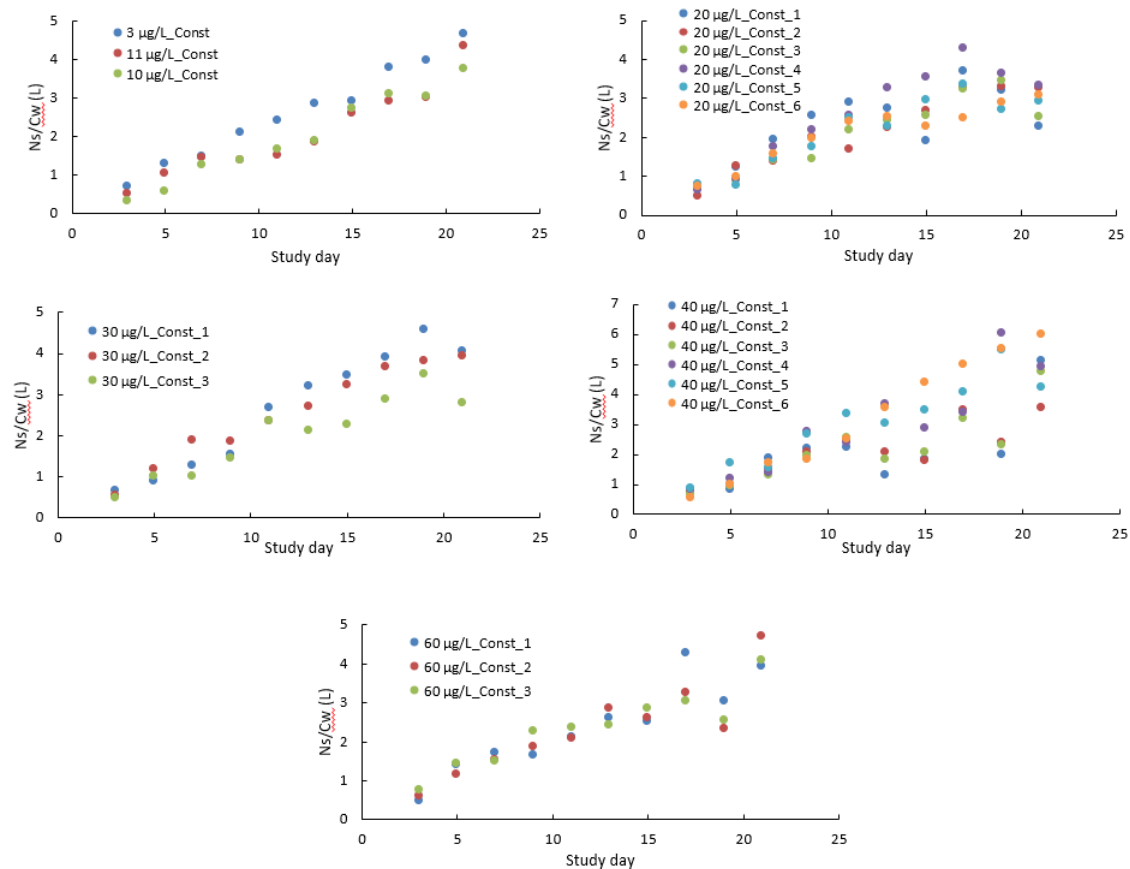


Figure D2. Atrazine POCIS uptake for constant concentration exposures ranging from 3 to 60 $\mu\text{g/L}$. The temperature and the flow velocity were held constant at 23 ± 2 $^{\circ}\text{C}$ and 10 cm/s , respectively.

