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A new passive surface water flux meter for simultaneous measurement of contaminant and water fluxes in streams and rivers

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A NEW PASSIVE SURFACE WATER FLUX METER FOR SIMULTANEOUS MEASUREMENT OF CONTAMINANT AND WATER FLUXES IN STREAMS AND RIVERS

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Dedicated to my wife, Jennifer Sassman, and four children Thalia, Matthew, Alexis, and Emilyann. Their love, support and patience throughout my time in graduate school has been invaluable. Also to Carol and Freddy Sassman who have been the best parents anyone could ask for.

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PREFACE

Measurement of concentration or flux of contaminants is essential for evaluating potential health risks to affected organisms and developing effective strategies for mitigating the effects of pollutants in the environment. For water-borne contaminants, concentrations have traditionally been measured by direct analysis of aqueous samples taken at discreet times. For systems in which concentrations exhibit a high degree of temporal variability, a discreet sampling approach may result in an inaccurate assessment of contaminant mass flux since a sample taken at any single point in time is not likely to be representative of the average concentration over a longer interval. Thus, pollutant monitoring strategies often require high frequency measurement resulting in a multitude of samples for analysis and soaring costs.

Since the mid 1970's, passive sampling techniques have steadily gained popularity because of their ability to provide comparable information about contaminant concentration or flux with far fewer samples. The vast majority of development in passive water sampling technology has focused on diffusive type samplers. This type of sampler is simple in design and yields a time-averaged concentration over the length of deployment of the device; however, if knowledge of contaminant mass flux or loading is desired, external measurement of water flow is necessary. In contrast, advective passive samplers have the capacity to directly measure the flux of contaminants without external measurement of water flow.

The research discussed herein describes the development and testing of a passive flux meter, which is a type of advective passive sampler in which the flux of water through the device is estimated by measuring the depletion of a suite of alcohol tracers that are pre-absorbed to granular activated carbon prior to deployment. Contaminant mass flux or flow weighted average concentration over the deployment period are then determined from the mass of contaminant absorbed by the device. While the majority

of previously designed passive flux meters have been developed to measure the flux of contaminants in groundwater, the passive surface water flux meter (PSFM) described herein is for assessment of contaminant concentration and flux in surface water bodies. This research focuses of first order streams affected by the application of manure and pesticides at the Purdue Animal Sciences Research and Education Center.

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SYMBOLS

Symbol	Definition/Units in terms of Mass (M), Length (L), and Time (T)
α	level of significance for statistical tests (dimensionless)
a	slope factor for relationship between darcy flux of water through flux meter and stream linear velocity (dimensionless)
A	cross sectional area of PSFM sorbent compartment (L^2)
b	linearity factor for relationship between darcy flux of water through flux meter and stream linear velocity (dimensionless)
c	slope factor for relationship between stream linear velocity and stream specific discharge (dimensionless)
C	concentration (M/L^3)
C_{final}^{GAC}	final concentration of tracer in the sorbent (M/L^3)
C_i	initial concentration (M/L^3)
C_i^{GAC}	initial concentration of tracer in the sorbent (M/L^3)
C_{ISCO}^{FWA}	flow weighted average concentration of contaminant measured in ISCO samples (M/L^3)
C_{PSFM}	flow weighted average concentration of contaminant measured using flux meter (M/L^3)
C_s	concentration of contaminant in stream (M/L^3)
C_s^{FWA}	flow weighted average concentration of contaminant in stream over flux meter deployment period (M/L^3)
C_t	tracer concentration (M/L^3)
C_w	concentration in aqueous phase (M/L^3)

d	linearity factor for relationship between stream linear velocity and stream specific discharge (dimensionless)
D	Damkohler Number (dimensionless)
E	error incurred due to sorption non-ideality when flux meter cumulative water flow is estimated using tracer retardation factor (dimensionless)
g	gravitational constant (L^3 M^{-1} T^{-2})
H	stream stage (L)
ΔH	change in head between inlet and outlet of flux meter (L)
θ	sorbent porosity (dimensionless)
κ	von Karman constant (0.4, dimensionless)
K_d	sorbent-water partition coefficient (L^3/M)
k_{eq}	sorption rate constant (T^{-1})
K_{eq}	sorbent-water partition coefficient at equilibrium (L^3/M)
K_f	Freundlich sorbent-water partition coefficient ($L^{3/N}/M^{1/N}$)
K_{ow}	octanol-water partition coefficient (dimensionless)
k_{PSFM}	saturated hydraulic conductivity of PSFM (L/T)
k_{sorp}	sorption rate (T^{-1})
λ	stream slope (L/T)
l	volume of aqueous phase (L^3)
L	length of sorbent packing (L)
m	slope factor for relationship between concentration in stream and specific discharge (dimensionless)
meq	milli-equivalents
M	contaminant mass (M)
M_{PSFM}	mass of contaminant captured by PSFM (M)
M_{liq}	mass of tracer in liquid phase (M)
M_{tot}	total mass of tracer in system (M)

n	linearity factor for relationship between concentration in stream and specific discharge (dimensionless)
N	Freundlich sorption linearity parameter (unitless)
p_1, p_2	static pressure at the flux meter inlet and outlet openings (M L^{-1} T^{-2})
Q	specific discharge (L/T)
q_{PSFM}	darcy flux of water passing through flux meter (L/T)
Q_{PSFM}	specific discharge of water through flux meter (L/T)
Q_{PSFM}^{Flume}	PSFM specific discharge estimated from stream velocity using the relationship between Q_{PSFM} and ambient velocity in a flume (L^3/T)
Q_{PSFM}^{ISCO}	PSFM specific discharge that would result in PSFM concentration estimate being equal to ISCO concentration estimate(L^3/T)
Q_s	stream specific discharge (L^3/T)
r	column radius (L)
R	retardation factor of tracer (unitless)
R^*	operational retardation factor of tracer (unitless)
ρ_b	sorbent bulk density (M/L^3)
s	mass of sorbent (M)
S	concentration in sorbent phase (M/M)
τ_{SMZ}	fraction of the total amount of SMZ contained in the flux meter that was extracted for contaminants (unitless)
t	time (T)
T	PSFM deployment duration (T)
v	volume of aqueous phase (L^3)
V	linear velocity of water moving through sorbent (L/T)
v_1, v_2	stream velocity at inlet and outlet openings of flux meter (L/T)
v_{60}	stream velocity at 60% stream depth (L/T)
v_{PSFM}	linear velocity of water passing through flux meter (L/T)

V_{PSFM}	pore volumes of water passed through flux meter (dimensionless)
v_s	stream velocity (L/T)
v_t	linear velocity of tracer (L/T)
v^*	friction velocity (L/T)
ϕ	sorbent total porosity (unitless)
x	distance traveled by tracer elution front (L)
X_1, X_2	proportionality constants relating v_1 and v_2 to v_s respectively (dimensionless)
ξ	pore volumes of water passed through flux meter (dimensionless)
Ω_R	fraction of tracer remaining (dimensionless)
z_0	depth of zero velocity (L)

ABBREVIATIONS

α	significance level
AA	atomic absorption
ASE	accelerated solvent extraction
ASREC	Agronomy Science Research and Education Center
atm	atmospheres
BTEX	benzene, toluene, ethylbenzene, and xylenes
°C	degrees Celsius
CAFO	confined animal feeding operation
CEC	cation exchange capacity
cm	centimeters
DI	de-ionized
ECEC	external cation exchange capacity
g	gram
GAC	granular activated carbon
h	hours
HDPE	high density polyethylene
HPLC	high performance liquid chromatography
ICP	inductively coupled plasma spectroscopy
ISCO	Teledyne Isco, Inc manufactures products for water pollution monitoring and abatement. For the purposes of this document, ISCO refers to samples collected using an automated water sampling unit manufactured by Teledyne Isco.
L	liters
LC/MS	liquid chromatography/ mass spectrometry

LOD	limit of detection
LOQ	limit of quantitation
m	meters
M	molar concentration
mg	milligrams
MIC	minimum inhibitory concentration
min	minutes
mL	milliliters
mm	millimeters
mol	moles
μg	micrograms
μL	microliters
ng	nanograms
PFM	passive flux meter
POCIS	Polar Organic Integrative Sampler
PSFM	passive surface water flux meter
psi	pounds per square inch
RCs	reference compounds
SDB	styrene divinylbenzene
sec	seconds
SMZ	surfactant modified zeolite
SPE	solid phase extraction
USD	United States Dollars
w	weight

NOMENCLATURE

ACN	acetonitrile
aE2	17α-estradiol
Ag^+	silver ion
$AgNO_3$	silver nitrate
Al	aluminum
ATZ	atrazine
ATZ-DE	desethylatrazine
ATZ-DIP	desisopropylatrazine
ATZ-OH	hydroxyatrazine
bE2	17β-estradiol
$CaCl_2$	calcium chloride
Cl^{-1}	chloride ion
CSF	chlorsulfuron
CPF	chlorpyrifos
CTAB	cetyltrimethylammonium bromide
DMF	dimethylformamide
DMP	2,4-dimethylpentanol
E1	estrone
E2	estradiol
E3	estriol
EtOH	ethanol
EtHexOH	2-ethyl-hexan-1-ol
H_2O	water
HDTMA	hexadecyltrimethylammonium bromide

IPA	isopropanol
MeOH	methanol
MTBE	methyl-t-butyl ether
MTC	metolachlor
Na^+	sodium ion
NaOAc	sodium acetate
NaOH	sodium hydroxide
NH_4OAc	ammonium acetate
NO_3^-	nitrate ion
Pb^+	lead ion
Si	silicon
TBA	t-butanol

ABSTRACT

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A passive surface water flux meter (PSFM) for measurement of contaminant concentration/flux in rivers and streams is described and tested. The novel PSFM design was developed for portability and ease of adaptability for a variety of contaminant classes. Although previous designs have been evaluated under constant flow conditions, the PSFM has never been used for measurement of pesticides or hormones and this is the first time that it has been tested under transient flow. Discharge through the PSFM is assessed by measuring miscible displacement of alcohol tracers from granular activated carbon (GAC). The tracer retardation factors (R) measured by miscible displacement were typically smaller (within 25%) than those estimated from batch studies with sorption of the larger tracers being more nonlinear. For calibration of the ratio of PSFM water flux to external flow velocity, water flux through the PSFM was measured in a flume under constant flow conditions at a range of velocities representative of those in streams and rivers. The relationship between PSFM water flux and external flow velocity in a flume was non-linear as predicted by Bernoulli's equation for velocity potential flow. However, in samples deployed in a natural stream, the relationship between PSFM water flux and external flow was weak with less flow passing through the PSFM under field conditions than predicted by measurements in a flume. The sorption and degradation of the contaminants of interest on surfactant modified zeolite (SMZ), the sorbent used for contaminant capture, were evaluated in laboratory and field experiments. PSFM performance was evaluated in a stream network at the Purdue Animal Sciences Research and Educa-

tion Center (ASREC). Sampling was focused on the steroid hormones and pesticides, which are present at trace concentrations in the stream network as a result of agricultural activity. Estimates of contaminant flow weighted average concentration obtained using the PSFM were compared to concentrations measured in water samples taken at regular intervals using automated sampling equipment. Concentrations of both estrogens and pesticides measured using the PSFM were generally higher than those measured in water samples. This difference was attributed primarily to the high temporal variability of contaminant concentration and flow in the stream resulting in large temporal inequality of transport which is not adequately sampled using discreet methods. Furthermore, it was hypothesized that non-equilibrium tracer desorption during periods of high stream velocity may cause underestimation of PSFM specific discharge and consequent overestimation of contaminant flux in some cases. The PSFM was used to measure contaminant concentration at five strategically located sampling stations over the course of two months. The flow weighted average concentrations of steroid estrogens measured using the PSFM were generally in the low ng/L range while that of the pesticides was in the $\mu g/L$ range. Estrogen concentrations were not correlated with manure application and were more highly variable relative to the pesticides. The highest estrogen concentrations were measured nearest the source zone following a prolonged period of high discharge. Conversely, the concentration of the pesticides atrazine, desethyl-atrazine, and metolachlor were not correlated with distance from the source zone, but increased dramatically with the first precipitation event following pesticide application suggesting disparate transport mechanisms for the compound classes.

1 INTRODUCTION

Measurement of contaminant concentration or loading in the environment has historically required a multitude of high frequency measurements within carefully defined spatial boundaries. Usually, water samples are taken at discreet intervals and either analyzed individually or combined into one or more composite samples. Because such sampling methodology only captures information about the contaminant at the moment and location when the samples were taken, these techniques often miss high flow events which contribute disproportionately to chemical mass flux or mean flow weighted average concentration, thus providing an inaccurate assessment of contaminant loading [35] and exposure of aquatic organisms [63, 88]. In the case of water born contaminants, which present significant challenges and expense related to collection, transportation, extraction, and analysis when using traditional methods such as discreet sampling, passive sampling presents a particularly attractive alternative with great potential for development of new techniques. Although flow-proportional sampling using automated equipment can improve estimates [34], many samples must still be taken to accurately measure contaminant loads and the expense of operation and maintenance of these systems can be prohibitive [126].

A cost comparison between discreet sampling using a Teledyne Isco (ISCO) automated water sampling unit and the herein described passive surface water flux meter (henceforth referred to as PSFM) reveals that the initial cost for automated water sampling is much higher than that of the PSFM. For example, an ISCO 3700 automated water sampler without refrigeration can currently be purchased for a minimum of about $3000 USD. Additionally, the ISCO unit must be supplied with some form of shelter and electricity, which often must be generated by expensive solar panels in remote areas. The cost of electricity and shelter will be neglected in the current assessment since these depend upon the desired sampling location. Initial costs for

the PSFM include the device housing, which can be custom fabricated by a machine shop for about $150 each, sorbents, chemicals, and screens, resulting in a total cost of about $250 per unit. Furthermore, the cost of routine analysis is about 50% higher for discreet sampling relative to the PSFM considering the sampling schemes used in the current study. Table 1.1 shows the cost accumulated over one week for collection, extraction, and analysis of water samples taken at 30 minute intervals using an ISCO sampler with 10 samples per 1 L bottle (about 34 composite samples per week) compared to a single PSFM unit deployed for 1 week. Furthermore, if flow weighted average concentration or measurement of contaminant loads is desired, stream discharge must be measured independently of concentration with traditional water sampling. However, since the PSFM has the capability to *directly* measure contaminant flux, external flow measurement is not necessary. Finally, if information about contaminant concentration or loading at multiple locations is desired, the initial cost of multiple automated water sampling units would greatly increase the initial cost of the monitoring budget. Hence, the PSFM has a particular cost advantage when measuring contaminant concentration or flux at multiple locations.

Table 1.1.: Cost comparison for sampling for one week at a single station using discreet sampling and the PSFM.

Expense Category	Discreet Sampling ($)		Passive Sampling ($)	
Sorbent	SPE cartridges	102	GAC Zeolite Surfactant	3 0.1 0.3
Extraction	Labor	170	Labor Extraction Solvent	80 12
Analysis	Nitrogen Gas Solvent HPLC vials HPLC Use/Repair	20 10 20 10	Nitrogen, Helium, Hydrogen, Air Solvent HPLC Vials HPLC Use/Repair	35 7 10 10
Total	Cost	230	Cost	157

In addition to project cost, the applicability of the acquired data to the overall objective of the research or monitoring effort must be considered. Passive sampling devices provide a time weighted or flow weighted average concentration which may be desirable for applications such as routine contaminant monitoring or evaluating chronic exposure of aquatic organisms; however, passive sampling devices are unable to provide information about concentration at smaller time scales. If contaminant concentration measurement at discreet temporal intervals is required, the PSFM is at a disadvantage. For example, if contaminant concentration must not exceed a pre-determined limit or if information about acute exposure of aquatic organisms is required, then discreet sampling would be the preferred approach. However, for monitoring of contaminant concentration or loads over extended time scales which is often the case with research, regulatory or routine monitoring efforts, passive sampling is far more cost effective.

Certain criteria are necessary for a well performing passive sampling unit. Most importantly, the device should be able to capture the contaminants of interest and there should be some mechanism to correlate the mass of contaminant sorbed with the external contaminant concentration. The sampler should resist bio-fouling and not allow for degradation of the analytes, and the compounds of interest should be readily extractable from the sorbent. Finally, the sampler housing should be inert with regards to potential interactions with the compound of interest.

There are two fundamental types of passive sampling, one relies on diffusion for transport of the contaminant from the bulk solution into the sorbent (diffusive samplers) and the other relies on advective movement of the sample though the sorbent phase where the analytes are taken up (advective sampler). Careful consideration of environmental parameters in addition to the overall purpose of measurement should be given before deciding which type of sample is more appropriate.

The diffusive passive sampler is simple in design with a variety of commercially available products. With diffusive samplers, the uptake rate for each contaminant of interest is measured in the laboratory and often assumed to be constant during the

deployment period of the device. External concentration is calculated from the measured uptake rate of a contaminant and the mass sorbed over the deployment of the device [11]. In a field setting, a number of factors can affect the contaminant uptake rate resulting in estimation error. Microbial growth on the surface of the sampler during deployment, also called bio-fouling, is a common problem in passive sampling [48, 133]. Bio-fouling causes loss of accuracy and precision because of its random formation and can act to increase mass transfer resistance due to blocked membrane pores in diffusion-limiting membranes [94]. Temperature must also be considered due to its affect on the uptake kinetics of contaminants with a positive correlation between increasing water temperature and sampling rate [53]. Turbulence can also influence contaminant uptake and the magnitude of this influence is dependent on factors including sampler materials, hydrophobicity of the contaminant and external flow conditions [19]. In many diffusive passive samplers, the sorbent phase is often separated from the aquatic environment by a semi-permeable membrane and permeation of compounds through the membrane is the rate-limiting step in contaminant sorption [22, 48, 53, 110]. With turbulence, the unstirred layer becomes thin causing enhanced uptake of non-polar compounds by the sampler. Depending upon the extent of the turbulence, at very high flow rates, poor dissolution of polar compounds into the membrane can result in decreased uptake rates.

Reference compounds (RCs) are often added to the sorbent before deployment of the sampler to help compensate for changes in uptake rates as a result of environmental factors such as bio-fouling, turbulence, flow variation and temperature changes [9, 10, 127, 133]. RCs can only be used if their dissipation rate is large enough so that the change in sorbed RC from the beginning of the exposure to the end of the exposure is measurable and small enough so that there is enough remaining RC to accurately determine the fraction remaining. Although reduced sampling rates can often be quantified by RCs, the reduction in mass captured by the device also affects the analytical sensitivity of the method. Whether or not reduced sampling rates are problematic depends on the ambient concentration of the contaminant, the exposure

time, and the sensitivity of the analytical equipment employed for the contaminant. Despite its potential limitations, the diffusive sampler is often the best choice, especially under near steady state conditions where a time averaged concentration is sufficient to describe contaminant concentration or flux over the deployment period.

In advective type passive samplers, dissolved contaminants flow through a porous sorbent where they are taken up by the device. Because of the influence of external flow, an advective sampler can be used for *direct* measurement of contaminant *flux* if it is operated in the kinetic time frame of the device (all contaminant passing through the device is captured) [126]. Water flux through the device can be directly measured or estimated by measuring the depletion of reference compounds, or 'resident tracers'. Under highly transient conditions such as those found in a stream or river, the advective sampler is more responsive to changes in ambient contaminant concentrations because it does not rely exclusively on diffusion of the contaminant into the sorbent which is slow relative to advection [95]. Furthermore, unlike diffusive samplers which measure only dissolved compounds, advective samplers are also capable of capturing particulate bound contaminants [25].

Currently, few commercially available advective passive water samplers exist. The SorbiCell passive sampler was commercialized in 2004 by SorbiSense (U.S. patent no. 7.325.443 B2) [25, 95, 126]. It is an advective passive sampler in which the depletion of a granular salt of low solubility is used to estimate water flow through the device. A number of different sorbents may be used in the device depending on the target contaminant including silica based materials, polymeric media, ion exchange resins, zeolites, and carbonaceous materials. After sampler deployment is completed, the mass of contaminant sorbed is measured by spectroscopic or chromatographic methods after extraction of the contaminant from the sorbent phase. The SobiCell sampler can measure time averaged concentration of various target contaminants including nitrate, phosphate, heavy metals, volatile organic compounds, polycyclic aromatic hydrocarbons, pesticides, and pharmaceuticals depending on the sorbent used [47]. Water flux through the SorbiCell sampler is dependent upon a pressure

gradient which is created by lowering a hollow tube, which is connected to the device inlet by a capillary, below the surface of the water. Since the pressure gradient is not influenced by external flow velocity, but instead by the diameter and length of the capillary and by the depth of the sampler inlet and outlet below the surface of the water, mass flux of contaminants in a stream or river cannot be directly measured using the SorbiCell sampler [126] without external knowledge about the flow characteristics of the sampling site. Because of the propietary nature of the Sorbicell device, the end user is required to ship the unit to an approved laboratory for analysis. Because of this, the Sorbicell is relatively expensive for routine monitoring applications and the contaminants which can be measured are limited to those for which approved laboratories have validated methods. Finally, the small size of the Sorbicell unit restricts the mass of sorbent that it can contain and hence the mass of contaminant that can be captured. Analytes present at very low concentrations may be undetectable due to this limitation.

The PSFM described in this document is based upon a passive flux meter developed at the University of Florida for measurement of water/contaminant flux in groundwater systems [5, 20, 44] which was later modified for use in surface water systems [55, 82]. This, previously developed surface water flux meter design was based upon a permanent housing which accepts removable cartridges containing granular activated carbon as a sorbent (GAC). The GAC is impregnated with alcohol tracers for estimation of water flow through the cartridge and contaminants are simultaneously absorbed by the GAC surface. A limitation of this design is that the device can only measure solutes which are sufficiently retained by GAC. For these reasons, there is a specific need for an easily portable, passive sampling device capable of directly measuring the flux of a wide variety of contaminants in streams and rivers under transient flow conditions.

The overall goal of the currently described research was to develop a PSFM for measuring concentration/flux of dissolved and particulate bound contaminants originating from many potential sources and to use this device for measurement of hormone

and herbicide fluxes in a ditch/stream network affected by CAFO activity. Various sorbent types were tested for capture of the contaminants of interest, design parameters optimized, and contaminant concentrations measured at various locations within the ditch stream network. Concentrations estimated using the Passive Surface Water Flux Meter (PSFM) were compared to flow weighted average concentrations determined from composite water samples taken at 30 min intervals. Our studies assess the potential utility of the PSFM as a tool for measurement of contaminant concentration or flux in streams and rivers. To this end, several primary hypotheses were developed to guide the proposed research:

- Cumulative specific discharge of water through the herein described PSFM under steady or transient external flow conditions can be estimated by measuring depletion of resident tracers given the retardation factor of each tracer relative to water.

- The flow weighted average (FWA) contaminant concentration measured using the PSFM will be of equal or similar magnitude to the FWA concentration measured in composite water samples collected by automated methods.

- Contaminant loads in a flowing stream can be directly measured using the PSFM without external estimation of stream discharge

- A series of PSFMs placed within a drainage ditch network affected by agricultural wastes may be used to quantify the transport of steroid hormones and atrazine from the source zone to affected areas downstream.

2 ESTIMATION OF PSFM CUMULATIVE SPECIFIC DISCHARGE OF WATER

2.1 Discharge From Depletion of Resident Tracers

The theoretical description of a passive flux meter for simultaneous measurement of water and contaminant fluxes was first developed by Hatfield et al. [44]. This work describes a permeable unit packed with a mixed hydrophobic/hydrophilic sorbent which captures target contaminants flowing through the device. The sorbent is impregnated with one or more resident tracers, which are displaced from the device at a rate that is proportional to water flux and inversely proportional to the affinity of the tracer(s) for the sorbent. Estimation of specific discharge through a passive flux meter by measurement of tracer displacement is based on a number of important assumptions: (1) the "resident tracers" are initially uniformly distributed within the device, (2) tracer transport within the device is homogeneous and parallel to the external water flow direction, (3) tracer sorption/desorption is linear, reversible, and instantaneous [44].

The PSFM described herein was constructed of anodized aluminum (removable end caps) and stainless steel (pipe) (Figure 2.1). These materials were chosen due to their relative inertness toward most environmental contaminants including the hydrophobic and polar organic compounds targeted in this study and because of their durability. The PSFM was designed to be easily adaptable to different contaminant classes by altering the sorbent material and small in size to facilitate ease of transport and deployment.

Granular activated carbon (GAC) was chosen as the sorbent for resident tracers because it has a hydrophobic surface with high sorptive capacity, is available in granular form, is inexpensive, is mechanically stable, and has been used in previous

Figure 2.1.: Photograph of Passive Surface Water Flux Meter.

versions of the flux meter [5, 20, 44, 55, 82]. Differing chain length alcohols, which were also used in previous flux meters, were chosen as resident tracers because they have a number of advantages over other potential choices: (1) the affinity of each individual tracer for the PSFM sorbent can be easily controlled by varying the alcohol carbon number, (2) they are easily extracted from GAC, (3) they are relatively non-toxic to aquatic organisms, (4) analysis by gas chromatography is facile, and (5) they are readily available and inexpensive. Uniform distribution of the resident tracers was confirmed by extraction of sorbent sub-samples which had been previously equilibrated with tracers. The long, tubular shape which is aligned parallel to the external flow and the placement of tracer loaded GAC within the unit ensures that flow in the GAC layer is homogeneous and parallel to stream flow (Figure 2.2).

Tracers were equilibrated with GAC prior to construction and deployment of the device. For packing, flux meters were securely closed using a stainless steel cap on the outlet side and oriented in the vertical position with the outlet side down. Flux meters were wet packed by adding water periodically to ensure that the packing constituents were always submerged. Packing constituents were added slowly while gently tapping on the sides of the unit to avoid the formation of preferential flow channels. The PSFM was packed in layers starting at the outlet side with a fine sand mixture consisting of a mixture of 75 and 250 mesh silica sands (2:1). Next

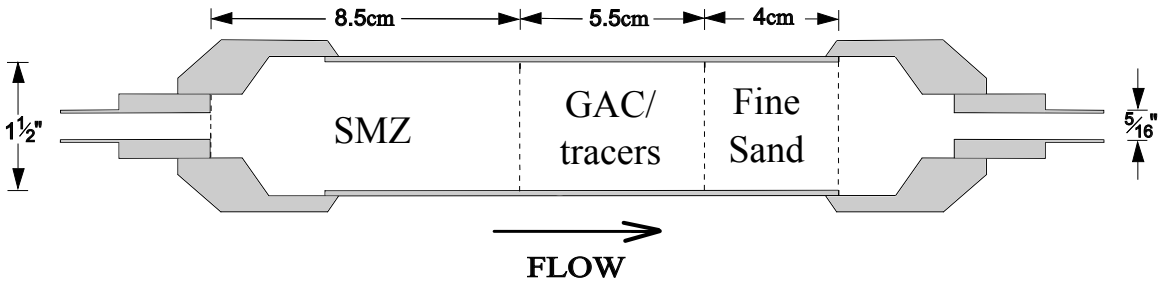


Figure 2.2.: Conceptual Diagram of Passive Surface Water Flux Meter. Silver impregnated surfactant modified zeolite (SMZ) is the sorbent for contaminants, granular activated carbon (GAC) is the sorbent for resident tracers which are used for measurement of water flow through the device, and fine sand on the outlet side functions to control hydraulic conductivity. Sorbent compartments are separated by steel mesh screens.

the tracer loaded GAC was added followed by the silver loaded surfactant modified zeolite layer (SMZ). Layers were separated from each other by stainless steel mesh screens. Further details of PSFM preparation are described in Appendices A, H, and L.

Four alcohol tracers were chosen for estimation of water flux in the surface water flux meter. Methanol (MeOH), ethanol (EtOH), isopropanol (IPA), and t-butanol (TBA) span a wide range of sorption affinity for the GAC surface, and hence, potentially allow for measurement of water flow over a wide range of external flow conditions. Branched chain alcohols are preferred over straight chain alcohols because of their greater resistance to bio-degradation via β-oxidation [108, 109]. A conservative tracer, 2,4-dimethylpentanol (DMP), which was assumed to be immobile within the sorbent during the deployment period, was added to GAC prior to deployment of the device and used as a surrogate standard to correct for possible tracer losses during deployment and extraction. Recovery of DMP was $90 - 110\%$ in $> 90\%$ of samples. Recovery of MeOH, EtOH, IPA, and TBA were normalized to the recovery of DMP prior to estimating PSFM discharge. After deployment of the device, tracers were extracted from the sorbent phase and the amount of each tracer remaining determined by gas chromatography using a J&W Scientific DB-624 capillary column (60m

x 0.53mm ID x 3μm film thickness) with helium carrier gas at 38 cm/sec linear velocity. 2-ethylhexanol was added to the solvent mixture used for extraction of tracers from GAC and used as an internal standard for correction of results due to slight changes in injection volume or instrument response. Further details of the methods used for extraction and analysis of the tracers are given in appendix D.

Figure 2.3 illustrates the displacement of a resident tracer from a flux meter packed with GAC. The velocity of each individual tracer ($v_t, L/T$) within the flux meter is related to the darcy flux of water through the PSFM ($q_{PSFM}, L/T$) by the retardation factor of each tracer (R, dimensionless):

$$v_t = \frac{x}{\Delta t} = \frac{q_{PSFM}}{\phi R} \tag{2.1}$$

where ϕ = sorbent porosity (dimensionless). Upon rearrangement and dividing through by the length of the PSFM (L), this yields:

$$\frac{q_{PSFM}}{\phi L} = \frac{x}{L}\frac{R}{\Delta t} \tag{2.2}$$

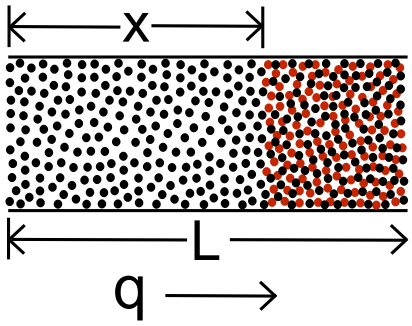


Figure 2.3.: Conceptual diagram of a resident tracer being eluted from a PSFM packed with sorbent. The alcohol tracer is represented by red dots while the sorbent is represented by black dots. L = length of PSFM sorbent, x = distance traveled by tracer elution front, q = darcy flux of water through the PSFM (L/T).

Assuming purely advective transport of tracers within the flux meter and instantaneous sorption/desorption kinetics, the quantity $\frac{x}{L}$ is equal to one minus the fraction of tracer remaining in the PSFM (Ω_R, dimensionless) :

$$\frac{x}{L} = 1 - \Omega_R \tag{2.3}$$

Substituting $[1 - \Omega_R]$ into equation (2.2), the expression for time averaged specific discharge of water through the PSFM as a function of fraction of tracer remaining is:

$$q_{PSFM} = [1 - \Omega_R]\frac{\phi LR}{t} \tag{2.4}$$

The tracer retardation factor (R, dimensionless) is a critical parameter in estimation of discharge through the PSFM and is defined as the ratio of the velocity water passing through the flux meter to the velocity of an individual tracer. R can be measured by performing an equilibrium batch sorption experiment or by measuring the elution of tracers from a packed column as water is pumped through at a known flow rate (miscible displacement).

In the batch equilibration method, the partition coefficient ($K_d, L^3/M$) of each tracer is determined by measuring the aqueous phase concentration of the tracer at equilibrium. Assuming that all of the mass of tracer lost from the initial aqueous solution is sorbed to the GAC with no degradation, K_d can be calculated using the formula:

$$K_d = \frac{v}{s}\,(\frac{M_{tot}}{M_{liq}} - 1) \tag{2.5}$$

where v is the volume of the aqueous phase, s is the sorbent mass, M_{tot} is the total mass of resident tracer in the system, and M_{liq} is the mass of tracer measured in the aqueous phase at equilibrium. R for each tracer is then determined from K_d by the equation:

$$R = 1 + \frac{\rho_b}{\phi} K_d \tag{2.6}$$

where ρ_b is the sorbent bulk density. Given the assumptions listed above, the fraction of tracer remaining in a packed column as a function of cumulative pore volumes of water passed through the column should be linear with x-intercept equal to the retardation factor which is related to the equilibrium K_d by equation 2.6. However, because of non-linear sorption behavior, the tracer retardation factor may depend not only on the tracer partition coefficient K_f ($M^{1-N}L^{3N}M^{-1}$), but also on the degree of sorption non-linearity N (dimensionless) and the tracer concentration in the liquid phase C_t (M/L^3). Assuming a Freudlich sorption isotherm:

$$S = K_f C_t^N \tag{2.7}$$

where S is the concentration of contaminant in the sorbed phase (M/L^3). In terms of the tracer retardation coefficient:

$$R = 1 + \frac{\rho_b}{\phi} K_f N C_t^{N-1} \tag{2.8}$$

Because hydrodynamic dispersion and molecular diffusion cause spreading of the tracer elution front, a (finite) concentration gradient develops near the front. This gradient, combined with dependence of R on concentration due to non-linear sorption, results in self spreading ($N < 1$) or self sharpening ($N > 1$) of the elution front as tracers are displaced from the PSFM. For example, if $N < 1$, decreasing solute concentrations near the elution front result in increasing K_d and hence solutes that are farther from the leading edge have slower velocity resulting in spreading of the front (dispersion) and consequent tailing of the elution profile [13]. If the "operational R" for a tracer, henceforth designated as R^* (dimensionless), is defined as the retardation factor estimated from the fraction of tracer remaining at any specific time point during elution, the value of R^* for a tracer exhibiting non-linear sorption behavior is time dependent and changes as the tracer becomes more depleted complicating the

estimation of cumulative flow from fraction of tracer remaining. For $N > 1$, the tracer elution front is self sharpening and tailing of the elution profile does not occur.

In addition to sorption linearity, sorption/desorption kinetics is also important to consider when estimating PSFM discharge from fraction of tracer remaining. Ideally, the PSFM should be designed so that the kinetics of tracer mass transfer between sorbent and dissolved phase is fast relative to the residence time of water in the PSFM. However, this may not be possible when the contaminants of interest are present at very low concentration. Instrumental sensitivity limits may require a large volume of water to be sampled to allow for accurate quantitation of analytes. If the sorption/desorption rate is slow relative to velocity of water flowing through the device, dispersion increases the magnitude of error in estimation of PSFM water flow from fraction of tracer remaining.

Therefore, to evaluate the effects of sorption non-linearity and non-equilibrium, it is instructive to measure the mass flux of both tracers and water from the PSFM outlet and plot the fraction of tracer remaining in the device as a function of cumulative pore volumes of water eluted. The shape of the tracer depletion profile can be examined to determine the range of tracer depletion for which flow estimation error is within acceptable bounds. Because the effects of dispersion become more severe as more waster passes through the flux meter, the initial part of tracer depletion profiles is linear and begins to tail with higher cumulative discharge. Retardation factors were determined from the depletion profiles by estimating the slope and the corresponding amount of flow estimation error over multiple ranges of tracer remaining. Then, the final retardation factor chosen to limit error within chosen bounds.

2.1.1 Measurement of Tracer Retardation Factors

Tracer retardation factors were estimated using both batch desorption and miscible displacement techniques (detailed experimental protocols are outlined in Appendices C and E respectively). For the batch experiments, tracer desorption kinetics

were first assessed to ensure that individual desorption steps were not kinetically constrained. Briefly, duplicate GAC samples were equilibrated at 23°C with a sterile aqueous solution containing 1% each of MeOH, EtOH, IPA, and TBA. Tracer concentrations in the aqueous phase were measured at 18, 29, and 48 hours, and it was found that the GAC-water partition coefficients did not change significantly after 18 hours (α=0.05). After 48 hours, the aqueous phase was decanted and fresh 0.005 M $CaCl_2$ solution added. The samples were mixed continuously using a rotary end-over-end mixer, and tracer concentrations in the aqueous phase measured at 0, 1, 2, 4, 8, and 24 hours and K_d values calculated assuming that all tracer not in the aqueous phase was sorbed (Fig. 2.4). GAC-water partition coefficients for IPA and TBA were 25-38% and 17-25% higher respectively at the 1 and 2 hour sampling times but did not change significantly thereafter (α=0.05) indicating that equilibrium was attained within 4 hours. The K_d for EtOH was 17% higher during the first sampling time but constant after 2 h, while the K_d for MeOH was constant for all sampling times.

Desorption isotherms were constructed to estimate R and to assess the degree of sorption non-linearity (Fig. 2.5). A detailed protocol for the desorption experiment is outlined in Appendix C. Briefly, GAC was equilibrated for 48 hours at 23°C with a sterile aqueous solution containing 1% each of methanol, ethanol, isopropanol, and t-butanol. Samples were prepared at 3 different solid/liquid ratios (1.5g/100mL, 6g/100mL, and 40g/100mL) in duplicate. After 24 hours of equilibration, the tracer concentration in the aqueous phase was measured, the aqueous phase decanted, and fresh 0.005 M $CaCl_2$ solution added. The sample was allowed to equilibrate for another 24 hours and tracer concentration determined. The aqueous phase was again decanted, fresh $CaCl_2$ solution added, and tracer concentration determined after 24 hours equilibration two more times for a total of four points on the desorption isotherm. Because the sorbed phase concentration (S), which was used to estimate the initial mass of tracer present during each equilibration period, was determined from the difference in aqueous concentration before and after the previous equilibration with the sorbent phase, the magnitude of potential experimental error increases with

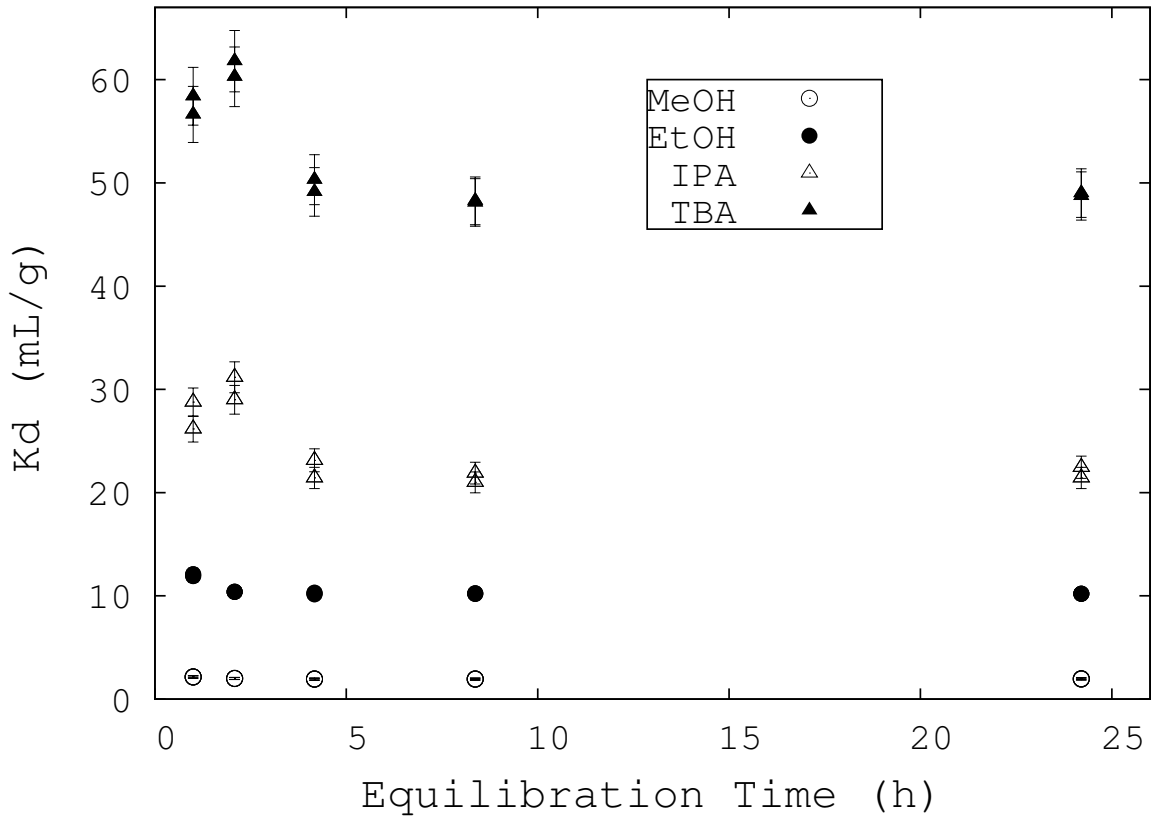


Figure 2.4.: Kinetics of Tracer Sorption on GAC. Sorbent = Si-GAC 989 20x50 mesh. Initial Concentration = 1%. Sorbent/Solution = 40g/100mL for MeOH and EtOH, 6g/100mL for IPA and TBA. Desorption time = 0, 1, 2, 4, 8, and 24 h. Error bars indicate the standard deviation of duplicate samples.

sequential desorption steps. Therefore, propagation of uncertainty was performed to evaluate the magnitude of potential error inherent in estimation of S. R statistical software (version 2.1.2.1) was used for fitting the data to the Freundlich isotherm using non-linear least squares minimization of error. Linear sorption coefficients (K_d) for MeOH and EtOH were determined by direct fitting of the desorption data. Due to the non-linear nature of the isotherms obtained for IPA and TBA, linearized K_d values were obtained by calculating the sorbed phase concentration predicted by the Freundlich isotherm at the aqueous phase concentration of tracer measured after preparation of tracer loaded GAC (the initial concentration for field deployed PSFM

units). Linear sorption partition coefficients along with retardation factors calculated from the desorption isotherms are presented in table 2.1.