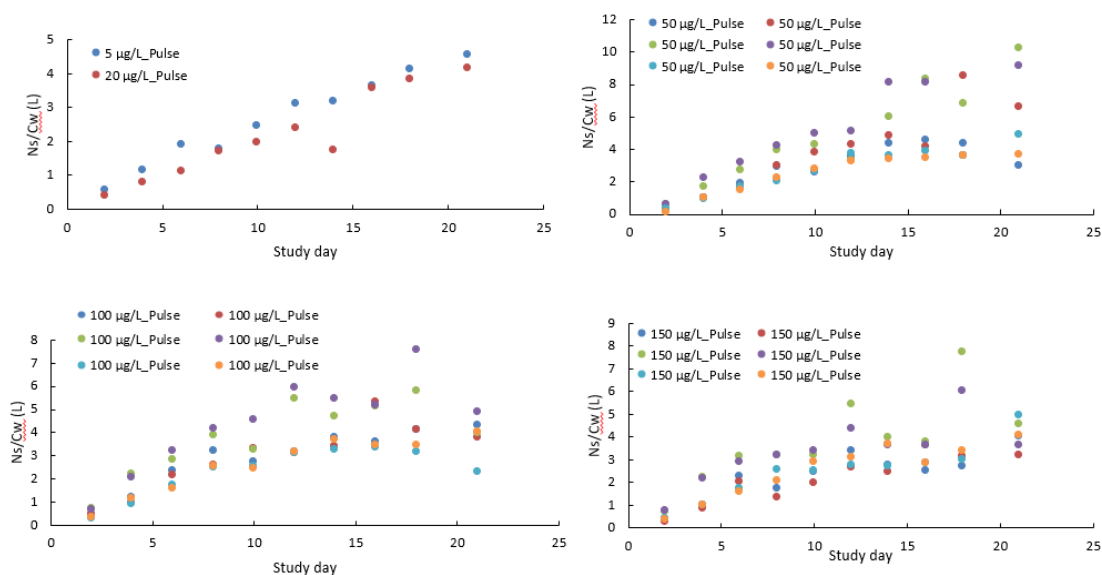


Figure D3. Atrazine POCIS uptake for multiple pulses concentration exposures with peak height ranging from 5 to 150 µg/L. The temperature and the flow velocity were held constant at 23 ± 2 °C and 10 cm/s, respectively.

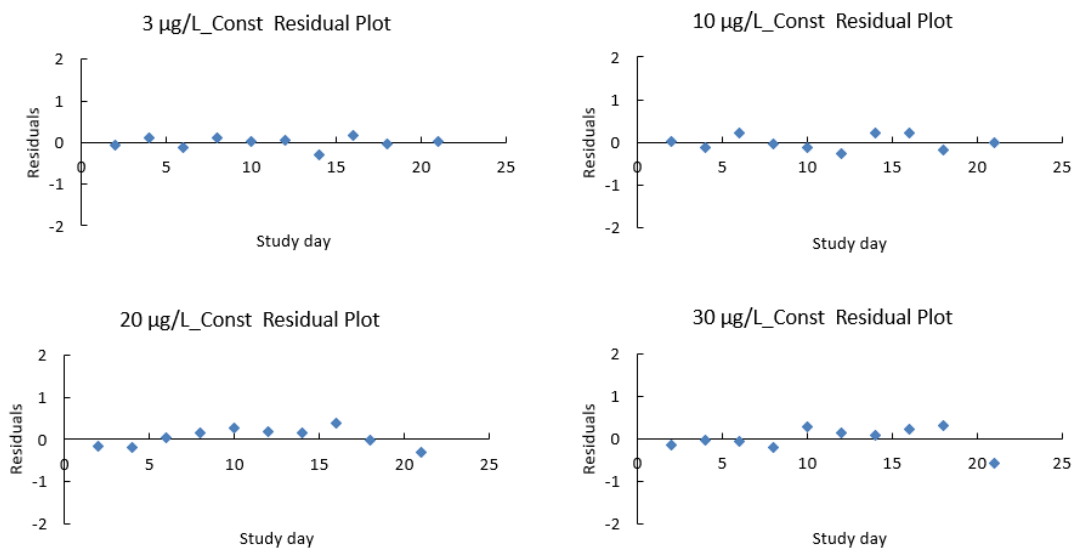


Figure D4. Atrazine POCIS uptake residual plots for constant and multiple pulses concentration exposures.

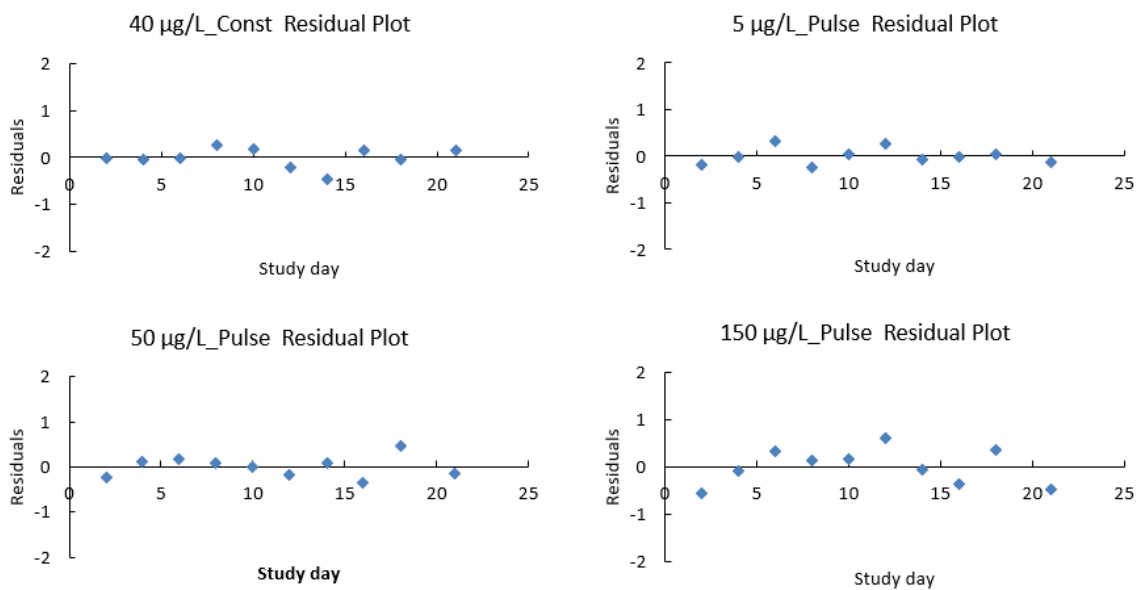


Figure D4 Continued. Atrazine POCIS uptake residual plots for constant and multiple pulses concentration exposures.

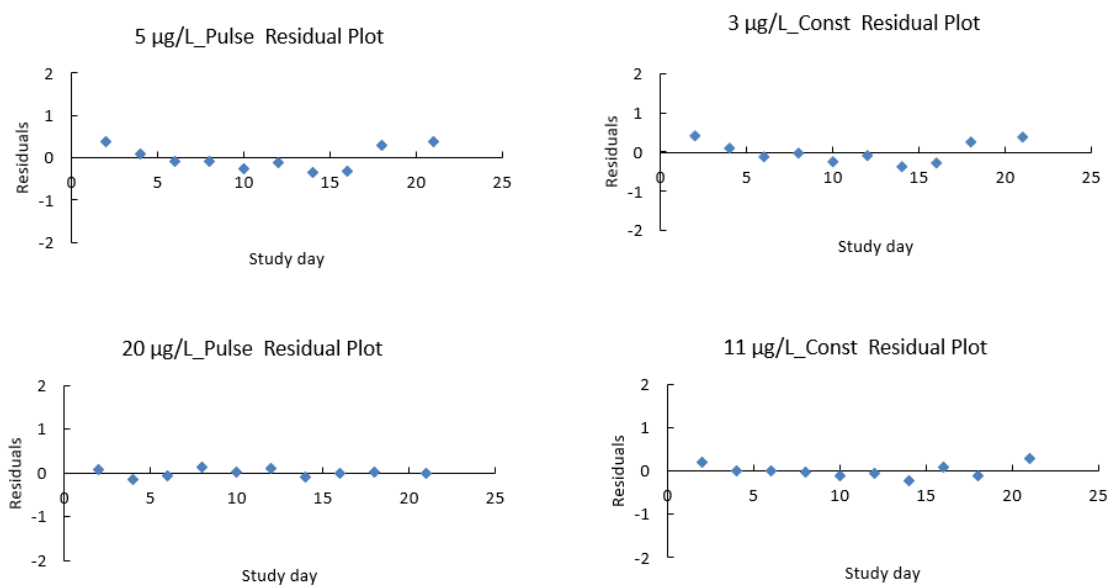


Figure D5. Azoxystrobin POCIS uptake residual plots for constant and multiple pulses concentration exposures.

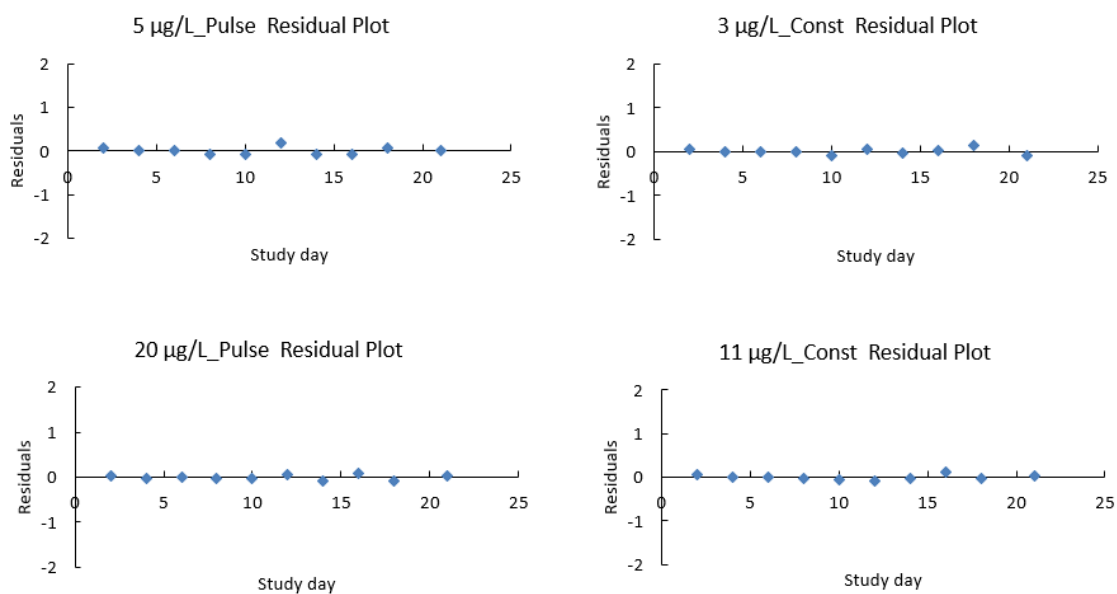


Figure D6. Bicyclopyrone POCIS uptake residual plots for constant and multiple pulses concentration exposures.