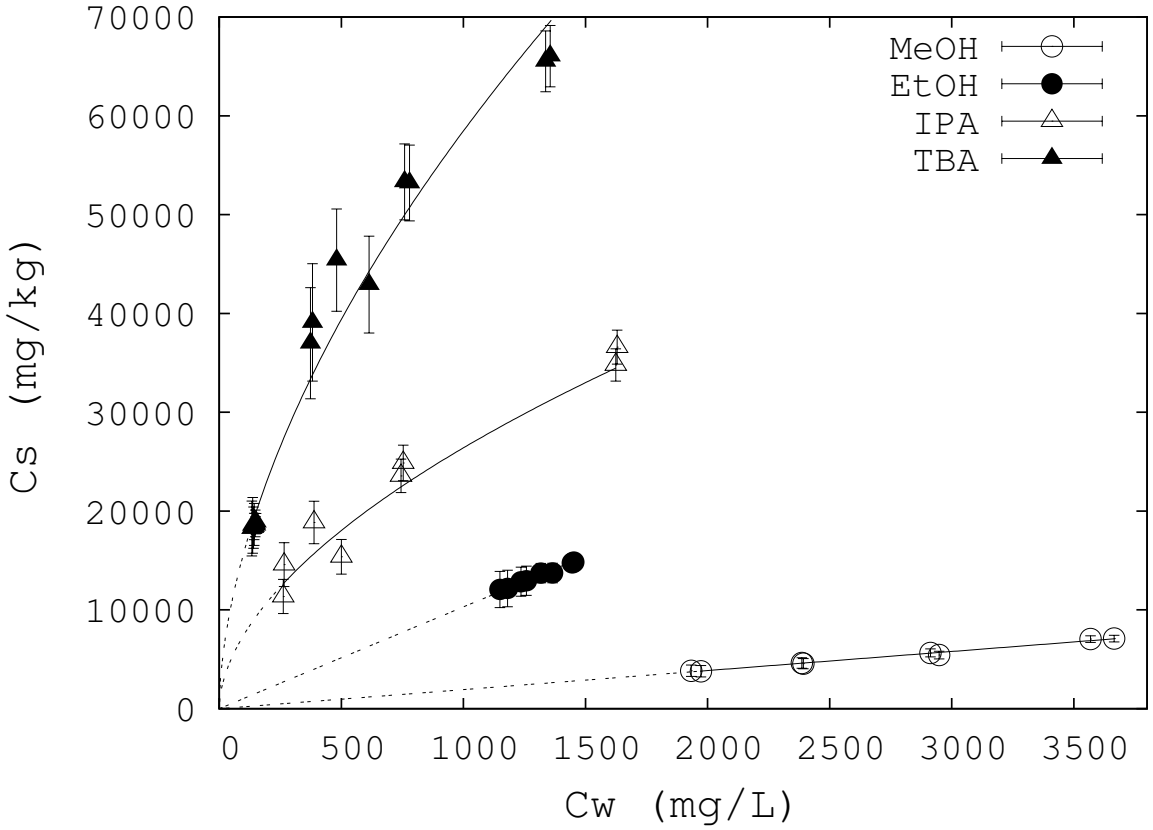


Figure 2.5.: Isotherm for Desorption of Tracers from GAC. Sorbent = Si-GAC 989 20x50 mesh. Initial Concentration = 1%. Sorbent/Solution = 1.5g/100mL, 6g/100mL, and 40g/100mL. Desorption time = 24 h.

A Damkohler number is a dimensionless measure relating the rate of a chemical reaction (sorption/desorption in the case of the PSFM) to the rate of transport. For the PSFM, the Damkohler number is $D = \frac{k_{sorp}L}{V}$ where k_{sorp} is the sorption/desorption rate (T^{-1}), L is the length of the sorbent, and V is the linear velocity of water moving through the sorbent (L/T). Modeling of solute transport in packed columns suggests that when the Damkohler number is greater than 10, the assumption of local equilibrium is a good approximation [52]. However, when $D < 10$, a non-equilibrium term was required to fit the data. Considering a moderately high PSFM water velocity

Table 2.1.: Sorbent-Water Partition Coefficients and Retardation Factors Determined From Desorption Isotherms.

Tracer	Linear		Freundlich	
	K_d [a]	R [b]	K_f [c]	N
MeOH	1.93 ± 0.02	2.25 ± 0.02	1.60 ± 0.56	1.02 ± 0.04
EtOH	10.3 ± 0.0	7.65 ± 0.00	21.5 ± 7.4	0.90 ± 0.05
IPA	41.3 ± 14.5	27.7 ± 9.7	591 ± 208	0.55 ± 0.05
TBA	138 ± 17	90.3 ± 11.1	1140 ± 140	0.57 ± 0.02

Mean ± standard error [a] L kg^{-1} [b] R determined from the linear partition coefficient estimated at the tracer concentration of the aqueous phase of freshly prepared tracer loaded GAC [c] $mg^{1-N}kg^{-1}L^{N}$

of 50 cm/d (based on flow rates experienced in field samples, see Figure 4.4), GAC sorbent length of 5.5 cm, and desorption rate of 0.25 hr^{-1} observed for the larger tracers, the Damkohler number is 0.7 suggesting potential non-equilibrium of the larger tracers under high stream flow conditions.

To better evaluate the affect of tracer sorption non-ideality on estimation of water flow, tracer retardation factors were also estimated by miscible displacement of tracers from columns packed with GAC under flow conditions similar to those experienced in the field. Details of the experimental protocol for miscible displacement experiments are given in Appendix E. Briefly, tracer loaded GAC was prepared by equilibrating GAC with a solution containing 1% each of MeOH, EtOH, IPA, and TBA. Tracer loaded GAC was added to the column using a wet packing method. The outlet side of the GAC column was then connected to a flow through cell which could be sampled by a gas chromatograph (GC) and the inlet side was connected to a pump capable of delivering a constant flow rate of 0.1-10 mL/min. Water was then pumped at a constant flow rate and the concentration of tracers leaving the column measured by GC with flame ionization detector against freshly prepared standards dissolved in sterilized water. The flow rate was determined gravimetrically at periodic intervals and the fraction of tracer remaining in the PSFM calculated.

Two tracer elution studies have been performed in our laboratory. In the first study, the darcy flux was initially adjusted to 5 cm/d to approximate base flow conditions. Later in the experiment, after MeOH, EtOH, and $\approx 60\%$ of IPA had eluted, the darcy flux was increased to 28 cm/d to approximate PSFM water flux under faster stream flow conditions (mean and median PSFM flow for all field deployments were 23 and 13 cm/d respectively). The results of this experiment are presented in Figure 2.6.

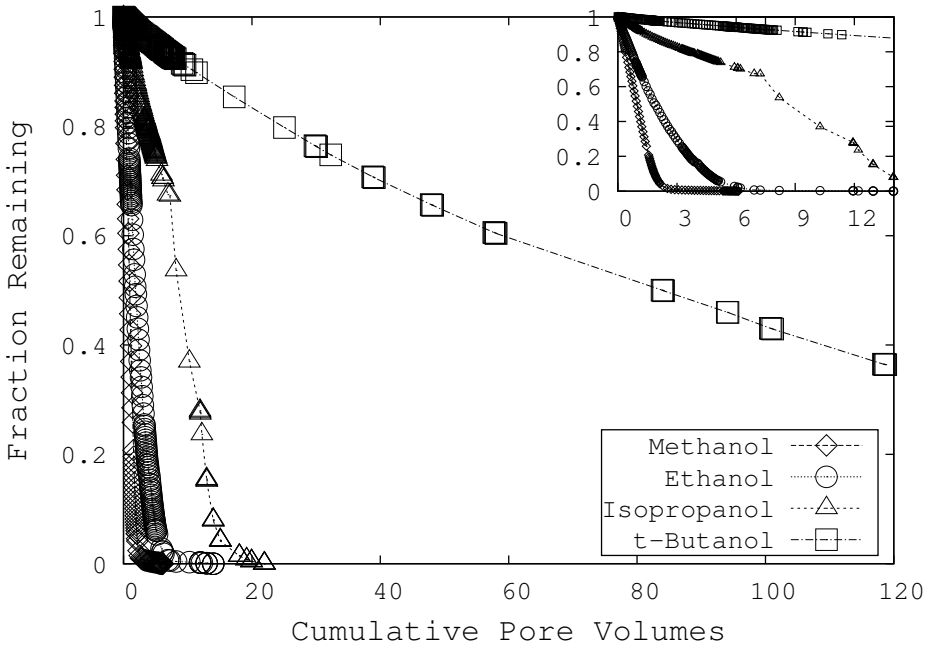


Figure 2.6.: Miscible Displacement of Tracers from GAC. Sorbent = Si-GAC 989 20x50 mesh. Darcy flux of water through column = 5 cm/d initially, increased to 28 cm/d after 11 pore volumes.

When the x coordinate of the tracer elution curves for each individual tracer are normalized to the retardation factor, ideal sorption-desorption predicts a line with a y-intercept of 1 and x-intercept of 1. Sorption non-linearity and/or non-equilibrium causes deviation from this expected behavior as previously described. From the normalized plot in figure 2.7, is is clear that the degree of sorption non-ideality is more severe for the larger tracers. Because of this, the departure from

reliable estimation of water flux becomes more severe as the tracer becomes more depleted and is greater for the larger tracers.

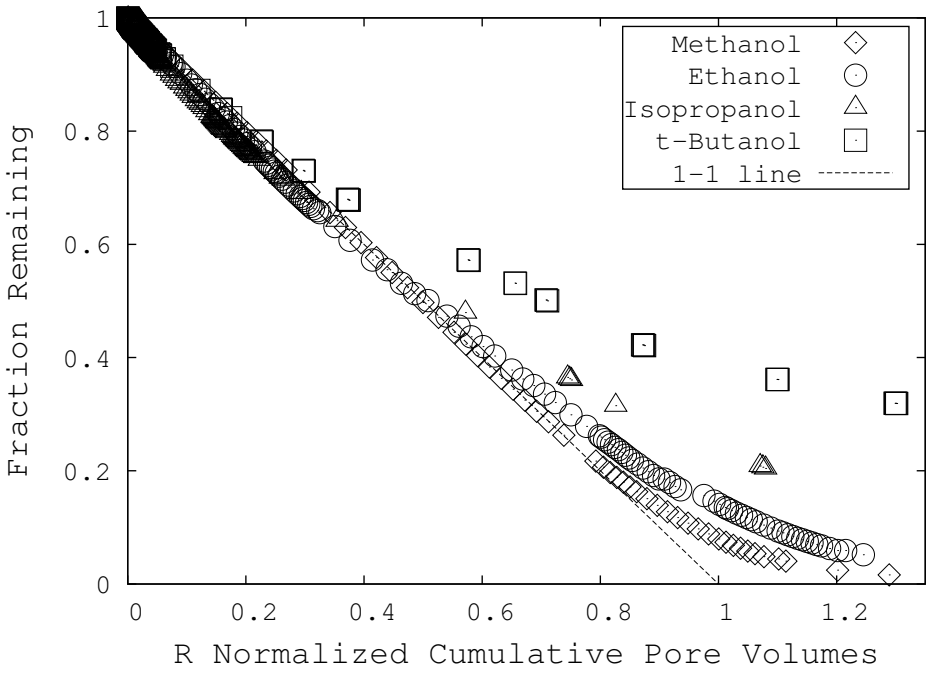


Figure 2.7.: Miscible Displacement of Tracers from GAC Normalized to Retardation Factor. Sorbent = Si-GAC 989 20x50 mesh, Darcy flux of water through column = 5 cm/d initially, increased to 28 cm/d after 11 pore volumes

A second tracer elution study was performed at a constant darcy flux of 9.1 cm/d to simulate low to moderate flow and near equilibrium conditions (Figure 2.8). Under these conditions, over 60% of IPA and over 80% of TBA were remaining in the PSFM at the conclusion of the experiment.

Due to sorption/desorption non-ideality resulting in some degree of non-linearity of the relationship between tracer remaining and cumulative discharge of water, least squares minimization was performed in order to determine values for R which limit estimation error to $< 25\%$ over a specific range of fraction of tracer remaining (Ω_R). Data from tracer miscible displacement experiments was used to estimate tracer retardation factors with R Statistical Software (www.r-project.org, version 2.12.1). Retardation factors were calculated over multiple ranges of cumulative specific discharge

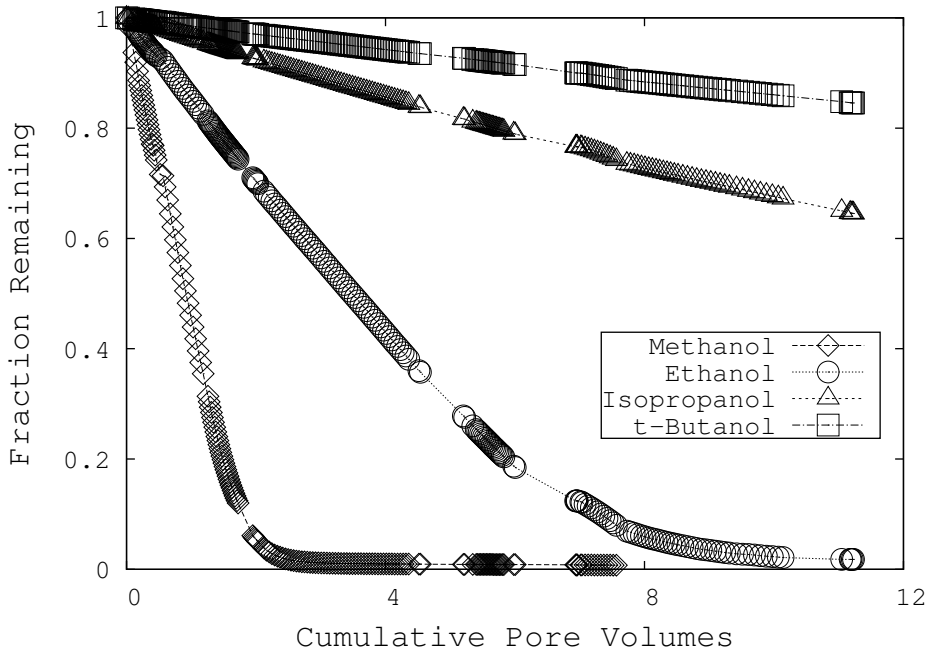


Figure 2.8.: Miscible Displacement of Tracers from GAC. Sorbent = Si-GAC 989 20x50 mesh, Darcy flux of water through column = 9.1 cm/d.

(ξ) by linear regression of tracer elution data with a fixed y-intercept of 1 (100% tracer remaining). For the retardation factor calculated over each range of ξ, the water flux estimation error at each measured data point was calculated:

$$E = \frac{\xi - [(1 - \Omega_R) \times R]}{\xi} \times 100\% \tag{2.9}$$

The range of flow over which each tracer will provide an accurate estimate of cumulative specific discharge (ξ) was determined by choosing R to minimize the error in flow estimation. Furthermore, the range of ξ for each tracer was chosen to allow entire suite of tracers to predict water flux over a sufficiently wide range of flow. A plot illustrating the maximum negative water flux estimation error, median error, and maximum positive error when R was estimated over various ranges of cumulative flow is illustrated in Figure 2.9 for the first column experiment and in Figure 2.10 for the second.

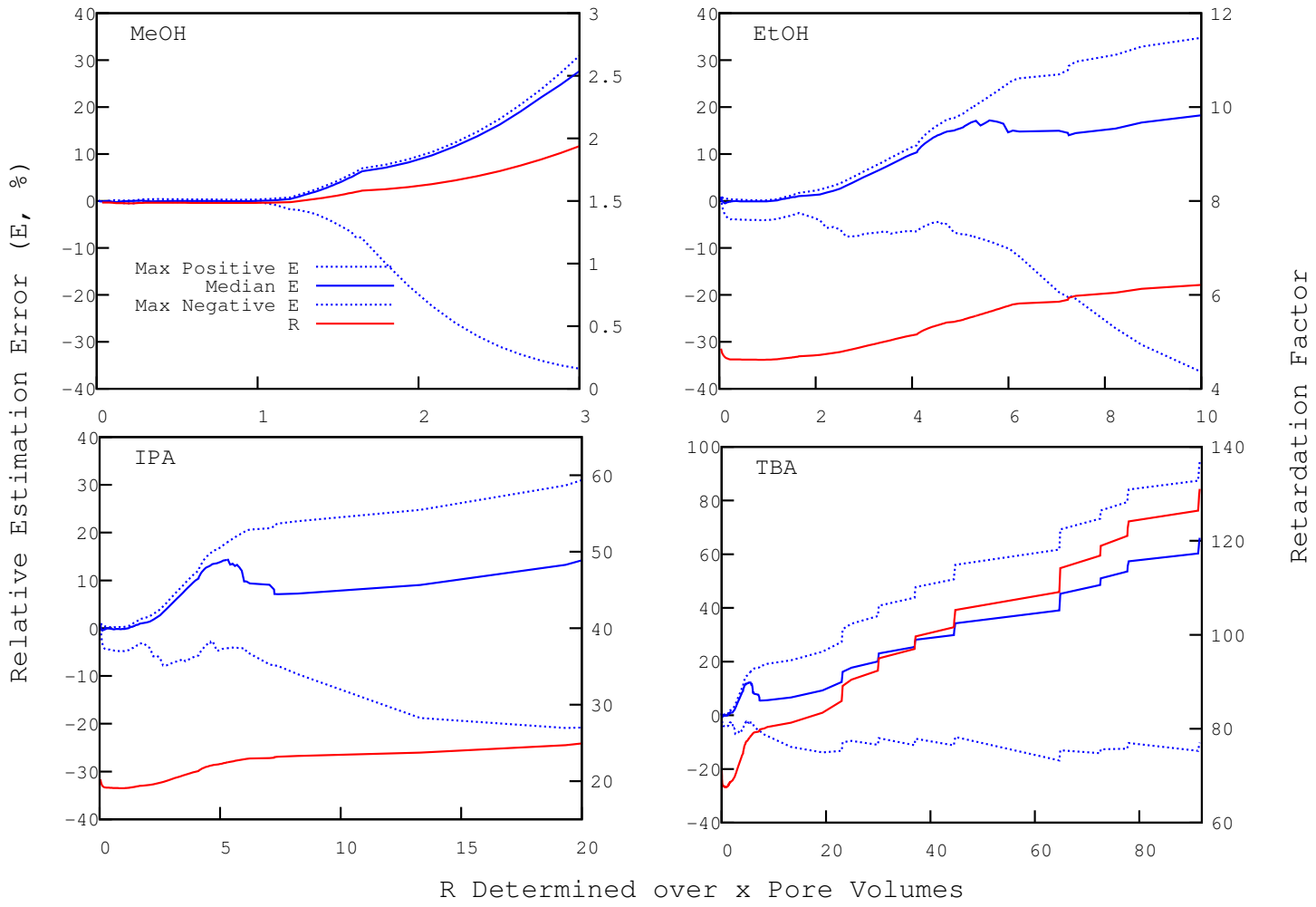


Figure 2.9.: Retardation factor calculated over multiple ranges of PSFM specific discharge from data collected during the first miscible displacement experiment (Figure 2.6) and statistics for relative estimation error.

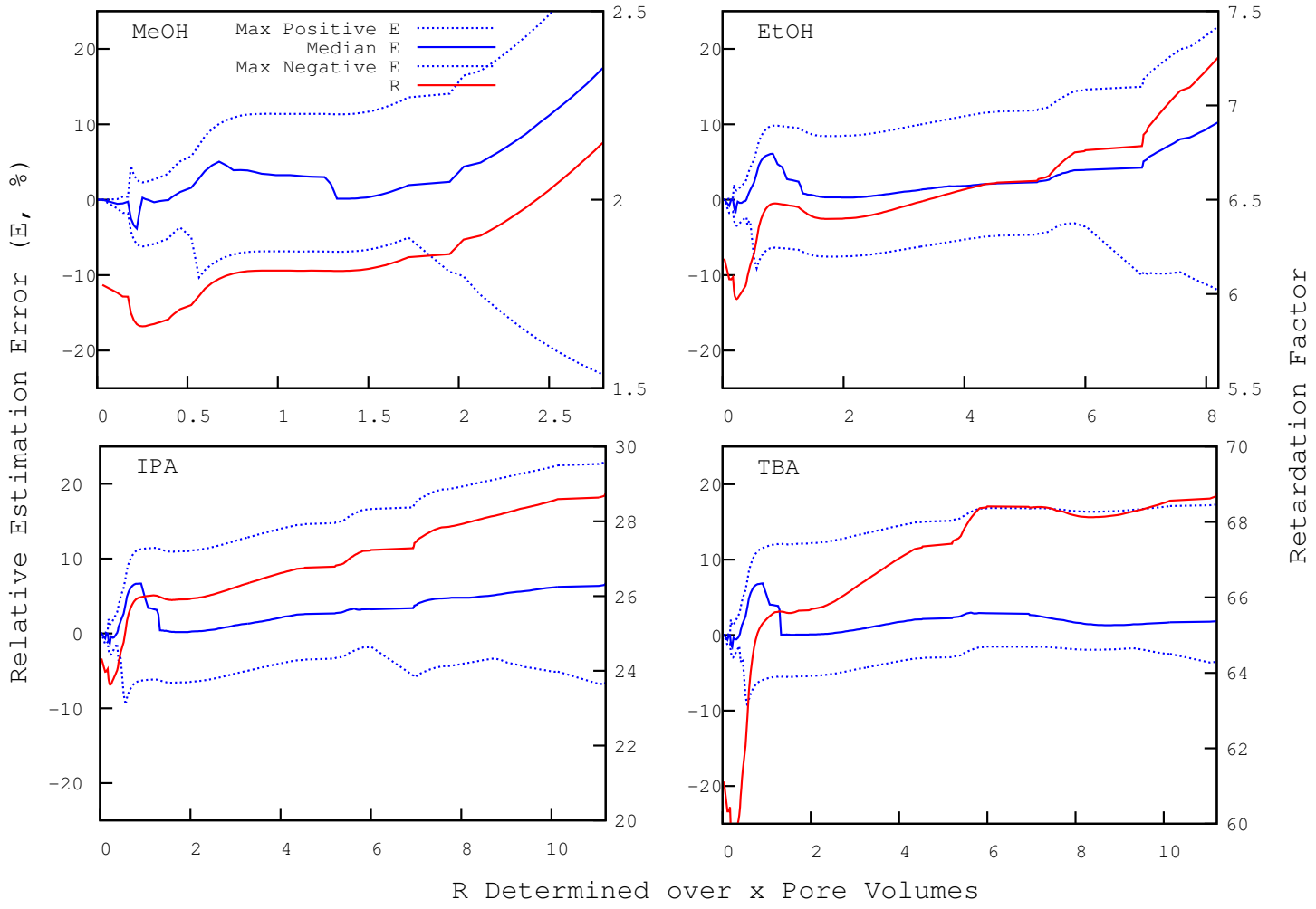


Figure 2.10.: Retardation factor calculated over multiple ranges of PSFM specific discharge from data collected during the second miscible displacement experiment (Figure 2.8) and statistics for relative estimation error.