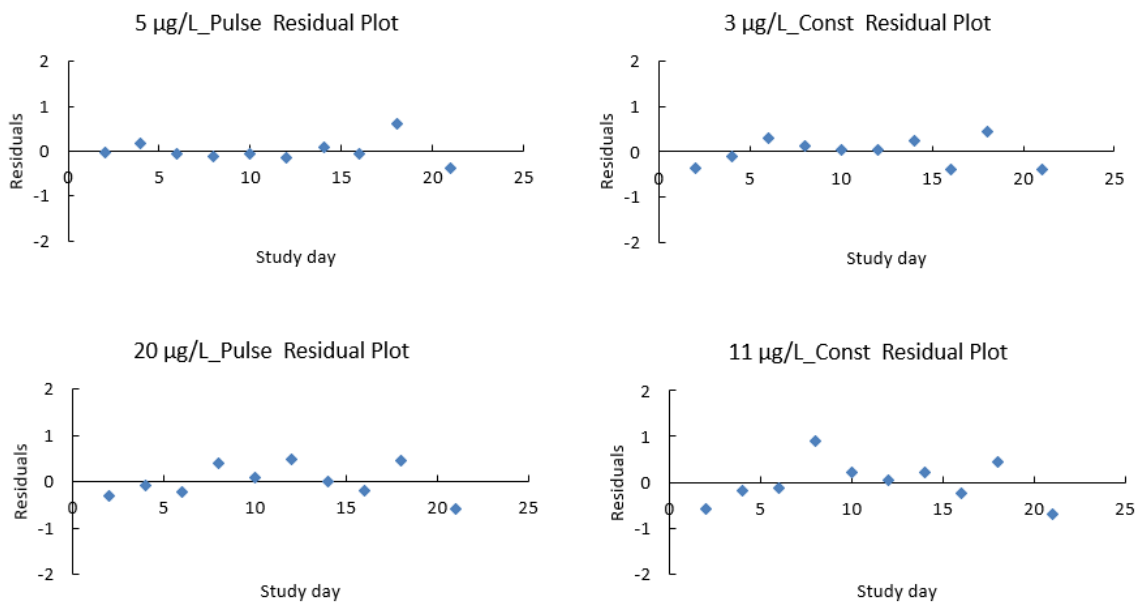


Figure D7. Cyproconazole POCIS uptake residual plots for constant and multiple pulses concentration exposures.

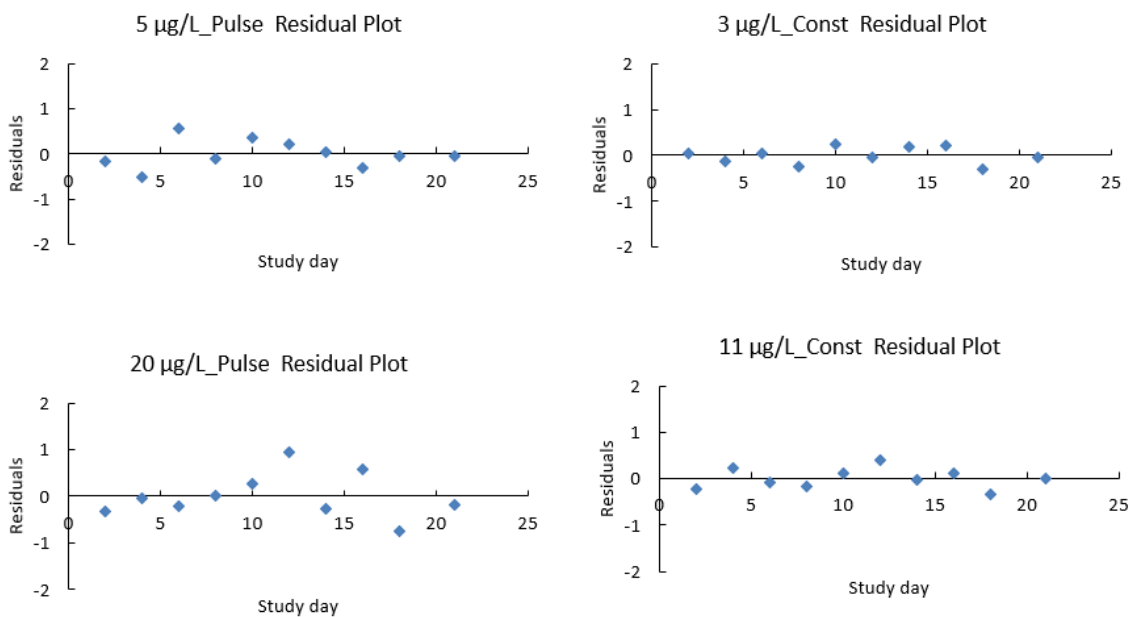


Figure D8. Fomesafen POCIS uptake residual plots for constant and multiple pulses concentration exposures.