The optimized R values, along with the range of ξ and Ω_R used to estimate R, are presented along with the maximum negative estimation error, median estimation error, and maximum positive estimation error, in Table 2.2. For field and flume deployed flux meters, any tracer having a fraction remaining within the range of Ω_R used to estimate R (the 'linear" range for that tracer) was used for estimation of PSFM cumulative PSFM water flux. If more than two tracers were within the linear range, the two tracers with Ω_R nearest the center of the linear range were used for estimation of PSFM water flux.

Table 2.2.: Retardation factors estimated over a range of specific discharge chosen to minimize water flux estimation error

Column Experiment	Tracer	Retardation Factor = R	Tracer Estimated Over Range		Relative Estimation Error (%)		
			ξ	Ω_R	Max Negative	Median	Max Positive
5-28 cm/d	MeOH	1.61 ± 0.02	0 - 2	0.01 - 1	-44.6	-9.5	17.4
	EtOH	5.76 ± 0.04	0 - 6	0.06 - 1	-58.8	-15.2	9.9
	IPA	23.73 ± 0.16	0 - 11	0.62 - 1	-57.5	-9.5	18.7
	TBA	93.84 ± 0.90	0 - 30	0.71 - 1	-72	-22.2	9.6
9.1 cm/d	MeOH	1.88 ± 0.01	0 - 2	0.04 - 1	-15.5	-3.6	9.9
	EtOH	6.76 ± 0.02	0 - 6	0.14 - 1	-14.6	-4	3.5
	IPA	28.47 ± 0.07	0 - 11	0.65 - 1	-22.7	-6.4	6.8
	TBA	68.84 ± 0.09	0 - 11.2	0.84 - 1	-17.6	-2	3.4

The relative water flux estimation error for each data point measured in the two miscible displacement experiments using the optimized R values for the tracers is shown in Figure 2.11.

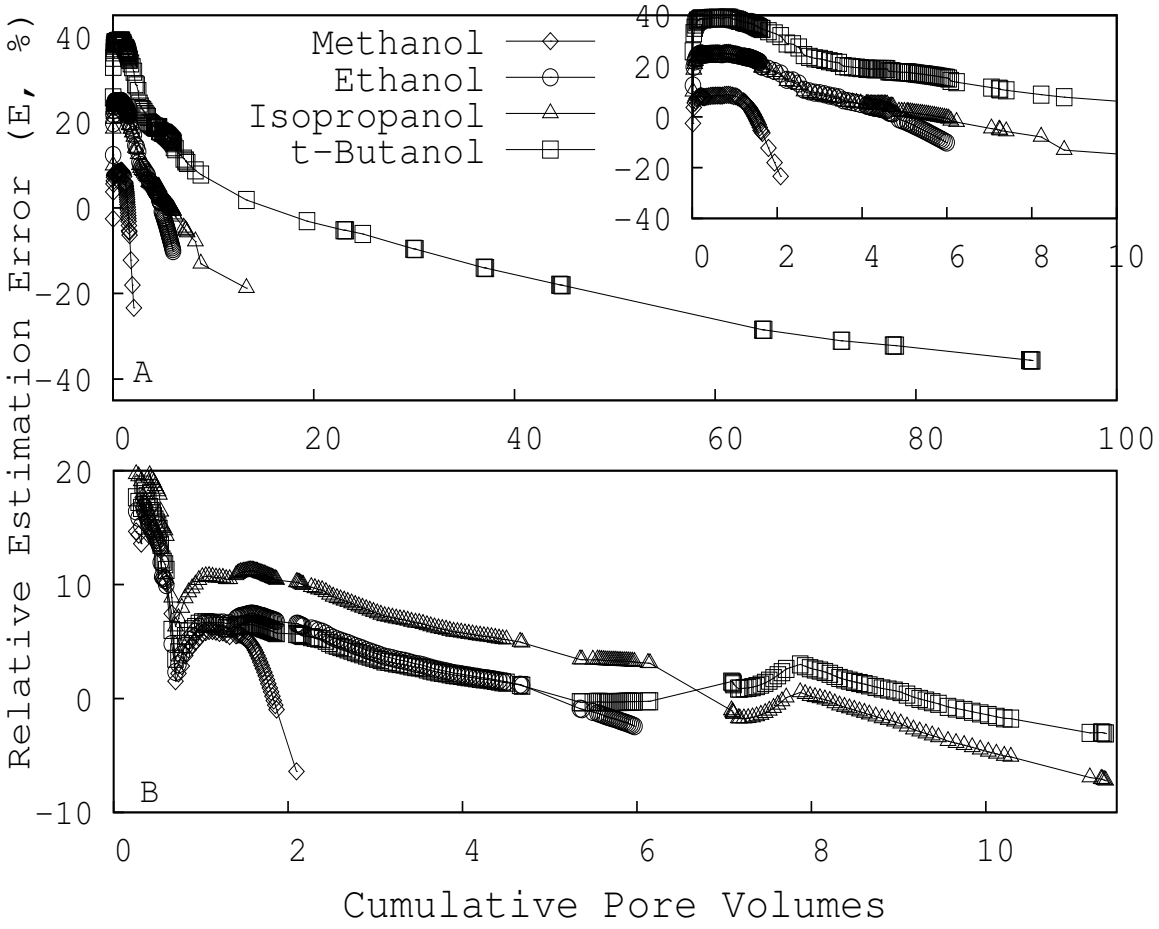


Figure 2.11.: Water flux estimation error for miscible displacement data from (A) column experiment 1 and (B) column experiment 2 using optimized R values

2.2 PSFM Fluid Dynamics and Estimation of Ambient Flow

Because of the streamlined shape of the PSFM and small inlet/outlet openings, only a small fraction of the water that is intercepted by the diameter of the unit passes through the sampler. Parameters affecting this "diversion factor" include the saturated hydraulic conductivity and length of the sorbent packing, the overall shape of the PSFM, and the size of the inlet and outlet openings. These are important design parameters that can be controlled to suit the range of external flow conditions as well as the constraints induced by the contaminants under investigation.

For example, under high flow conditions, it may be desirable to limit flow through the PSFM to avoid tracer non-equilibrium and early breakthrough of contaminants. The advantages of limiting water flux under high external flow conditions are multi-fold: (1) because the cumulative PSFM water flux will be relatively small, less hydrophobic tracers (with faster desorption kinetics and more linear behavior) can be used for estimation of flow, (2) lower linear velocity of water passing through the PSFM results in higher Damkohler number (less non-equilibrium), (3) the opportunity for contaminant breakthrough due to advective/dispersive transport is decreased, and (4) bio-fouling and/or decrease in permeability due to deposition of sediments and organic matter in the sorbent layers will be reduced. Conversely, in instances where contaminant concentrations are very low (as with hormones and pesticides), it may be desirable to allow *more* flow through the device to increase the mass of contaminant absorbed and improve detection limits. In cases where tracer desorption kinetics are limited relative to water flux and more flow cannot be allowed through the device, it may be better to deploy flux meters over longer time periods resulting in an equivalent amount of discharge while maintaining acceptable linear flow velocity.

Varying sorbent particle size to achieve the desired hydraulic conductivity is the most straight forward method of controlling PSFM water flux. Although this simple approach may be the most desirable from a mechanistic viewpoint, it may be difficult to obtain many sorbents in appropriate mesh sizes. Flow can also be reduced by introducing a layer of sand at the outlet which has smaller particle size than the sorbent. Controlling the size of the PSFM inlet and outlet or attaching a pressure controlling device to the outlet are other potential options. In the currently described study, flow was limited to allow for balance between sufficient contaminant mass capture and minimization of tracer sorption/desorption non-ideality by placing a layer of fine sand at the PSFM outlet (Figure 2.2). The fine sand layer consisted of an intimate mixture of 75 mesh and 250 mesh silica sands in a 2:1 ratio.

The saturated hydraulic conductivity of PSFM units packed with GAC, SMZ-GAC, and SMZ-GAC-Sand were measured using a constant head apparatus (Table

Table 2.3.: Saturated Hydraulic Conductivity of PSFM Units Packed with Several Configurations of Sorbent Layers

GAC layer (cm)	SMZ layer (cm)	Fine sand layer (cm)	ΔH (cm)	Δt (sec)	Q_{PSFM} (m/d)	k_{PSFM} (m/d)
15.2	NA	NA	41.7	60	134	48.9
15.2	NA	NA	38.0	60	142	56.4
15.2	NA	NA	38.0	60	153	61.3
6.3	8.9	NA	39.3	60	119	46.0
5.6	5.6	4	35.5	10290	0.367	0.16

NA = Not Applicable

2.3). The effective saturated hydraulic conductivity of the PSFM with each packing configuration (k_{PSFM}) was then determined from the specific discharge using Darcy's Law:

$$k_{PSFM} = \frac{q_{PSFM} \times L}{\Delta H} \tag{2.10}$$

A previously developed PSFM for measuring contaminant and water fluxes in surface waters was developed by Klammler and later modified by Padowski [55, 82]. The original design by Klammler used an aerodynamically shaped hydrofoil for housing of PSFM cartridges which were attached by tubes to openings at specific points along the outside of the hydrofoil. Because the shape of the hydrofoil was defined by the Joukowsky profile, the flow properties around the hydrofoil can be described mathematically [55, 82]. ΔH is related to the flow properties around the hydrofoil [specifically, the velocity of water passing the inlet and outlet openings v_1 and v_2, (L/R)] and the static pressure at the PSFM inlet and outlet openings [p_1 and p_2, (M/LT^2)] by Bernoulli's equation for velocity potential flow (Eq. 2.11).

$$\Delta H = \frac{1}{\rho g}(p_1 - p_2) = \frac{1}{2g}(v_2^2 - v_1^2) \tag{2.11}$$

where ρ = density of water (M/L^3) and g = acceleration due to gravity (L/T^2). If the velocity at the inlet and outlet openings are expressed as a multiple of the undisturbed stream velocity ($v_1 = X_1 v_s$ and $v_2 = X_2 v_s$) and the equation is solved for v_s, we obtain:

$$v_s = \sqrt{\frac{2g\Delta H}{X_1^2 - X_2^2}} \tag{2.12}$$

ΔH is estimated from the fraction of tracer remaining after PSFM deployment using Darcy's law with Eq. 2.4 substituted for q (Eq.2.13):

$$\Delta H = \frac{q_{PSFM} L}{k_{PSFM}} = \frac{[1 - \Omega_R]\phi R L^2}{k_{PSFM} t} \tag{2.13}$$

In a constant flow field, the quantity $\frac{2g}{X_1^2 - X_2^2}$ is constant and q_{PSFM} is shown to vary with the square of the undisturbed stream velocity:

$$v_s^2 \propto q_{PSFM} \tag{2.14}$$

Although the currently discussed design does not use a hydrofoil housing, because of the PSFM's streamlined shape, q_{PSFM} should be proportional to the external stream velocity in a similar manner. To evaluate this relationship, q_{PSFM} was measured at several different constant external water velocities in a flume. For estimation of the fraction of each tracer remaining in the GAC sorbent after deployment in the flume, the concentration of tracer alcohols in GAC samples (C^{GAC}) was determined by gas chromatography after solvent extraction to recover the tracers from the sorbent as outlined in Appendix D:

$$C^{GAC} = \frac{C_{GC}^{PFM} \times V_{extr}}{M_{GAC}^{extr}} \tag{2.15}$$

where C^{GAC} is the concentration of tracer in the GAC sorbent on a dry mass basis, C_{GC}^{PFM} is the concentration of tracer measured in the GC sample, V_{extr} is the sum of the volume of extraction solvent added and water present in the portion of GAC

sorbent taken for analysis, M_{GAC}^{extr} is the dry mass of GAC extracted. The fraction of tracer remaining in the GAC after deployment was then calculated using equation 2.16:

$$\Omega_R = \frac{C_{final}^{GAC}}{C_i^{GAC} \times \Omega_{DMP}} \tag{2.16}$$

where C_i^{GAC} and C_{final}^{GAC} are the concentrations of tracer remaining in the sorbent at the beginning and end of deployment respectively and Ω_{DMP} is the fraction of DMP remaining in the sorbent after deployment determined from initial and post-deployment measurement by gas chromatography as explained above. The mean specific discharge of water passing through the PSFM during the deployment period was then calculated using equation 2.17.

$$q_{PSFM} = \frac{(1 - \Omega_R)\phi LAR}{\Delta t} \tag{2.17}$$

where L is the length of the GAC layer, A is the cross sectional area of the GAC layer, and Δt is the PSFM deployment time.

The observed non-linear relationship between PSFM darcy flux and external velocity (Figure 2.12) has important implications for estimation of both external stream velocity and contaminant concentration using the PSFM. The PSFM measured value is always weighted disproportionately toward external flow or concentration occurring during periods of high flow. This phenomenon will be explored in more depth in Chapter 4.

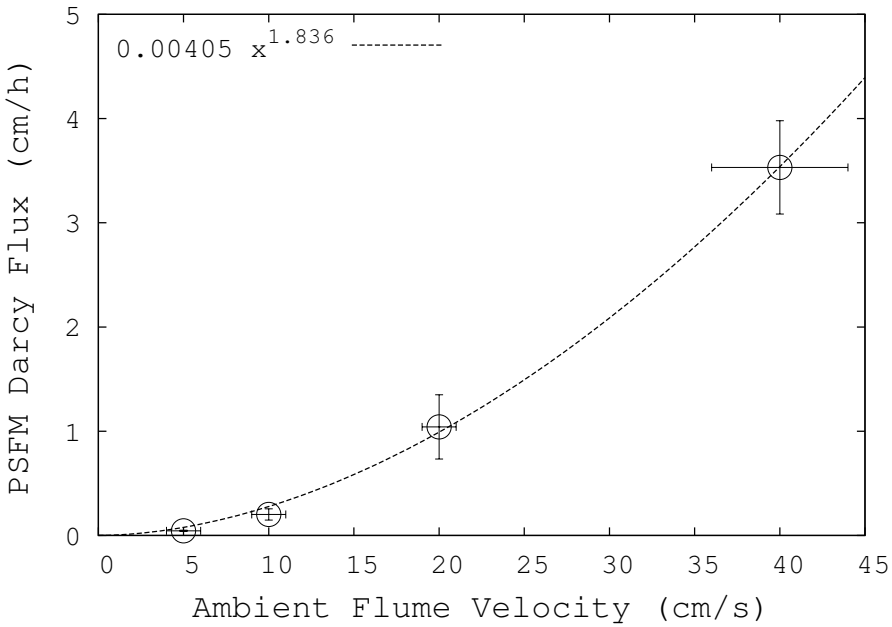


Figure 2.12.: PSFM Water Flux as a Function of Flume Velocity

2.3 PSFM Water Flux in Field Deployed Flux Meters

Flux meters were deployed at various locations in a stream network at the Purdue Animal Sciences Research and Education Center (ASREC) and the cumulative specific discharge of water passing through the PSFMs estimated from the fraction of each tracer remaining at the end of deployment (Table 2.4). Either one or two PSFM units were affixed to a steel T-style post using an adjustable T-bolt band clamp. Samplers were situated with the length of the PSFM unit parallel to the direction of stream flow and at 60% of stream stage at the time of deployment. PSFM units were assembled following the protocol outlined in Appendix L. Flux meters were wet packed starting at the outlet side and working toward the inlet. After packing/assembly, flux meters were refrigerated (4°C) for a maximum of 40 hours prior to deployment. Flux meters were kept filled with water and in the upright position (outlet side down) until deployment. After completion of the sampling period, subsamples of the GAC contained in the PSFM (2 g wet mass) were taken in duplicate

or triplicate, transfered to 35 mL glass vials with teflon lined closures, extracted using 2-butanol:4-methyl-2-pentanone (1:1), and analyzed by gas chromatography with flame ionization detector as outlined in Appendix D. The cumulative discharge of water passing through the flux meter over the deployment period was then estimated as described above.

The tracers used for estimation of specific discharge were chosen based on the linear range of the tracer elution profile measured in miscible displacement experiments. The linear range of fraction of tracer remaining (Ω_R) was 1 - 0.05, 1-0.15, 1-0.35, and 1-0.60 for MeOH, EtOH, IPA, and TBA respectively. When Ω_R for multiple tracers were within the linear range, two tracers were used for estimation of PSFM specific discharge. If more than two tracers were within the linear range, only the two tracers with Ω_R closest to the center of their linear range were used. The tracers used for estimation of water flux for each deployment are highlighted in bold in Table 2.4. Estimates of PSFM flow from individual tracers were generally in good agreement when the PSFM specific discharge was < 1000 mL. For PSFM units where two tracers were used for estimation of discharge and the cumulative specific discharge was < 1000 mL, 88% of the estimated discharge values for individual tracers were within 20% of the calculated mean. However, when the PSFM cumulative discharge was > 1000 mL and two tracers were used for estimation of PSFM flow, the deviation of flow estimates given by individual tracers was $> 25\%$ in all cases (7 occurrences). In cases of very high flow (> 2000 mL), all tracers were depleted well beyond the linear range ($\approx 20\%$ of PSFM samples). In these cases, the PSFM discharge is underestimated when using the retardation factor determined from the linear part of the tracer elution profile. These results reiterate the need for limiting flow to achieve accurate estimation of specific discharge. However, as previously discussed, a sufficient mass of the contaminants of interest must be captured to allow for detection using the available analytical instrumentation.

At the P1 and P4 sampling stations, flux meters were always deployed in pairs with two PSFM units attached to a single T-style fence post. For these flux meters,

the PSFM cumulative discharge was used to calculate the mean head differential to remove any dependence upon hydraulic conductivity due to slightly different lengths of flow restricting sand layer. The data, presented in table 2.5, shows that in $\approx 80\%$ of flux meters, the head differential for replicate flux meters was within 40% of the mean. In $\approx 43\%$ of flux meters, the head differential for replicate flux meters was within 17% of the mean. There was no apparent correlation of deviation from the mean for replicate flux meters with either deployment time or mean stream velocity.