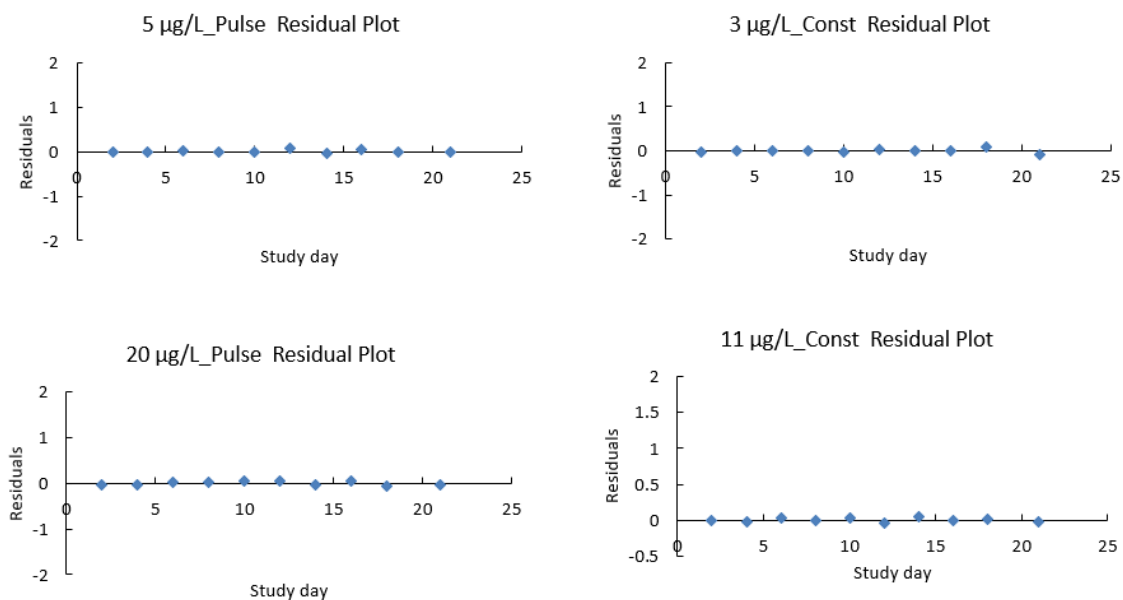


Figure D9. Mesotrione POCIS uptake residual plots for constant and multiple pulses concentration exposures.

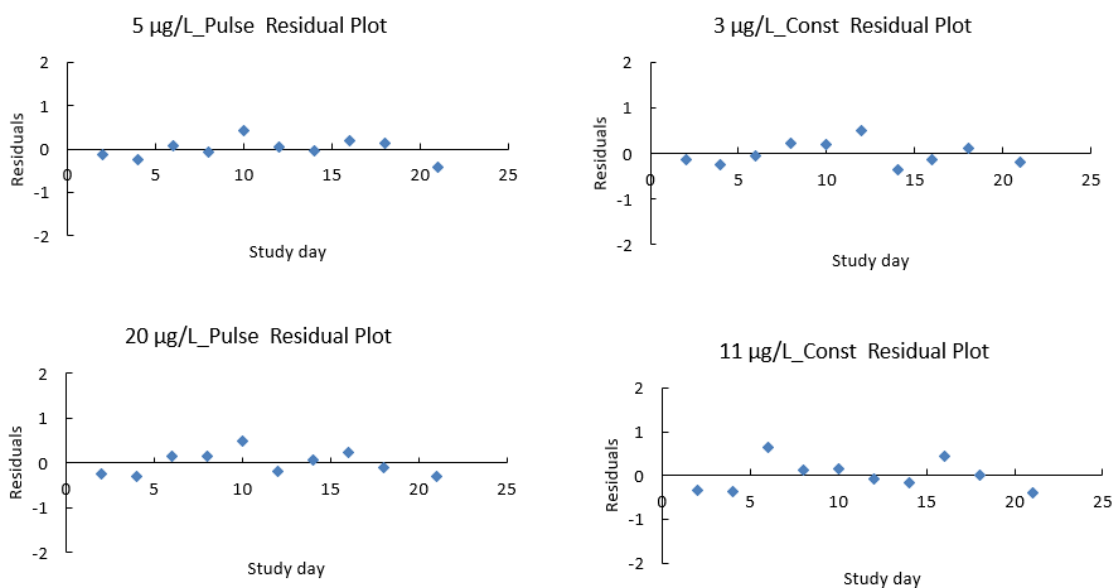


Figure D10. S-Metolachlor POCIS uptake residual plots for constant and multiple pulses concentration exposures.