Table 2.4.: Fraction of tracer remaining and estimate of PSFM water flux along with estimates from each individual tracer

Deployment Duration (h)	Cumulative Discharge (mL)	Ω_{MeOH}	MeOH Discharge (mL)	Ω_{EtOH}	EtOH Discharge (mL)	Ω_{IPA}	IPA Discharge (mL)	Ω_{TBA}	TBA Discharge (mL)
68	28 ± 12	**0.75**	**20**	**0.87**	**37**	1.06	NA	1.05	NA
92	46 ± 17	**0.63**	**33**	**0.82**	**58**	0.93	95	0.99	44
92	46 ± 11	**0.56**	**37**	**0.82**	**54**	0.88	160	0.94	178
76	49 ± 9	**0.45**	**43**	**0.80**	**56**	0.91	105	0.98	63
92	52 ± 20	**0.54**	**37**	**0.78**	**66**	0.85	191	0.95	146
68	61 ± 20	**0.39**	**47**	**0.73**	**75**	0.99	8	1.00	NA
73	92 ± NA	0.30	55	**0.67**	**92**	0.95	57	0.97	91
55	98 ± 5	0.17	73	**0.68**	**101**	**0.93**	**94**	0.97	90
72	114 ± NA	0.25	58	**0.59**	**114**	0.98	27	1.01	NA
102	131 ± 62	0.40	46	**0.69**	**86**	**0.85**	**175**	0.94	168
69	148 ± 40	0.18	64	**0.37**	**177**	**0.90**	**120**	0.97	30
69	153 ± NA	0.26	58	**0.46**	**153**	0.97	38	0.95	57
76	156 ± 33	ND	NA	**0.53**	**132**	**0.85**	**179**	0.96	113
55	163 ± 1	ND	NA	**0.48**	**163**	**0.88**	**163**	0.95	168
102	175 ± 77	0.24	58	**0.56**	**121**	**0.80**	**230**	0.92	228
73	179 ± 24	0.25	59	0.10	252	**0.86**	**162**	**0.93**	**196**
76	187 ± 12	ND	NA	**0.30**	**195**	**0.85**	**179**	0.94	171
76	202 ± 28	ND	NA	**0.35**	**182**	**0.81**	**222**	0.95	153
102	205 ± 40	0.21	64	**0.39**	**177**	**0.81**	**233**	0.92	226
52	226 ± 2	ND	NA	0.25	210	**0.81**	**228**	**0.92**	**225**
76	239 ± 18	ND	NA	0.22	220	**0.79**	**252**	**0.92**	**227**
92	245 ± 4	0.25	59	0.15	241	**0.80**	**242**	**0.91**	**247**
52	282 ± 26	ND	NA	0.07	260	**0.75**	**301**	**0.91**	**264**
68	312 ± 117	0.26	58	ND	NA	**0.81**	**230**	**0.86**	**395**
102	314 ± 11	0.19	71	0.33	213	**0.77**	**306**	**0.90**	**322**
96	322 ± 59	0.22	65	0.15	255	**0.78**	**281**	**0.88**	**364**
68	365 ± 121	0.25	61	ND	NA	**0.77**	**280**	**0.85**	**450**
55	380 ± 18	ND	NA	0.19	260	**0.73**	**367**	**0.88**	**392**
52	393 ± 19	ND	NA	ND	NA	**0.68**	**379**	**0.86**	**407**
92	394 ± 67	0.21	63	0.10	258	**0.71**	**346**	**0.85**	**441**
77	425 ± 11	ND	NA	0.13	243	**0.65**	**417**	**0.85**	**433**
77	429 ± 26	ND	NA	0.15	242	**0.66**	**411**	**0.85**	**448**
77	440 ± 26	ND	NA	0.13	257	**0.66**	**421**	**0.85**	**458**
102	504 ± 65	0.19	69	ND	NA	**0.64**	**458**	**0.82**	**550**
76	521 ± 40	ND	NA	ND	NA	**0.58**	**493**	**0.81**	**549**
77	522 ± 49	ND	NA	0.12	245	**0.59**	**487**	**0.81**	**556**
77	539 ± 21	ND	NA	0.12	283	**0.61**	**524**	**0.83**	**553**
96	569 ± 38	ND	NA	0.33	200	**0.53**	**595**	**0.82**	**542**
52	574 ± 36	ND	NA	ND	NA	**0.54**	**548**	**0.79**	**599**
212	584 ± 5	ND	NA	0.19	226	**0.51**	**581**	**0.79**	**587**
96	671 ± 174	0.20	66	0.16	248	**0.56**	**547**	**0.74**	**794**
55	748 ± 53	ND	NA	0.11	260	**0.42**	**711**	**0.73**	**785**
69	750 ± 172	0.26	57	ND	NA	**0.47**	**628**	**0.26**	**871**
68	759 ± 44	ND	NA	0.08	277	**0.43**	**728**	**0.74**	**790**
69	774 ± 131	0.25	58	ND	NA	**0.42**	**681**	**0.27**	**867**
68	778 ± 50	ND	NA	0.10	281	**0.43**	**743**	**0.74**	**814**
212	801 ± 65	ND	NA	0.07	267	**0.38**	**755**	**0.71**	**848**
96	846 ± 81	ND	NA	0.10	275	**0.39**	**789**	**0.71**	**903**
102	1045 ± 414	0.23	61	0.03	277	**0.37**	**753**	**0.54**	**1338**
73	1057 ± 548	0.25	58	ND	NA	**0.43**	**670**	**0.49**	**1445**
212	1148 ± NA	ND	NA	0.13	270	0.25	979	**0.64**	**1148**
96	1212 ± 416	0.15	74	0.14	267	**0.30**	**918**	**0.52**	**1506**
72	1213 ± 637	0.20	62	ND	NA	**0.35**	**763**	**0.42**	**1663**
52	1233 ± NA	ND	NA	ND	NA	0.26	873	**0.57**	**1233**
68	1245 ± 694	0.23	58	0.09	246	**0.34**	**754**	**0.37**	**1736**
212	1420 ± NA	ND	NA	0.07	266	0.14	1045	**0.52**	**1420**
52	1649 ± NA	ND	NA	ND	NA	0.08	1085	**0.42**	**1649**
73	1675 ± 1250	0.26	57	ND	NA	**0.33**	**791**	**0.10**	**2559**
92	1759 ± 1212	0.24	64	ND	NA	**0.30**	**902**	**0.16**	**2616**
212	1992 ± NA	ND	NA	0.08	258	ND	NA	**0.30**	**1992**
92	2041 ± NA	0.21	56	ND	NA	0.26	794	**0.21**	**2041**
96	2124 ± NA	ND	NA	0.15	255	0.04	1217	**0.31**	**2124**
212	2189 ± NA	ND	NA	0.08	285	ND	NA	**0.31**	**2189**
55	2295 ± NA	ND	NA	ND	NA	ND	NA	**0.24**	**2295**
55	2670 ± NA	ND	NA	ND	NA	ND	NA	**0.09**	**2670**
102	2684 ± NA	0.22	62	ND	NA	0.26	887	**0.08**	**2684**
68	2759 ± NA	ND	NA	0.09	275	ND	NA	**0.10**	**2759**
55	2901 ± NA	ND	NA	ND	NA	ND	NA	**0.08**	**2901**
96	2927 ± NA	ND	NA	0.25	236	ND	NA	**0.09**	**2927**

Tracer remaining and flow estimates from individual tracers shown in bold were used for calculation of PSFM cumulative discharge. Ω_R = Fraction of tracer remaining, ND = Not detected, NA = Not applicable

Table 2.5.: Cumulative discharge and head differential in side-by-side deployed PSFM units.

Deployment Date	Location	Deployment Duration (h)	Stream Mean Velocity (cm/s)	Cumulative Discharge (mL)	Mean Cumulative Discharge (mL)	PFM Head Drop (cm)	Difference from Mean Head Drop (fraction)
3/7 - 3/10	P1	69	31	148 153	150	1.19 1.23	0.01
3/19 - 3/22	P1	73	18	1057 92	575	8.09 0.71	0.84
4/4 - 4/7	P1	76	18	187 156	171	1.36 1.13	0.09
4/12 - 4/14	P1	52	48	282 574	428	3.04 6.18	0.34
4/14 - 4/23	P1	212	40	584 1148	866	1.79 3.30	0.30
4/23 - 4/26	P1	77	42	425 440	432	2.70 2.96	0.04
5/6 - 5/10	P1	92	23	52 46	49	0.31 0.24	0.13
5/10 - 5/14	P1	102	21	205 504	354	0.98 2.54	0.44
5/25 - 5/29	P1	96	29	569 322	445	2.97 1.77	0.25
6/3 - 6/5	P1	55	32	2901 2670	2786	29.4 27.1	0.04
3/7 - 3/10	P4	69	ND	774 750	762	6.27 6.07	0.02
3/19 - 3/22	P4	72	ND	114 1213	664	0.88 9.32	0.83
4/4 - 4/7	P4	76	ND	239 202	221	1.74 1.47	0.08
4/12 - 4/14	P4	52	ND	393 226	310	4.23 2.44	0.27
4/14 - 4/23	P4	212	ND	1420 2189	1805	3.94 5.58	0.17
4/23 - 4/26	P4	77	ND	429 522	476	3.04 3.78	0.11
4/26 - 4/29	P4	68	ND	312 759	536	2.75 6.21	0.39
5/6 - 5/10	P4	92	ND	2041 394	1217	13.1 2.54	0.68
5/10 - 5/14	P4	102	ND	314 175	245	1.67 0.89	0.31
5/25 - 5/29	P4	96	ND	2927 1212	2069	15.7 7.19	0.37
6/3 - 6/5	P4	55	ND	163 380	271	1.71 3.85	0.38

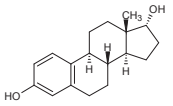
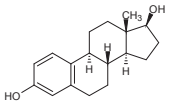
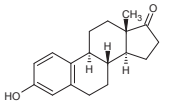
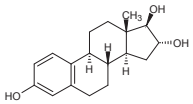
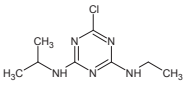
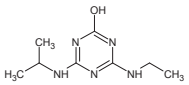
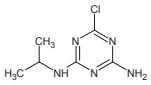
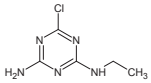
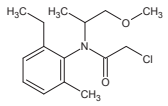
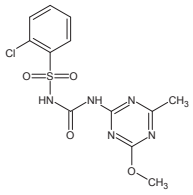
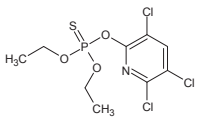
3 CHARACTERIZATION OF CONTAMINANTS AND SORBENTS

3.1 Physicochemical Description of Contaminants

Steroid hormones and the herbicides atrazine and metolachlor, which are commonly present in agronomic environments, were chosen for investigation of PSFM performance (Table 3.1). The steroid hormones 17α-estradiol, 17β-estradiol, estone, and estriol are present in animal manures which are frequently applied to arable land as fertilizer and as a means of disposal. Although these compounds are naturally occurring in all vertebrates and some insects [26, 71, 96], they are known to disrupt the endocrine system when absorbed from the environment because of their high estrogenic potency [60, 72, 81, 101]. Aquatic species inhabiting surface water bodies affected by agricultural activity are particularly likely to be exposed to significant levels of steroid hormones due to their immediate proximity to fields where manures are applied.

Atrazine is an herbicide which is banned in several European counties, but is still used extensively in the United States for control of broadleaf weeds [120, 121]. Although atrazine has been controversially implicated in feminization of male frogs [45] and in skewing of sex ratios in Daphnia species [27], other researchers have found no significant endocrine effects on frogs [56] or Daphnia [80, 83] at concentration levels typically found in streams and rivers and the United States Environmental Protection Agency recently concluded that atrazine does not adversely affect amphibian reproductive function [122]. The popular herbicide is also controversial because of its occurrence in surface and drinking water and its reputed effects on prenatal development of children [1, 69, 131]. The PSFM was evaluated as a tool for measuring the concentration of atrazine and three of its degradation products, along with the herbicides metolachlor and chlorsulfuron, and the insecticide chlorpyrifos.

Table 3.1.: Contaminants of Interest with pK_a values for ionizable compounds (NI = not ionizable from pH = 0-14) and log K_{ow} at neutral pH

Contaminant Name	**Structure**	pK_a	**Log** K_{ow}
17α-Estradiol(aE2)		10.3[29, 49, 54]	3.7[90]
17β-Estradiol (bE2)		10.4[54, 62]	3.8[90]
Estrone (E1)		10.6[29, 49, 54, 62]	3.5[90]
Estriol (E3)		10.4[49]	2.8[135]
Atrazine (ATZ)		1.71[125]	2.6[32, 86]
Hydroxyatrazine (ATZ-OH)		5.15[125]	1.6[18]
Desethylatrazine (ATZ-DE)		1.65[125]	1.5[32, 86]
Desisopropylatrazine (ATZ-DIP)		1.58[125]	1.1[32, 86]
Metolachlor (MTC)		NI[2]	3.4[97, 137]
Chlorsulfuron (CSF)		3.6[105]	0.2[92]
Chlorpyrifos (CPF)		NI[87]	4.2[119]

3.2 Contaminant Sorption

The collection of contaminants by a passive sampler can be described as partitioning between the sorbing phase and the external environment [53, 115, 134]. High sorptive capacity for the contaminants of interest and reversibility of sorption (extractability) are important factors when considering a sorbent for use in a PSFM. In the case of steroid hormones and atrazine, which have low to moderate polarity, a hydrophobic sorbent is required. Since particulate laden stream water must be able to pass through without a decrease in permeability, a highly porous or granular sorbent is desirable. A number of potential candidates were considered for the PSFM including granular activated carbon (GAC), surfactant modified zeolite (SMZ), styrene/divinylbenzene copolymer beads, solid phase extraction disks, and organic coated glass beads or sand.

3.2.1 Granular Activated Carbon

Granular activated carbon (GAC) has been used in previous passive flux meter designs because of its high sorptive capacity, micro-porosity, and because GAC is available in many different particle sizes [5, 20, 44, 82]. Porosity and bulk density of GAC were determined gravimetrically (Appendix B). In order to test the suitability of GAC as a sorbent for the contaminants of interest, batch sorption experiments were conducted at 23°C in glass centrifuge tubes with teflon-lined closures. Details of the experimental protocol are in Appendix F. Briefly, GAC (0.1 g) was equilibrated for 20 hours with hormones dissolved in 0.005 M $CaCl_2$ (initial concentrations of 20, 50, 100, 200, and 400 ng/L). All hormone lost from aqueous solution was assumed to be sorbed to GAC since a suitable extraction protocol had not yet been developed. The results, presented in table 3.2, indicate that the hormones are strongly sorbed to GAC and breakthrough of hormones from the PSFM should not occur if equilibrium conditions prevail. For example, given a sorption partition coefficient of $K_d = 200 L/kg$, sorbent

Table 3.2.: Measured GAC/Water Sorption Coefficients for Hormones on GAC

Analyte	K_d [a]	K_f [b]	N
E1	233 ± 12	205 ± 43	1.08 ± 0.13
a-E2	482 ± 13	500 ± 44	0.97 ± 0.06
b-E2	257 ± 14	212 ± 52	1.12 ± 0.15
E3	482 ± 27	540 ± 40	1.27 ± 0.15

Sorbent = Si-989 GAC 20x50 mesh, [a] Lkg^{-1} [b] $mg^{1-N}L^{N}kg^{-1}$

porosity of $\phi = 0.73$ and bulk density of $\rho = 0.5\ g/cm^3$, the retardation factor is equal to:

$$R = 1 + K_d\frac{\rho_b}{\phi} = 138 \tag{3.1}$$

Considering a darcy flux of water through the PSFM of 2.5 cm/h (high flow conditions) and sorbent length of 14 cm, the contaminant would not break through for 32 days assuming purely advective transport under equilibrium conditions. However, non-equilibrium conditions or sorption non-linearity can result in dispersion and consequent premature breakthrough relative to what is predicted by the retardation factor measured under equilibrium conditions.

Given that sorbent-water partition coefficients for the hormones were sufficiently high to allow for capture of the contaminants using the PSFM (neglecting dispersion effects), development of a suitable extraction protocol was attempted. A variety of solvents including methanol, dichloromethane, acetone, butanone, isopropyl ether, octanol, ethyl acetate, acetonitrile, methyl-t-butyl-ether, and mixtures of these were screened for extraction efficiency (Table 3.3). GAC (170 mL) was wetted with deionized water (170 mL) in a 250 mL jar overnight under vacuum (25 in Hg). Wet GAC (1.5 g) was transferred to a 35 mL centrifuge tube along with the appropriate extraction solvent (25 mL) and 1 mL of a mixture of hormones (8 mg/L each) in acetonitrile. After 4 h mixing on a rotary end-over-end mixer, samples were centrifuged

Table 3.3.: Batch Extraction of Hormones from GAC

Extraction Solvent	aE2	bE2	E3
	recovery (%)		
dichloromethane	1	1	0
methanol	1	2	2
dichloromethane/ acetonitrile (7/3)	1	2	1
ethyl acetate	2	2	2
dichloromethane/ acetone (1/1)	2	2	0
diisopropyl ether	3	3	0
methyl-t-butyl-ether/ methanol (8/2)	3	5	1
ethyl acetate/ methanol (8/2)	3	3	3
acetone	3	3	4
diisopropyl ether/ methanol (8/2)	4	3	2
butanone	7	5	4
dichloromethane/ acetone (7/3)	7	4	5
butanone/ methanol (6/4)	7	5	8
dichloromethane/ butanone (1/1)	8	5	4
butanone/ methanol (8/2)	8	20	9
dichloromethane/ butanone (7/3)	9	6	3
dichloromethane/ methanol (9/1)	9	7	6
butanone/ methanol (9/1)	10	5	9
dichloromethane/ acetone (1/1)	11	6	6
dichloromethane/ methanol (75/25)	14	10	19
dichlromethane/ methanol (1/1)	16	10	23
dichloromethane/ methanol (7/3)	18	12	25

Sorbent/ extractant = 1.5 g/ 25 mL, extraction time = 4 h, extraction temp = 23°C, initial hormone concentration = 333 ng/mL.

(750 g, 20 min) and a 2 mL aliquot of supernatant was evaporated to dryness under a gentle stream of nitrogen in a 2 mL HPLC vial. The samples were reconstituted in 0.5 mL methanol and analyzed for hormones by HPLC with fluorescence detection. A solvent mixture of dichloromethane:methanol (7:3) resulted in higher extraction recovery of all hormones than any other solvent or solvent mixture tested.

Accelerated solvent extraction of hormones from GAC was performed in an attempt to improve extraction recovery. GAC (1 g) was weighed into a 35 mL centrifuge tubes in triplicate along with a 1 mL aliquot of a solution containing hormones (8 mg/L) dissolved in acetonitrile. The mixture was allowed to sit at room temperature for 1 h. A glass fiber filter was placed at the bottom of an ASE extraction cell, and the cell was filled half way with a mixture of sand/ silica gel (15/2). The hormone amended GAC was transferred to the extraction cell, and the cell was filled with the sand/ silica gel mixture and topped with a glass fiber filter. Two 5 min extraction cycles were performed with dichloromethane:methanol (7:3) at 100°C (5 min heating time, 70% volume). The extracts were washed with 50 mL water, dried with anhydrous sodium sulfate, and concentrated to $\approx$ 50% volume by rotary evaporation. A 2 mL aliquot was transferred to an HPLC vial, evaporated to dryness under a gentle stream of nitrogen, and reconstituted in 0.5 mL methanol. Samples were analyzed by HPLC with fluorescence detection. Recovery was 86$\pm$33, 67$\pm$27, 51$\pm$19 for aE2, bE2, and E3 respectively.

Although recoveries were adequate when extracting 1 g of GAC using ASE, larger amounts of the sorbent needed to be extracted to meet detection limits for hormones and pesticides in a stream due to the very low concentrations of these contaminants. For example, a PSFM with internal volume of 145 mL and GAC density of 0.5 g/mL will contain 72.5g of dry GAC. In a stream where the hormone concentration is 0.1 ng/L and 1 L of water flows through the PSFM, 0.1 ng of hormone will be trapped on the packing. If only 1 g of GAC is extracted, the result is 0.1 ng X (1/72.5) = 1.4 pg of hormone in the extract. If concentrated down to 0.5 mL, the final concentration is 2.8 pg/L, which is below the limit of detection. However if 7 g of GAC is extracted, the final concentration will be 20 pg/L which is above the LOD for all hormones except for E3.

Another test using ASE was performed to determine if hormones could be extracted from a larger amount of the sorbent. GAC (8 g dry mass) was transferred to a 100 mL beaker along with diatomaceous earth (15 g) and a solution containing

hormones (8 mg/L) dissolved in acetonitrile (0.5 mL). The mixture was transferred to an ASE extraction cell and extraction with dichloromethane/ methanol (75/25) was performed with two extraction cycles of 5 min each and 75% flush volume. Extraction was performed at 60, 70, 80, 90, 100, and 125 °C to evaluate the affect of temperature on extraction efficiency. Recovery of aE2, bE2, E1, and E3 was <25% for all hormones and all temperatures.

Although adsorption of apolar compounds on GAC is generally considered to be by a non-specific hydrophobic or $\pi - \pi$ bonding mechanism, compounds with additional functionality can also interact with oxygen containing groups at the surface. Many studies have examined the forces involved in phenol sorption on GAC which is generally considered to be a combination of physi-sorption ($\pi - \pi$ bonding and hydrophobic) and chemi-sorption (charge transfer bonding with surface oxygens)[76, 77, 116, 124]. In addition to surface adsorption, coupling reactions of phenolic compounds on the GAC surface can be catalyzed by molecular oxygen [111, 116, 117, 128–130]. Because the estrogens also contain a phenolic group, such processes cannot be ruled out as a possible explanation for low extraction recovery. Other researchers have suggested that surface carboxyls and/or basic functional groups play an important role in phenol sorption and may be at least partially responsible for the sorption hysteresis commonly seen on activated carbons[116, 117]. Of particular interest is a study comparing nonylphenol and phenol sorption on GAC[76]. In this work, it was discovered that nitric acid treatment of the surface increased nonylphenol sorption while decreasing phenol sorption indicating different mechanisms at work. It was theorized that with nonylphenol, strong bonding of the phenolic group to surface OH, COOH, and SiO2 is likely a dominant mechanism while phenol binds primarily via $\pi - \pi$ interactions. Irrespective of the precise mechanism, the low extraction recovery of the estrogens from GAC deems it an unsuitable sorbent for these contaminants in the PSFM. Because of extensive previous work characterizing retention and extraction behavior of the tracers on the sorbent; however, GAC was used as a sorbent for estimation of PSFM water flux by measurement of tracer depletion. Furthermore, the

addition of a separate sorbent phase for contaminants allows for different sorbents to be used depending on the type of target contaminant increasing the versatility of the PSFM.

3.2.2 Surfactant Modified Zeolites

Zeolites are a diverse group of micro-porous, aluminosilicate minerals with high surface area and cation exchange capacities [38, 107]. Zeolites have a permanent negative surface charge due to isomorphous substitution of Al for Si in the crystal lattice [28]. The cation exchange capacity for zeolites can vary from 1 - 3 meq/g depending on the degree of substitution [73]. Cation exchange sites are located primarily in channels and cavities throughout the zeolite structure that are only accessible to small ions and molecules. The exclusion of larger ions and molecules is called ion or molecular sieving [73].