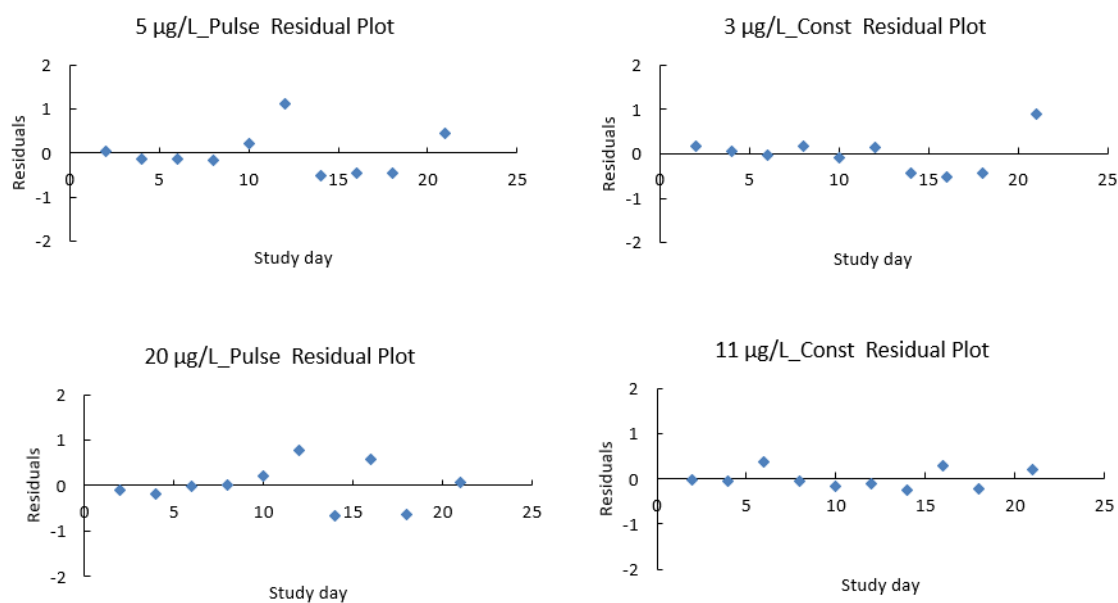


Figure D11. Propiconazole POCIS uptake residual plots for constant and multiple pulses concentration exposures.

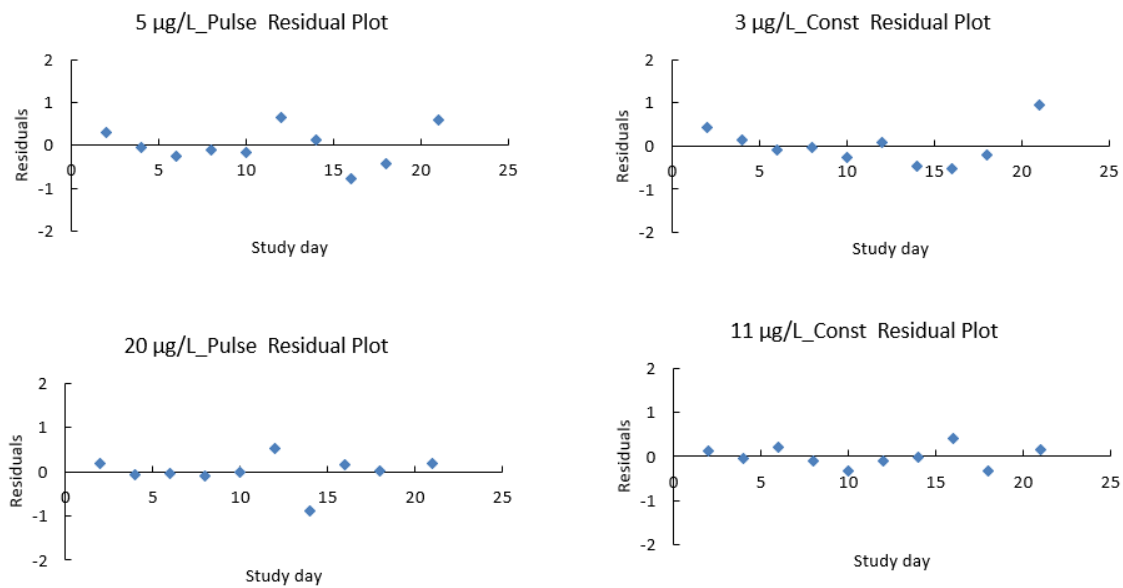


Figure D12. Sedaxane POCIS uptake residual plots for constant and multiple pulses concentration exposures.