Although, the negative charge makes zeolites effective sorbents for cations, they have low affinity for hydrophobic or negatively charged species. However, substitution of surface cations for cationic surfactants resulting in surfactant modified zeolite, or SMZ, can impart hydrophobic character to the zeolite surface [28, 99, 100, 107]. Because of the large size of surfactant molecules, they cannot penetrate to interior cation exchange sites. If surfactant loading increases beyond that required to fill all external exchange sites, the hydrophobic tails of surfactant molecules will begin to align with one another leaving the positively charged end of one of the molecules at the exterior surface of the sorbent. This configuration allows for not only sorption of hydrophobic compounds, but also anionic species. Since the internal zeolite pores are not accessible to surfactant molecules, the zeolite still carries a net negative charge resulting in a sorbent capable of attracting cations, anions, and hydrophobic molecules (Figure 3.1).

Porosity and bulk density of zeolite was determined gravimetrically as outlined in Appendix B. SMZ with 70% monolayer surfactant coverage was prepared according

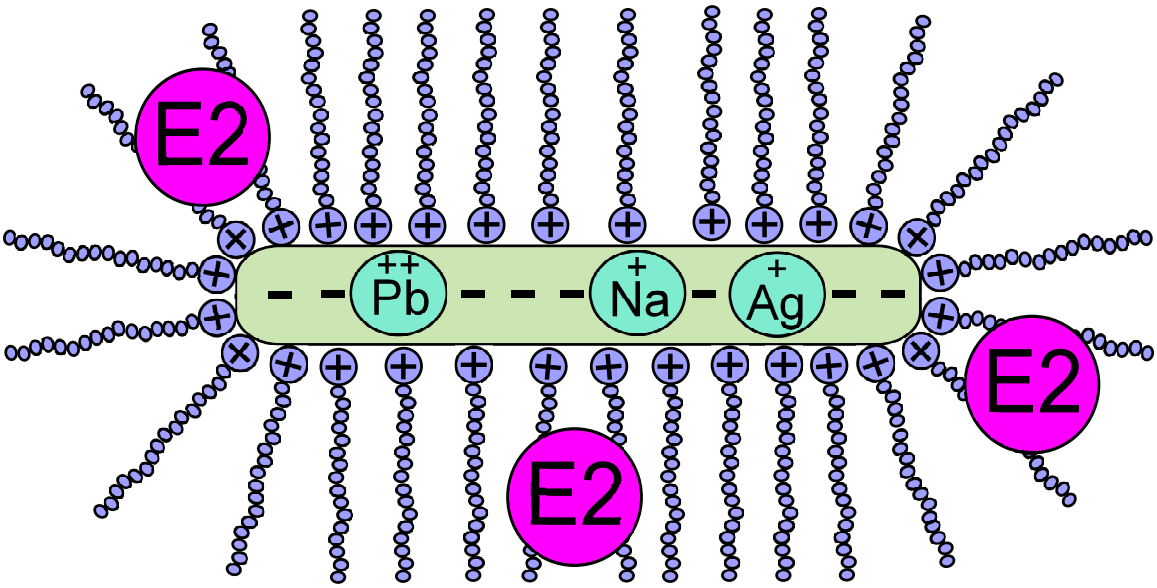


Figure 3.1.: Graphical Representation of SMZ surface showing absorbed cationic surfactant, estradiol (E2), and the cations lead (Pb^{++}), sodium (Na^{+}), and silver (Ag^{+}).

to the procedure outlined in Appendix H. Zeolite was washed with sodium acetate to saturate all exchange sites with Na^{+}, the Na^{+} saturated zeolite was then equilibrated with an amount of silver nitrate to cover 15% of the total exchange sites, and finally, the silver-zeolite was equilibrated with sufficient cetyltrimethylammonium bromide (CTAB) to cover 70% of the external cation exchange sites.

Sorption of estrogens and pesticides on SMZ was measured to evaluate the suitability of SMZ as a sorbent for these contaminants in the flux meter. SMZ was equilibrated with a sterile aqueous solution containing a mixture of aE2, bE2, E1, E3 (17 ng/mL each), ATZ (26 ng/mL), ATZ-DE (47 ng/mL), ATZ-DIP (76 ng/mL), ATZ-OH (155 ng/mL), MTC (110 ng/mL), CSF (25 ng/mL), and CPF (34 ng/mL). SMZ-water partition coefficients (K_d) for pesticides were measured after equilibration for 0 (no SMZ controls), 1, 2, 4, 10, 27, and 72 h while K_d for hormones was measured at 0, 2, 4, 10, 24, and 72 h to evaluate sorption kinetics (Figures 3.2 and 3.3). After the prescribed time interval, samples were centrifuged, and 0.5 mL of

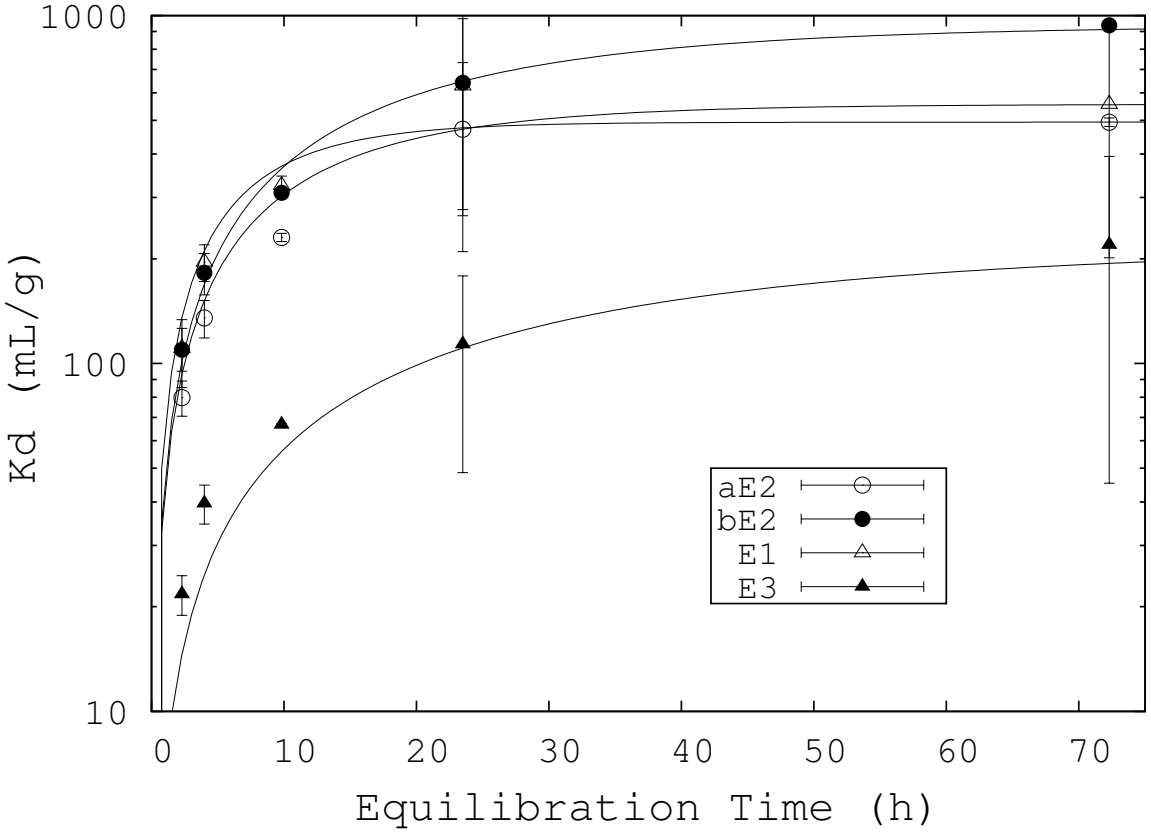


Figure 3.2.: Sorbent-water partition coefficients (K_d) for sorption of estrogens on SMZ as a function of time with fist order kinetic fits. Isotherm temp = 23°C, sorbent/ solution = 0.1 g / 38 mL, Initial conc = 17 ng/mL.

the aqueous phase transferred to a 2 mL HPLC vial using a volumetric glass pipet, 0.5 mL of methanol was added as a preservative and the aqueous phase analyzed by LC/MS. The remaining aqueous solution was decanted and SMZ extracted with 35 mL of methanol. After centrifugation, methanol extracts were analyzed by LC/MS. A detailed protocol for the sorption experiment is given in Appendix J.

For all contaminants except ATZ and its degradates, SMZ-water sorption coefficients were > 100 mL/g. Under equilibrium conditions, breakthrough would therefore take at least 10 days under high flow conditions (sorbent length = 8.5 cm, PSFM water velocity = 2.5 cm/hr, $\phi = 0.76$, $\rho_b = 0.5$ g/cm^3). However, ATZ and its degradates have much lower K_d and breakthrough of these compounds could occur in as little

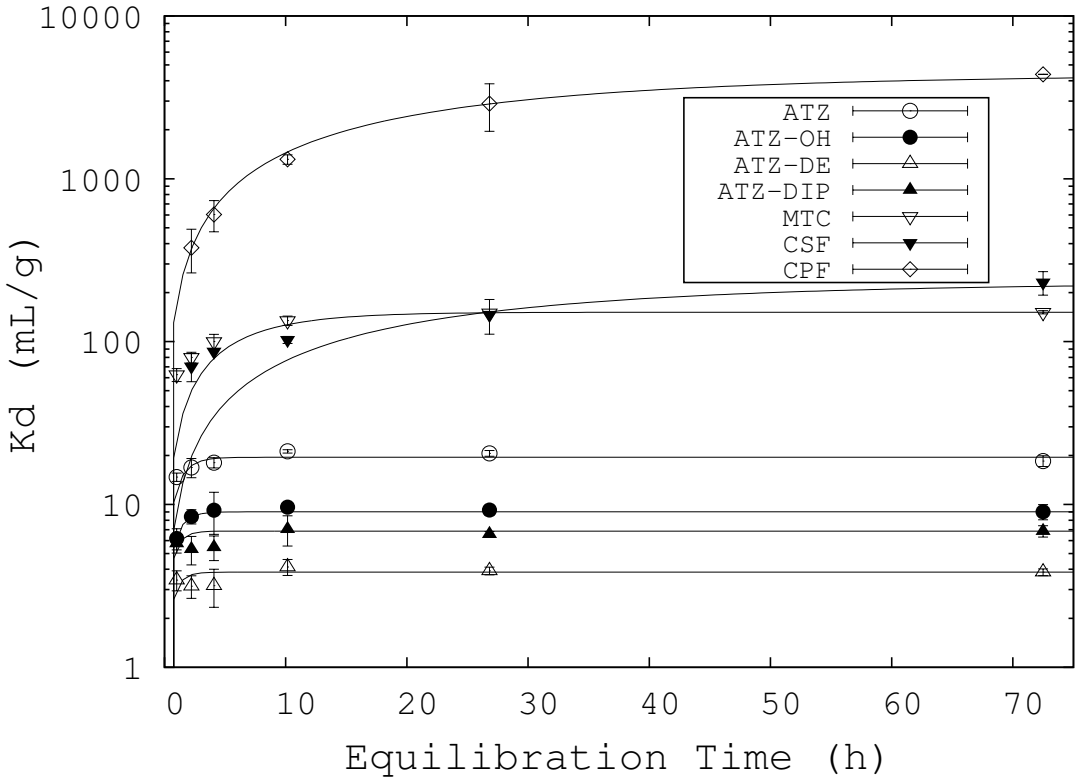


Figure 3.3.: Sorbent-water partition coefficients (K_d) for sorption of pesticides on SMZ as a function of time with fist order kinetic fits. Isotherm temp = 23°C, sorbent/ solution = 8 g / 33 mL, Initial conc: ATZ = 26 ng/mL, ATZ-DE = 47 ng/mL, ATZ-DIP = 76 ng/mL, ATZ-OH = 155 ng/mL, MTC = 110 ng/mL, CSF = 25 ng/mL, CPF = 34 ng/mL.

as 0.4 - 2 days under high flow conditions (assuming equilibrium sorption). In the case where sorption non-equilibrium is significant (retention time of water in PSFM is short relative to sorption rate), though, increased solute dispersion may result in premature breakthrough of contaminants.

Sorption data was fit to a first order kinetic model to obtain a sorption rate constant (lines in Figures 3.2 and 3.3):

$$K_{d,t} = K_d^{\infty}(1 - e^{-kt}) \tag{3.2}$$

Table 3.4 lists the sorption rate constants along with Damkohler numbers for several flow rates representative of those experienced in the field. Clearly, non-equilibrium is a concern for all compounds except for ATZ and its degradates at low flow rates. While it is possible to decrease PSFM darcy flux of water by measures previously discussed thereby reducing the degree of non-equilibrium, increasing PSFM deployment time is the only viable option for compounds such as steroid hormones and pesticides which are present in very low concentrations and require a large sampling volume to allow for sufficient mass capture. If contaminants are shown to be stable for the duration of the extended deployment times, this option should allow for more accurate concentration/flux estimates and reduce costs.

Table 3.4.: Rate constants for sorption of hormones and pesticides on SMZ and Damkohler numbers at several flow rates representative of those typical in field deployed PSFMs

Compound	Kd (mL/g)	α (hr^{-1})	Damkohler Number at V_m^* 0.2cm/hr	0.79cm/hr	3.2cm/hr
aE2	494	0.032	0.9	0.2	0.1
bE2	937	0.021	0.6	0.1	0.0
E1	556	0.029	0.8	0.2	0.1
E3	219	0.055	1.5	0.4	0.1
ATZ	18	0.28	8	2.0	0.5
ATZ-OH	9.0	0.46	13	3.2	0.8
ATZ-DE	3.8	0.81	22	5.7	1.4
ATZ-DIP	6.9	0.55	15	3.8	1.0
MTC	152	0.07	1.9	0.5	0.1
CSF	231	0.05	1.4	0.4	0.1
CPF	4382	0.01	0.2	0.1	0.0

Sorbent length = 8.5 cm

3.3 Extraction of Contaminants from SMZ and Stream Water

Because of the low concentrations of these contaminants in stream water, a large amount of SMZ from field deployed flux meters must be extracted to allow for accurate quantitation. With batch extraction, this would require either a very large volume of solvent or soxhlet type extraction. Accelerated solvent extraction (ASE) is a method by which solid matrices can be extracted efficiently using elevated temperature and pressure effectively minimizing the volume of solvent required.

Hormones and pesticides were extracted from SMZ using methanol. ASE extraction parameters including extraction temperature, number of extraction cycles, extraction cycle time and flush volume were optimized for the compounds of interest (Table 3.5). A flush volume of 60% was used for all extractions since further increasing the flush volume did not result in greater yields. Estrogens were extracted in $> 75\%$ yield with temperatures $\geq 75°C$. Performing 2 extraction cycles appeared to increase yield slightly while using 3 extraction cycles did not seem to provide any additional benefit. Increasing extraction time from 5 to 10 or 15 minutes did not

improve recovery. Recovery of ATZ was also maximized at temperatures above 75°C. ATZ-DE recovery was optimal at 75°C while maximum recovery of both ATZ-DIP and ATZ-OH was obtained at the highest temperature (125°C). As with the estrogens, 2 extraction cycles resulted in a recovery increase for ATZ and its degradates, but 3 extraction cycles did not further increase yield. Longer extraction times did not result in better recovery for ATZ, ATZ-DE, or ATZ-DIP, but may benefit extraction of ATZ-OH. Extraction recovery of MTC, CSF, and CPF were maximized at lower temperature (60 or 75°C). Both MTC and CSF appeared to benefit from longer extraction times and multiple extraction cycles, although 3 cycles did not improve recovery for CSF. Recovery of CPF was very low under all conditions tested presumably because the extremely hydrophobic compound could not be extracted from the wet sorbent using methanol. Given these results, field samples were extracted using two extraction cycles of 5 min each at 75°C, heating time of 5 min, and flush volume of 30%. A detailed protocol for extraction of contaminants from SMZ is outlined in Appendix I. Briefly, a glass fiber filter was placed at the bottom of the ASE extraction cell with a 1 cm layer of pelletized diatomaceous earth, SMZ was weighed and transfered to the extraction cell. A glass fiber filter was placed at the top of the extraction cell and the cell was closed tightly. Three extractions were required to extract all SMZ from each flux meter. All extracts from each flux meter were combined into a single sample.

Table 3.5.: Accelerated Solvent Extraction of Estrogens and Pesticides from Surfactant Modified Zeolite

Extraction			Recovery (Fraction of Applied)									
Temp (^{o}C)	Time (m)	Cycles	aE2	bE2	E3	ATZ	ATZ-DE	ATZ-DIP	ATZ-OH	MTC	CSF	CPF
60	5	1	0.66	0.59	0.67	0.54	0.88	0.26	0.12	0.84	0.62	0.16
75	5	1	0.82	0.76	0.85	0.66	1.06	0.53	0.23	0.83	0.69	0.04
90	5	1	0.75	0.76	0.82	0.69	0.95	0.83	0.31	0.74	0.62	0.08
105	5	1	0.80	0.74	0.85	0.68	0.85	0.73	0.32	0.69	0.40	0.04
120	5	1	0.83	0.75	0.85	0.70	0.85	0.85	0.48	0.68	0.19	0.00
75	5	1	0.88	0.79	0.86	ND	0.86	1.11	0.61	0.69	0.37	0.00
75	5	2	0.93	0.81	0.90	ND	1.02	1.12	0.72	0.72	0.43	0.00
75	10	1	0.85	0.75	0.83	ND	0.88	0.74	0.64	0.80	0.40	0.00
75	10	2	0.92	0.80	0.91	ND	0.97	0.92	0.86	0.77	0.56	0.00
75	10	3	0.78	0.88	0.92	ND	0.99	1.25	0.83	0.83	0.46	0.00
75	15	1	0.86	0.71	0.77	ND	0.73	0.92	0.79	0.72	0.46	0.00
75	15	2	0.73	0.82	0.87	ND	0.81	1.19	0.72	0.80	0.46	0.00

Contaminants were extracted from stream water samples using solid phase extraction (SPE). Recovery of contaminants from estrogen and pesticide amended stream water samples are presented in Table 3.6. Stream water samples (1 L) were collected in HDPE bottles, filtered (VWR glass fiber filter, Grade 696, 1.2 μm exclusion size) through a B*ü*chner funnel, amended with either 0.5 mL of a solution containing 8.4 ng/mL aE2, 8.1 ng/mL bE2, 6.3 ng/mL E1, 4.3 ng/mL E3 dissolved in methanol or 50 μL of a solution containing 11.9 mg/L ATZ, 11.4 mg/L ATZ-DE, 11.4 mg/L ATZ-DIP, 13.3 mg/L ATZ-OH, 9.74 mg/L CPF, 11.4 mg/L CSF, and 11.4 mg/L MTC dissolved in methanol. Samples were mixed by turning end-over-end several times and extracted immediately using solid phase extraction with Phenomenex SDB-L cartridges (200 mg, 3 mL). After extraction, samples were evaporated to dryness under a gentle stream of nitrogen, reconstituted in methanol, and analyzed by LC/MS with electrospray ionization. Details of the extraction and LC/MS analysis are given in in Appendices K and M respectively. All compounds were recovered in $> 70\%$ yield except for ATZ-DIP which was likely not hydrophobic enough to be captured by the SPE sorbent.

3.4 Stability of Contaminants

3.4.1 Stability in PSFM

Ideally, a passive sampling device should have some mechanism to preserve contaminants after they have been captured by the sampler. Many studies have shown that sorption to soils effectively shields chemicals from bio-degradation [36, 39, 79, 102]. Consequently, contaminants being transported in the PSFM are expected to be degraded only in the dissolved state making the relationship between sorption kintetics, sorption coefficient, and degradation rate critical for compound stability. Preservation of dissolved species by addition of an anti-microbial agent to the PSFM may further increase stability. Addition of anti-microbial to the sorbent phase which slowly desorbs over the course of deployment is a simple method applicable to the

Table 3.6.: Solid Phase Extraction Recovery of Estrogens and Pesticides from Stream Water

Contaminant	SPE Recovery (Fraction of Applied)
aE2	0.79 ± 0.04
bE2	0.72 ± 0.03
E1	0.74 ± 0.04
E3	0.76 ± 0.06
ATZ	1.10 ± 0.03
ATZ-DE	0.91 ± 0.06
ATZ-DIP	0.21 ± 0.05
ATZ-OH	1.10 ± 0.03
MTC	1.04 ± 0.01
CSF	0.94 ± 0.07
CPF	0.89 ± 0.03

PSFM. Although numerous anti-microbial agents exist, one with low toxicity toward aquatic life is necessary for a device for sampling surface water.

In the case of GAC, silver impregnation has been used for some time to control bacterial growth in water filtration systems [7, 89]. For this reason, GAC that has been infused with nano-silver (0.026%) was initially chosen as a sorbent for the PSFM. Previous work has shown that the minimum bactericidal concentrations for silver nano-particles to be in the range of 1 - 50 mg/L depending on bacterial species and the sugar substrate used in the incubation broth [85]. A later study investigating the anti-bacterial properties of silver-GAC on E-coli showed complete inhibition only at $> 9\%$ (w/w) metallic silver. Much lower concentrations of silver resulted in slight or negligible bactericidal activity [7]. Given this information, it is not clear whether the relatively low silver content of the GAC being used will significantly inhibit microbial activity in the PSFM. Furthermore, silver nano-particles could be lost during washing

of GAC to remove fine particulates during sorbent preparation (Appendix A) or washed out of the sampler as water passes through during use.