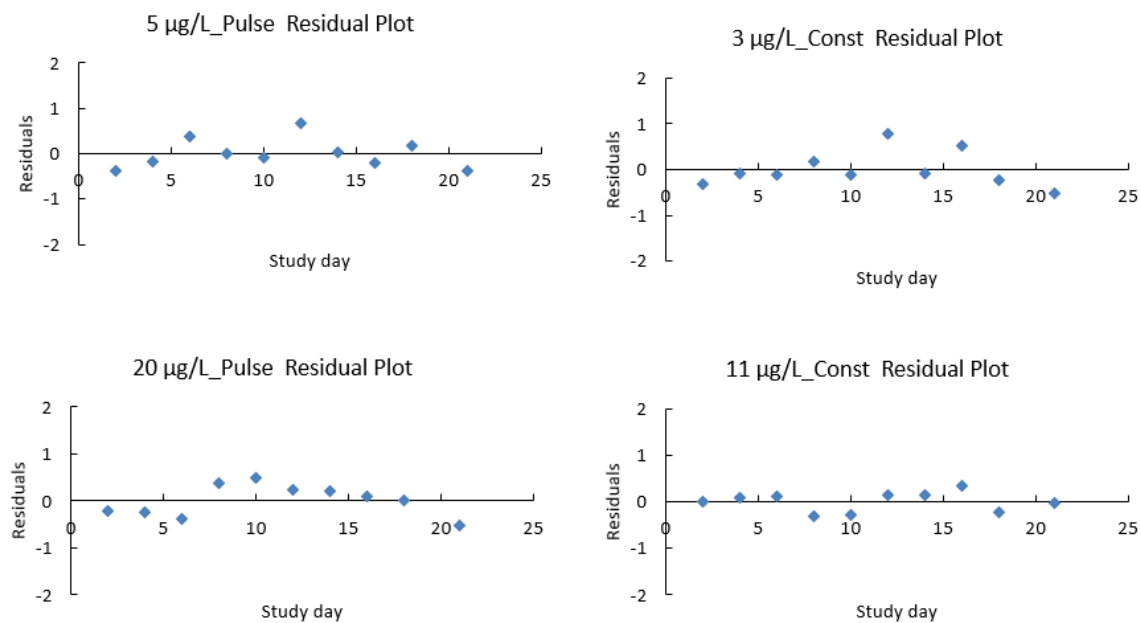


Figure D13. Simazine POCIS uptake residual plots for constant and multiple pulses concentration exposures.

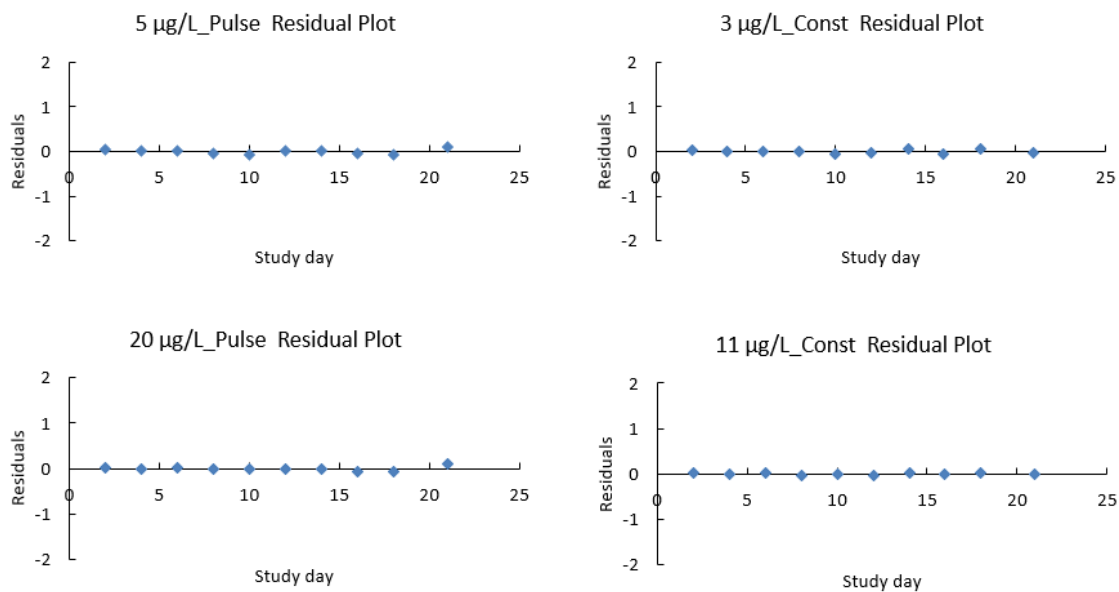


Figure D14. Solatenol POCIS uptake residual plots for constant and multiple pulses concentration exposures.

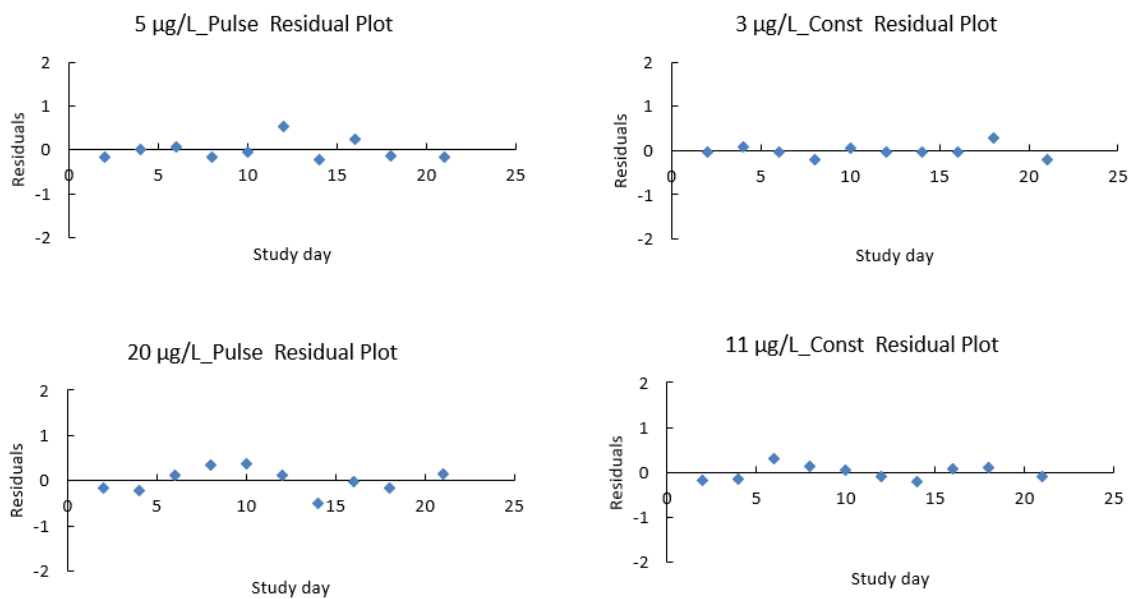


Figure D15. Thiamethoxam POCIS uptake residual plots for constant and multiple pulses concentration exposures.

Sorption Isotherm Experiment

Sorption isotherm between atrazine and Oasis HLB was carried out by contacting 1 mg of Oasis HLB with 5 mL of atrazine with concentration ranging from 0.005 to 50 mg/L in amber vials . The vial was shaken for 48 hours in an incubator with temperature set at 22 °C. Samples were analyzed by LC-MS/MS. Langmuir and Freundlich sorption isotherm models were used to interpret the data.

- The Langmuir model is based on the assumption that the sorption energy of each molecule is the same, occurs on localized sites and involves no interaction between adsorbed molecules. This leads to the deposition of a single layer of sorbate on the surface of the sorbent with maximum adsorption resulting in the formation of monolayer coverage:

$$q_e = \frac{q_{max}bC_e}{1 + bC_e}$$

Where q_e is the amount of pesticides adsorbed (mg/g) at equilibrium, q_{max} is the maximum adsorption capacity (mg/g), b is the Langmuir equilibrium constant (L/mg), and C_e is the residual pesticides concentration (mg/L) at equilibrium.

- The Freundlich isotherm model is based on the assumption that the adsorption process takes place on an heterogeneous surface. It can be applied to the formation of multilayer during the adsorption process with non-uniform distribution of the adsorption heat and affinity over the heterogeneous surface:

$$q_e = K_f C_e^{1/n}$$

Where q_e is the amount of pesticides adsorbed (mg/g) at equilibrium, K_f is a relative indication of the adsorption capacity (mg/g), C_e is the residual pesticides concentration

(mg/L) at equilibrium and $1/n$ is the adsorption intensity, and indicates the sorbent heterogeneity.

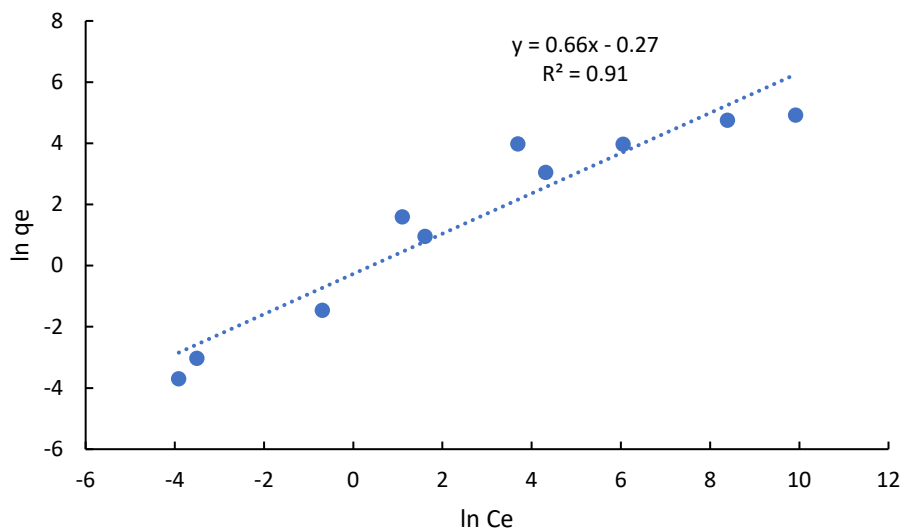


Figure D16. Freundlich sorption isotherm fit for atrazine on Oasis HLB.

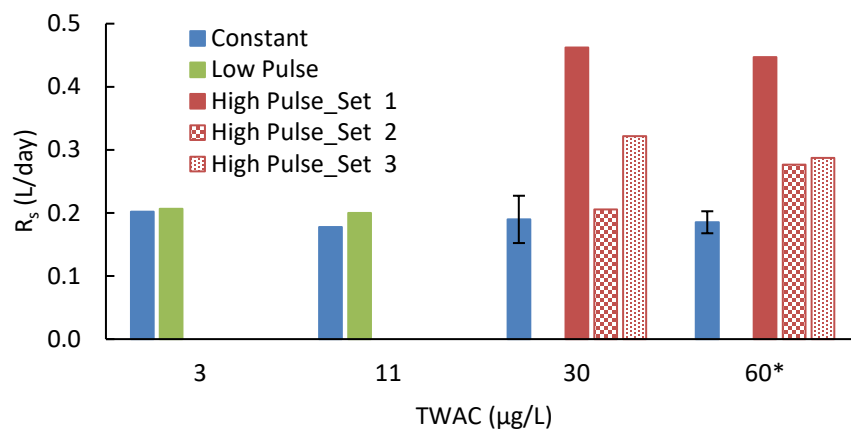


Figure D17. Atrazine sampling rates comparison between constant and pulse concentration exposures, where (*) indicates that sampling was determined from a 12-day exposure time period. The error bars represent one standard deviation for n number of replicates.

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