Recent studies have found that silver ions sorbed on montmorillonite reduced the number of bacterial colonies by 4-10 orders of magnitude within 24 hours [64]. They found the anti-bacterial activity to be due to desorption of Ag^+ into solution. Zeolites, which also have high cation exchange capacity, should have similar bactericidal properties if treated with Ag^+. As water flows through the PSFM, silver ions are released from the surface by cation exchange and function as anti-bacterial agents in solution.

Stability of the target contaminants in field deployed PSFM units was evaluated by measuring recovery from PSFMs amended with hormones and pesticides prior to deployment. The mass of each contaminant spiked into flux meters was > 100 times the amount expected to be captured to avoid significant error due to absorption of contaminants from stream water. Sorbents were prepared according to the protocol outlined in Appendices A and H and flux meters packed in the same manner as for field samples. Immediately prior to PSFM deployment, contaminants dissolved in 100 μL of 2-butanol were spiked into the inlet of the flux meter using a gas-tight syringe. Eleven PSFM units were amended with all compounds. Two PSFM units were amended with only aE2, bE2, E3, ATZ, MTC, CSF, and CPF and two were amended with only E1, ATZ-DE, ATZ-DIP, and ATZ-OH to evaluate the potential for interconversion between parent and degradate species. After the deployment period, SMZ was extracted using ASE and the fraction of each contaminant recovered measured by LC/MS with electrospray ionization.

Median recovery of estrogens was approximately 65% for all four compounds. In flux meters amended with only aE2, bE2, and E3, no conversion to E1 was observed. However, in flux meters amended with E1, a small amount of E3 was recovered ($\approx$ 3%) suggesting possible E1$\rightarrow$E3 conversion. Recovery of ATZ and its degradates appeared to be inversely correlated with compound hydrophobicity. CPF was not detected in extracts and therefore not reported here. Because CPF is very hydropho-

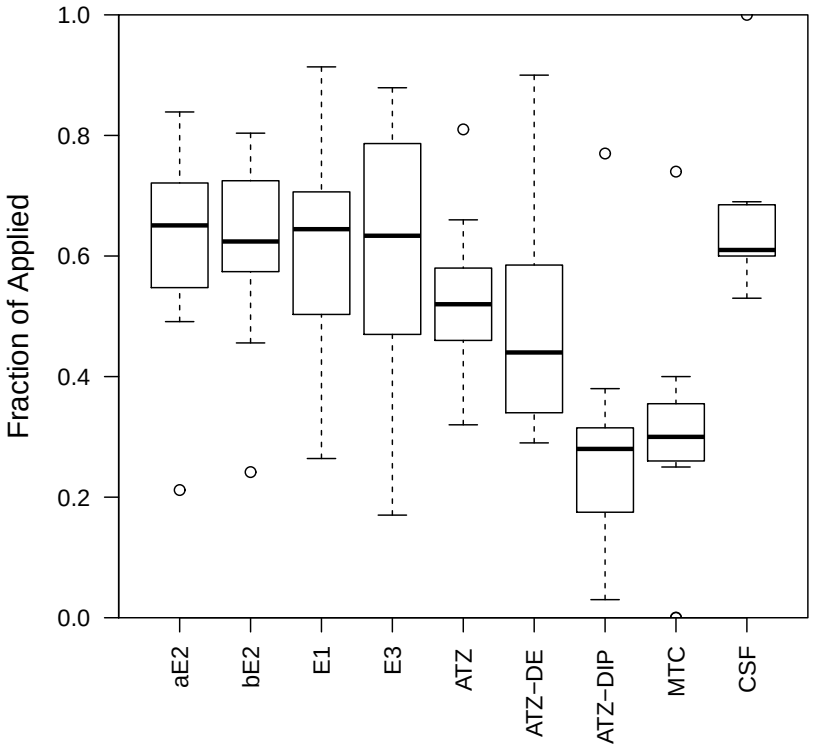


Figure 3.4.: Recovery of estrogens and pesticides from flux meters amended with the contaminants prior to deployment. Estrogens (13 mg/L), ATZ (17 mg/L), ATZ-DE (31 mg/L), ATZ-DIP (50 mg/L), ATZ-OH (100 mg/L), MTC (83 mg/L), CSF (19 mg/L), and CPF (26 mg/L) dissolved in 100 μL 2-butanol were spiked into the PSFM inlet using a syringe immediately prior to deployment. PSFM deployment times varied from 2-9 days. No CPF was recovered from any of the PSFM units.

bic, it is probably not extracted from the wet sorbent using methanol. Recovery was not significantly correlated ($\alpha = 0.05$) with PSFM specific discharge, PSFM cumulative discharge, or deployment time. For contaminants where breakthrough of contaminants from the PSFM sorbent occurs, recovery might be expected to be correlated with PSFM specific discharge or cumulative discharge. For contaminants where degradation was occurring, a negative correlation between deployment time and compound recovery is expected. Since neither PSFM flow nor deployment time

appear to be correlated with recovery, more likely explanations of low apparent recovery for ATZ-DE, ATZ-DIP, and MTC may be LC/MS signal suppression caused by the sample matrix, transformation of the analytes, or simply less than ideal extraction recovery.

3.4.2 Stability in ISCO samples

Stability of contaminants in stream water was measured for samples collected using automated ISCO equipment. Stream water (1 L) was collected into HDPE bottles and sterilized by addition of sulfuric acid (0.5 mL) or autoclave (1 h, 15 psi, 121°C). Samples were amended with contaminants dissolved in 100 μL of 2-butanol. Initial concentrations were 1.3 μg/L for estrogens, 1.7 μg/L for ATZ, 3.12 μg/L for ATZ-DE, 5.04 μg/L for ATZ-DIP, 10.3 μg/L for ATZ-OH, 8.3 μg/L for MTC, 1.9 μg/L for CSF, and 2.6 μg/L for CPF. Sub-samples (0.5 mL) were collected at periodic intervals and diluted with methanol (0.5 mL). Hormone and pesticide concentrations were measured by LC/MS using the protocol outlined in Appendix M.

Estrogens, MTC, ATZ, and ATZ degradates were all stable during the 5-6 day incubation period in both acidified and autoclaved stream water (Figures 3.5 and 3.6). CSF was stable in autoclaved water but dissipated with a first order half-life of 8.3 hours in acidified stream water, presumably because of acid hydrolysis. CPF concentration decreased in acidified and autoclaved stream water with first order half lives of 27 and 21 hours respectively. Given the hydrophobicity of CPF (log K_{ow} = 4.2, [119]), sorption to the plastic surfaces of ISCO bottles is likely. Significant loss by volatilization is unlikely given reported Henry's constant values of $3.8x10^{-6}$ - $3.6x10^{-5}$ atm m^3 mol^{-1} [17, 93]. Since neither CSF nor CPF were measured in un-spiked field samples; however, their instability is not significant to the reported data.

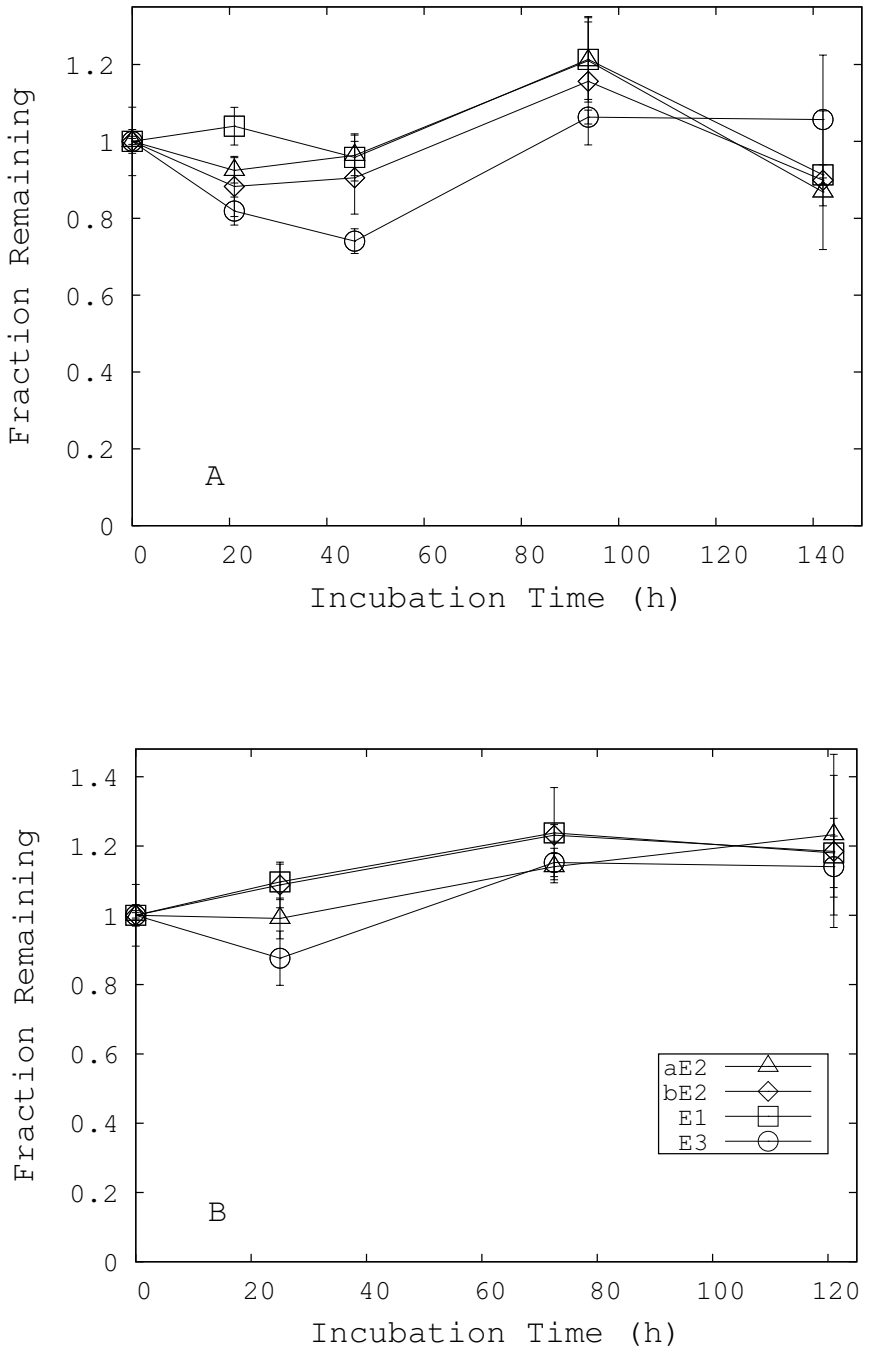


Figure 3.5.: Stability of estrogens in [A] acidified and [B] autoclaved stream water samples. Acidified samples contained 0.05% H_2SO_4, autoclaved samples sterilized at 15 psi (121°C) for 1 hour. Incubation temperature 23±3°C.

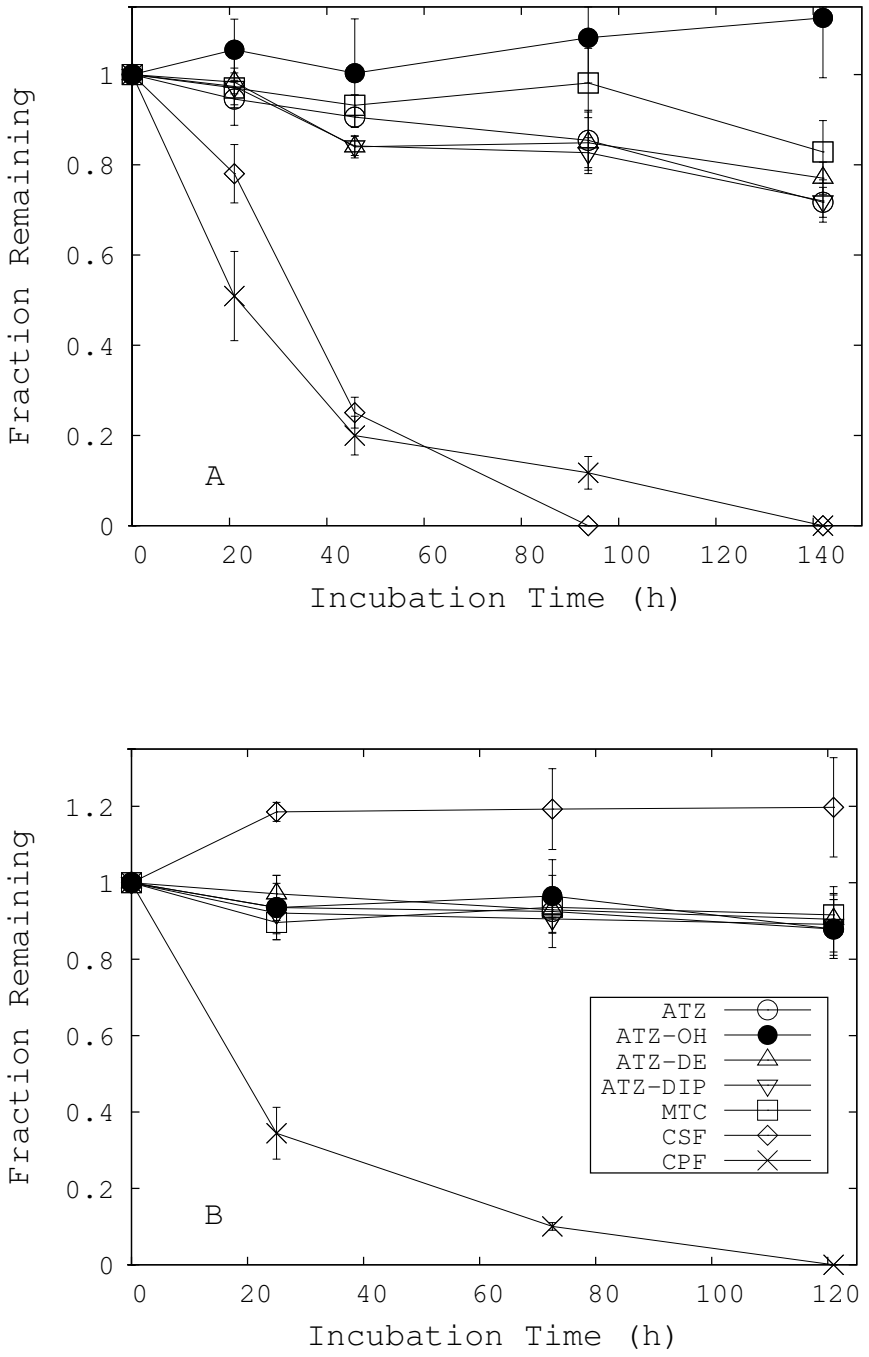


Figure 3.6.: Stability of pesticides in [A] acidified and [B] autoclaved stream water samples. Acidified samples contained 0.05% H_2SO_4, autoclaved samples sterilized at 15 psi (121°C) for 1 h. Incubation temperature 23±3°C.

4 COMPARISION OF CONCENTRATIONS MEASURED USING THE PSFM TO CONCENTRATIONS MEASURED IN ISCO WATER SAMPLES

4.1 Deployment, collection, processing, and analysis of PSFM and ISCO samples

PSFM measured concentrations were compared to flow weighted average concentrations estimated from discreet water samples taken at regular intervals over the PSFM deployment period. Each PSFM unit was affixed to a steel T-style post using an adjustable T-bolt band clamp. Samplers were situated with the length of the PSFM unit parallel to the direction of stream flow and at 60% of stream stage at the time of deployment. Either one or two PSFM units were affixed to a steel T-style post. PSFM units were assembled following the protocol outlined in Appendix L. Flux meters were wet packed starting at the outlet side and working toward the inlet. After packing/assembly, flux meters were refrigerated (4°C) for a maximum of 40 hours prior to deployment. Flux meters were kept filled with water and in the upright position (outlet side down) until deployment.

The concentration of tracer alcohols in GAC samples (C^{GAC}) was determined by gas chromatography (GC) after solvent extraction to recover the tracers from the GAC sorbent as outlined in Appendix D. The concentration of tracers in GAC was then calculated using Equation 4.1.

$$C^{GAC} = \frac{C_{GC}^{PFM} \times V_{extr}}{M_{GAC}^{extr}} \tag{4.1}$$

where C^{GAC} is the concentration of tracer in the GAC sorbent on a dry mass basis, C_{GC}^{PFM} is the concentration of tracer measured in the GC sample, V_{extr} is the sum of the volume of extraction solvent added and water present in the portion of GAC sorbent taken for analysis, M_{GAC}^{extr} is the dry mass of GAC extracted. The fraction of tracer remaining in the GAC after deployment is calculated using equation 4.2:

$$\Omega_R = \frac{C_{final}^{GAC}}{C_i^{GAC} \times \Omega_{DMP}} \tag{4.2}$$

where C_i^{GAC} and C_{final}^{GAC} are the concentrations of tracer remaining in the sorbent at the beginning and end of deployment respectively and Ω_{DMP} is the fraction of DMP remaining in the sorbent after deployment determined from initial and post-deployment measurement by gas chromatography as explained above. The cummulative discharge of water passing through the PSFM during the deployment period was then calculated using equation 4.3.

$$Q_{PSFM} = (1 - \Omega_R)\phi LAR \tag{4.3}$$

where L is the length of the GAC layer, A is the cross sectional area of the GAC layer, and Δt is the PSFM deployment time.

SMZ was extracted and analyzed for estrogens and pesticides as described in Appendix I. Briefly, SMZ from flux meters was homogenized and transfered to 33 mL ASE extraction cells. Three extraction cells were required to extract all SMZ from a single flux meter. Two sequential extractions were performed at 75°C for 5 minutes each and combined for each extraction cell (60% flush volume). After all three cells for each flux meter had been extracted, the extracts were combined to result in a single sample for each flux meter ($\approx$ 150 mL of extract). SMZ extracts were analyzed directly for pesticides without pre-concentration while SMZ extracts for hormone analysis required further processing due to much lower concentrations relative to pesticides. For hormone analysis, oven dried molecular sieves (type 3a, 2 g) were added and mixed with the extract for several minutes to remove water and poorly hydrated salts. The treated extract was decanted and molecular sieves washed with 20 mL of ethyl acetate/ ethanol (1/1). Extracts were combined with washes and evaporated to $\approx$ 4 mL in a rotary evaporator with nitrogen gently blowing into the round bottom flask during evaporation at 50°C. The concentrated sample was then passed through a small column containing 3 g of anhydrous sodium sulfate over 1.5

g of silica gel (both dried at 150°C overnight) to further clarify the final sample. The sodium sulfate/silica gel column was washed with 2 mL of ethyl acetate/ethanol (1/1). The combined eluent and washings were transferred to a 5 mL conical vial and evaporated to dryness under a gentle stream of nitrogen. Samples for hormone analysis were then reconstituted in methanol (1 mL) prior to analysis.

Water samples were collected immediately adjacent to the PSFM using automated ISCO equipment at the P1 sampling location. Water samples were preserved by acidification with sulfuric acid (0.5 mL), which was added to the 1 L high density polyethylene (HDPE) collection bottles prior to initiation of sampling. Water samples were collected in the HDPE bottles at 30 minute intervals using ISCO equipment. Ten 100 mL water samples were combined in each 1 L bottle resulting in a single composite sample per 5 hour time period (final concentration of sulfuric acid was 0.05% and the pH of the final sample was $\approx$ 2.2). At the end of the PSFM deployment period, water samples were stored at 4°C for a maximum of 24 hours, neutralized to pH 6.5 using sodium bicarbonate, extracted by solid phase extraction (SPE) with Phenomenex SDB-L cartridges (200 mg, 3 mL) using the procedure outlined in Appendix K, and reconstituted in methanol (1 mL) prior to analysis.

PSFM and extracted water samples were analyzed for estrogens, metolachlor, atrazine and atrazine degradates by LC/MS with electrospray ionization using a Phenomenex Gemini C18 column (150mm length x 2.0 mm ID x 5μm particle diameter), Sciex API-3000 mass spectrometer, and Shimadzu HT-C liquid chromatography system as outlined in Appendix M. Flow weighted average contaminant concentrations in the stream (C_{PSFM}) were estimated from the concentrations measured in the SMZ extracts and the cumulative discharge of water passing through the PSFM determined in equation 4.3:

$$C_{PSFM} = \frac{C_{LCMS}\, V_{extr}}{Q_{PSFM}\, \tau_{SMZ}} \tag{4.4}$$

where C_{LCMS} is the concentration of contaminant measured in the LC/MS sample, V_{extr} is the volume of the extracted sample as prepared for analysis ($\approx$150mL for

pesticides and 1 mL for hormones) and τ_{SMZ} is the fraction of the total amount of SMZ contained in the PSFM that was extracted.

Concentrations estimated using the PSFM were compared to flow weighted average concentrations estimated from water samples (C_{ISCO}^{FWA}) using continuous discharge data:

$$C_{ISCO}^{FWA} = \frac{\sum_i Q_{s,i}\, C_{ISCO,i}\, \Delta t_i}{\sum_i Q_{s,i}\, \Delta t_i} \tag{4.5}$$

where $Q_{s,i}$ is the mean specific discharge of water in the stream during the ith sampling period and $C_{ISCO,i}$ is the concentration of contaminant measured in the composite water samples collected during the ith sampling period. Each ISCO sample is a composite of 10 individual samples taken at 30 minute intervals for a total sampling period of 5 hours. Stream discharge was estimated by means of a rating curve delineated over the range of stream stage observed during flux meter deployments (Appendix N). For development of the rating curve, a Flo-Mate 2000 portable flow meter (Marsh-McBirney, Inc) was used to measure velocity at 60% of stream depth at 1 ft segments across a transect of the stream at various levels of stream stage, and the stage-discharge relationship was determined [123]. Thereafter, stream stage was monitored at 15 minute intervals using a Campbell Scientific shaft encoder pulley system and discharge was estimated from stage.

4.2 Comparison of concentration estimates from PSFM and ISCO water samples

Figures 4.1 and 4.2 illustrate flow weighted average concentrations of pesticides (ATZ, ATZ-DE and MTC) and estrogens (E1, aE2, bE2, and E3) respectively at P1 measured using the PSFM and concentrations of these contaminants in composite water samples taken concurrently and immediately adjacent to the PSFM. PSFM measured flow weighted average concentrations are depicted by horizontal lines encompassing the time period of PSFM deployment. Concentrations of samples for

which the time weighted average PSFM discharge exceeds that which is within the linear range of the resident tracers are depicted using dashed lines while concentrations of samples which were within the linear range of tracers are shown with solid lines. For water samples, dissolved concentrations are shown with open symbols while the concentration of particulate bound contaminants are depicted with solid symbols. Each water sample is a composite of ten individual discreet samples taken at regular intervals over a 5 hour period. A large flood event occurring during the 4/14 - 4/23 sampling period prevented access to the ISCO sampling equipment, and consequently, no data for ISCO water samples is presented for this sampling period. The hydrograph recorded at P1/S2 is also shown along with the hyetograph. Tables 4.1 and 4.2 show the same data but with flow weighted averages calculated for water sample concentrations using the discharge data presented in figures 4.1 and 4.2 and equation 4.8. The mean and maximum concentration of suspended sediments in ISCO water samples is also presented in Tables 4.1 and 4.2. Hormones were not detected in any of the PSFM samples collected under base flow conditions since not enough water was sampled by the device to allow for detection of hormones by LC/MS (Figure 4.2 and Table 4.2).

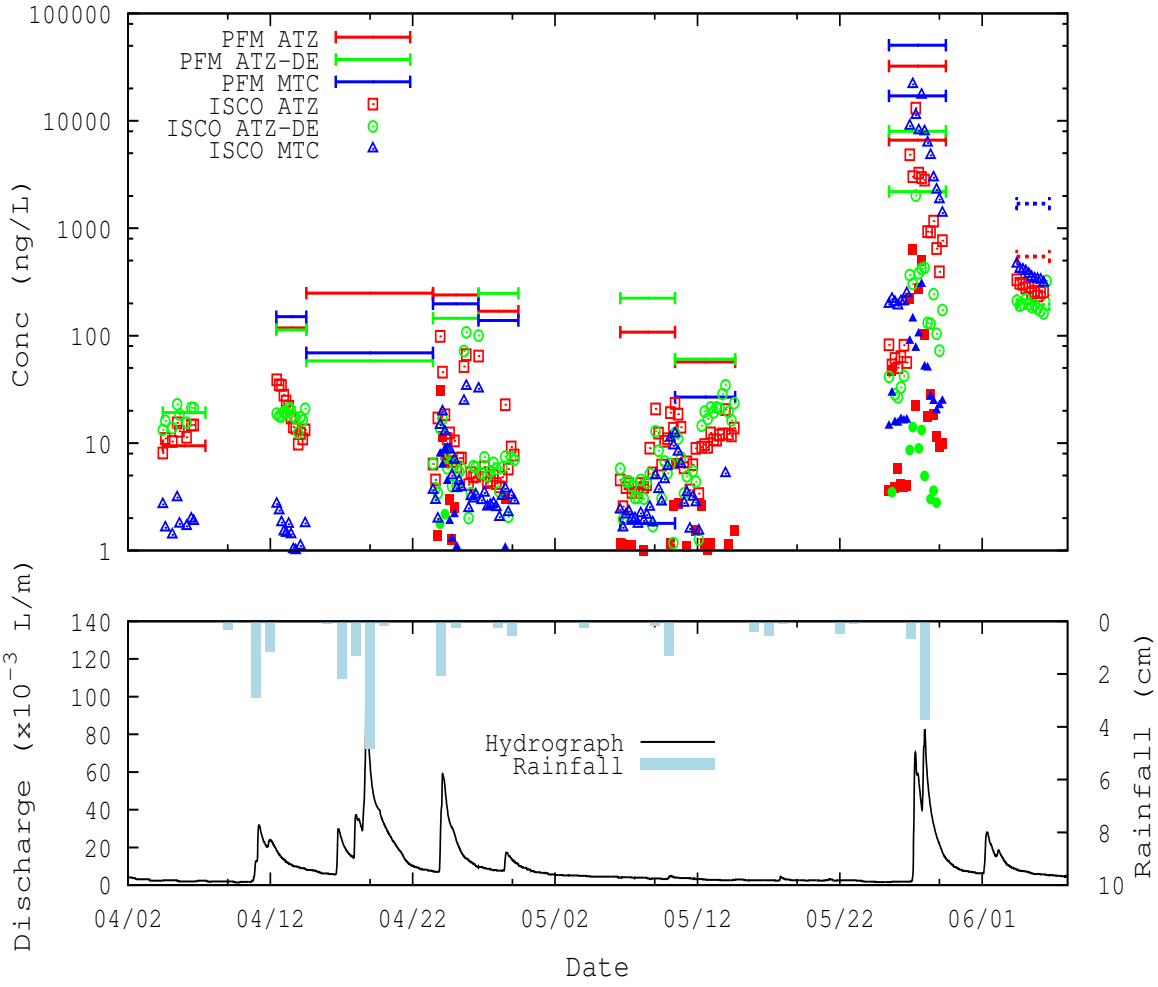


Figure 4.1.: Concentration of pesticides measured using ISCO and PSFM at P1. The hyetograph and hydrograph at the P1 sampling station are shown in the bottom graph. For ISCO samples, dissolved concentration of pesticides is represented by open symbols while particulate bound concentration is represented by closed symbols. Access to the ISCO sampling equipment was prevented by a flood event occurring during the 4/14 - 4/23 sampling period, and consequently, data for ISCO water samples is not presented for this sampling period. PSFM measured concentrations are represented by lines. For PSFM data, samples for which the cumulative water flux was beyond the linear range of all tracers are represented by dashed lines while those within the linear range of tracers are shown using solid lines.

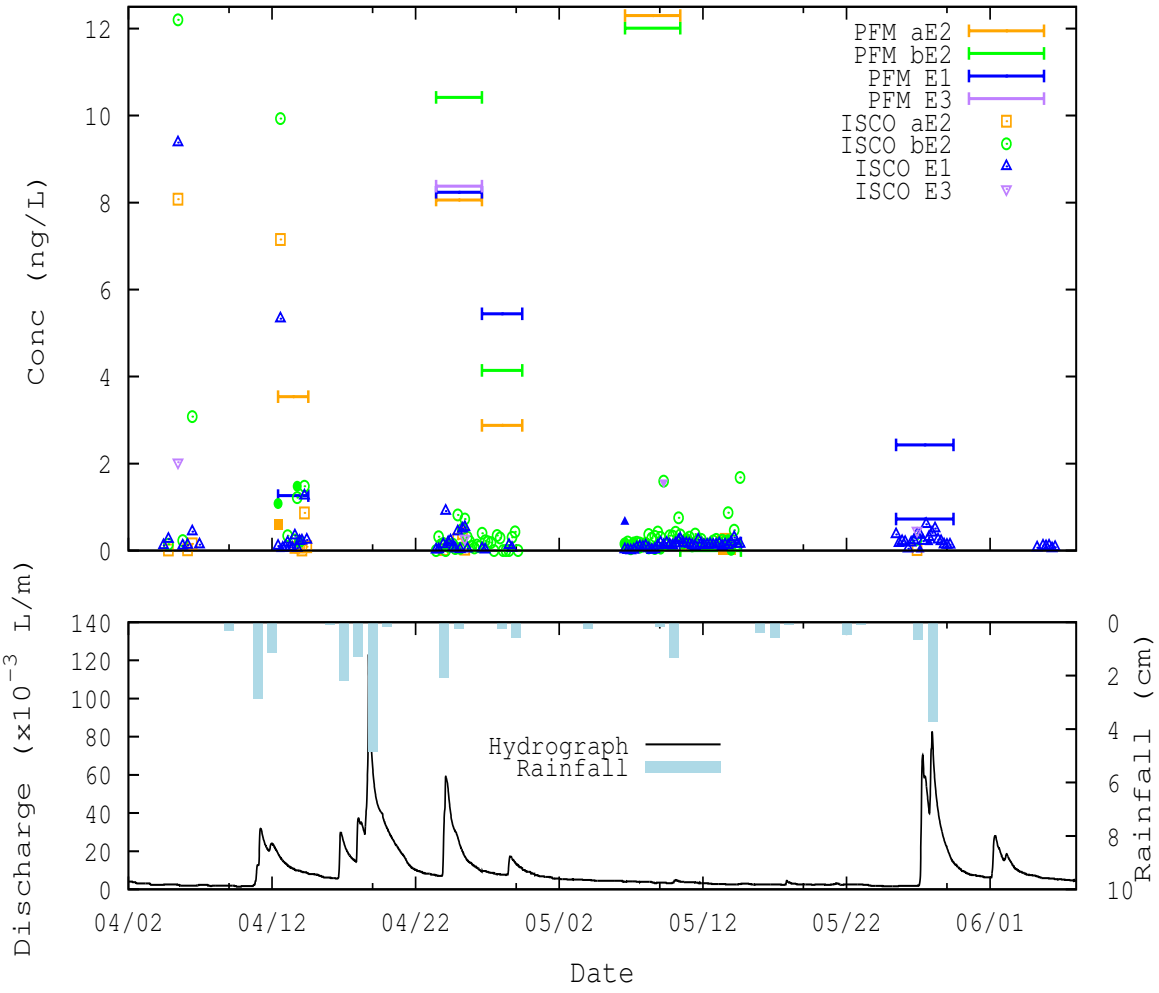


Figure 4.2.: Concentration of estrogens measured using ISCO and PSFM at P1. The hyetograph and hydrograph for the P1 sampling station are shown in the bottom graph. For ISCO samples, dissolved concentration of estrogens is represented by open symbols while particulate bound concentration is represented by closed symbols. Access to the ISCO sampling equipment was prevented by a flood event occurring during the 4/14 - 4/23 sampling period, and consequently, data for ISCO water samples is not presented for this sampling period. PSFM measured concentrations are represented by lines. For PSFM data, samples for which the cumulative water flux was beyond the linear range of all tracers are represented by dashed lines while those within the linear range of tracers are shown using solid lines. Hormones were not detected in any of the PSFM samples collected under base flow conditions since not enough water was sampled by the device to allow for detection of hormones by LC/MS.

Table 4.1.: PSFM parameters, sediment loads in ISCO samples, and pesticide concentrations in PSFM and ISCO samples at P1

ISCO Sampling Dates	Deploy Time	PFM Cumulative Specific Discharge	PFM K_{eff}	PFM ΔH	ISCO Sediment Conc (mg/L)		ATZ (ng/L)			ATZ-DE (ng/L)			MTC (ng/L)		
							PFM	ISCO		PFM	ISCO		PFM	ISCO	
	(d)	(mL)	(cm/d)	(cm)	mean	max		Diss	Sed		Diss	Sed		Diss	Sed
4/4 - 4/7	3.2	187	72	1.4	ND	ND	9	13	ND	19	22	ND	0	2	ND
4/12 - 4/14	2.1	282	72	3.0	10	52	118	16	0	113	22	0	150	1	0
4/23 - 4/26	3.2	425	83	2.7	240	1,436	240	29	6	145	18	1	198	11	3
4/26 - 4/29	2.8	365	83	2.6	26	97	169	13	1	248	16	0	138	5	0
5/6 - 5/10	3.9	52	72	0.3	1	4	108	8	1	224	6	0	2	3	0
5/10 - 5/14	4.2	504	78	2.5	0	0	57	12	1	61	18	0	27	3	0
5/25 - 5/29	4.0	569	80	3.0	163	994	6,621	3,815	175	2,192	644	7	17,046	9,098	52
5/25 - 5/29	4.0	322	76	1.8	163	994	32,325	3,815	175	8,010	644	7	50,566	9,098	52
6/3 - 6/5	2.3	2,901	72	29	11	13	549	293	1	194	231	0	1,709	374	0
6/3 - 6/5	2.3	2,670	72	27	11	13	540	293	1	215	231	0	1,681	374	0

ND = Not determined, Diss = Dissolved concentration, Sed = Concentration in suspended sediments. For ISCO samples collected during the 4/4-4/7 time period, dissolved and particulate bound concentrations were not measured separately. However, very little suspended sediment was present in water samples collected during this time. K_{eff} was calculated from the lengths of GAC, SMZ, and flow restricting sand layer and from the saturated hydraulic conductivity of GAC, SMZ, and a fully assembled flux meter.

Table 4.2.: PSFM parameters, sediment loads in ISCO samples, and estrogen concentrations in PSFM and ISCO samples at P1

ISCO Sampling Dates	Deploy Time	PFM Cumulative Specific Discharge	PFM Keff	PFM ΔH	ISCO Sediment Conc (mg/L)		aE2 (ng/L)			bE2 (ng/L)			E1 (ng/L)			E3 (ng/L)		
							PFM	ISCO		PFM	ISCO		PFM	ISCO		PFM	ISCO	
	(d)	(mL)	(cm/d)	(cm)	mean	max		diss	sed		diss	sed		diss	sed		diss	sed
4/4 - 4/7	3.2	187	72	1.4	ND	ND	0	0.5	ND	0	1.0	ND	0	0.8	ND	0	0.1	ND
4/12 - 4/14	2.1	282	72	3.0	10	52	3.5	1.2	0.1	0	2.0	0.2	1.3	1.4	0	0	0.1	0
4/23 - 4/26	3.2	425	83	2.7	240	1436	8.1	0	0	10	0.2	0	8.2	0.3	0	8.4	0	0
4/26 - 4/29	2.8	365	83	2.6	26	97	2.9	0	0	4.1	0.2	0	5.4	0	0	0	0	0
5/6 - 5/10	3.9	52	72	0.3	1	4	12.3	0	0	12.0	0.4	0	12.6	0.1	0	0	0	0.1
5/10 - 5/14	4.2	504	78	2.5	0	0	0	0	0	0	0.2	0	0	0.1	0	0	0	0
5/25 - 5/29	4.0	569	80	3.0	163	994	0	0	0	0	0	0	0.7	0.4	0	0	0	0
5/25 - 5/29	4.0	322	76	1.8	163	994	0	0	0	0	0	0	2.4	0.0	0	0	0	0
6/3 6/5	2.3	2901	72	29.4	11	13	0	0	0	0	0	0	0	0	0	0	0	0
6/3 - 6/5	2.3	2670	72	27.1	11	13	0	0	0	0	0	0	0	0	0	0	0	0

ND = Not determined, Diss = Dissolved concentration, Sed = Concentration in suspended sediments. For ISCO samples collected during the 4/4-4/7 time period, dissolved and particulate bound concentrations were not measured separately. However, very little suspended sediment was present in water samples collected during this time. Hormones were not detected in any of the PSFM samples collected under base flow conditions since not enough water was sampled by the device to allow for detection of hormones by LC/MS. K_{eff} was calculated from the lengths of GAC, SMZ, and flow restricting sand layer and from the saturated hydraulic conductivity of GAC, SMZ, and a fully assembled flux meter.

In general, estrogen and pesticide concentrations measured using the PSFM are higher than those measured in water samples. A number of possibilities may contribute to differences between PSFM measured concentrations and those measured in water samples. Given negligible degradation of pesticides and estrogens in acidified water samples (Figures 3.5 and 3.6) and high recovery during extraction of water samples by SPE (Table 3.6), the disparity cannot be explained by differences in ISCO water sample preparation. Because recovery from amended, field deployed PSFMs ranged from 30-60% for estrogens, ATZ, ATZ-DE, and MTC (Fig. 3.4), PSFM measured concentrations are actually expected to be smaller than water samples if only analyte recovery is taken into account. Furthermore, since all data reported here are corrected for extraction recovery/degradation, these effects do not contribute to the differences in concentration observed between ISCO and PSFM samples.

For contaminants with highly transient behavior, it is likely that discreet sampling methods underestimate concentrations since they can miss spikes that may occur in between sampling times [23, 98, 126]. In a study measuring estrogenic in surface waters from 19 headwater basins using both the Polar Organic Integrative Sampler (POCIS, a commercial passive sampler) and discreet sampling, estrogens were detected much more frequently in POCIS samples [4]. Differences in concentration estimates between discreet sampling methods and passive sampling methods will become greater as the variability of contaminant concentration increases and the frequency of discreet sampling is decreased. Figure 4.3 illustrates the variability of contaminant concentration measured in ISCO samples for estrogens and pesticides. The mean concentration in ISCO samples during each PSFM deployment period was determined and the deviation of each individual ISCO measurement from the mean for the corresponding deployment period was calculated in units of % for each data point.

For the estrogens, the greatest observed differences between PSFM and ISCO measured concentrations occurred during the 4/23-4/26, 4/26-4/29, and 5/6-5/10 sampling periods (Table 4.2). These dates correspond with periods of high variability

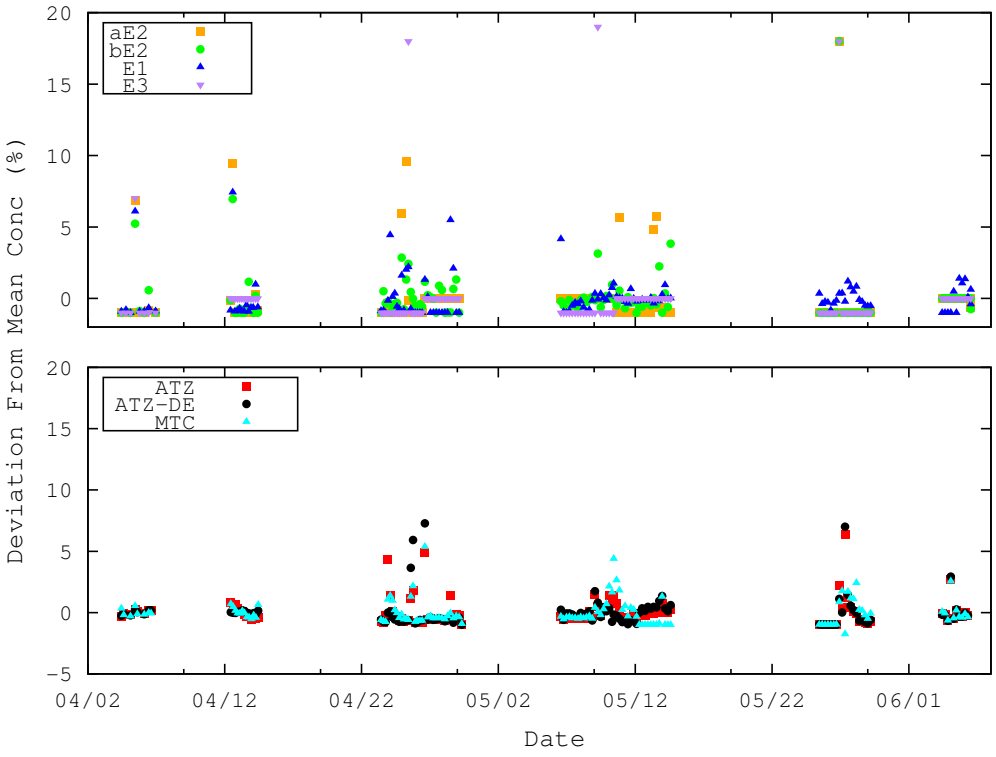


Figure 4.3.: Variability of ISCO sample concentrations. The deviation from the mean concentration of each contaminant in each ISCO sample was computed by dividing the difference of each concentration from the mean concentration for that sampling period by the mean concentration for that sampling period.

in ISCO measured estrogen concentrations (Figure 4.3). For ATZ and ATZ-DE, the highest amount of variability in ISCO sample concentrations occurred during the 4/23-4/26, 4/26-4/29, and 5/25-5/29 sampling periods (Table 4.3). This high variability correlates well with large differences between PSFM and ISCO measured concentrations observed during these time frames (Figure 4.1). With the exception of the 4/12-4/14 sampling period, differences in MTC concentrations measured using the PSFM and ISCO also correlate well with the variability of measured concentrations in ISCO samples (Table 4.1 and Figure 4.3).

Underestimation of PSFM water flux because of tracer sorption/desorption non-equilibrium provides another possible reason why contaminant concentrations mea-

sured using the PSFM are higher than those measured in water samples. At high flow rates, increased dispersion and tailing of the tracer elution profile may result as a consequence of sorption non-equilibrium thereby reducing the range of flow over which a specific tracer is capable of accurately predicting flow. Consequently, PSFM cumulative discharge may be underestimated under high flow conditions. The apparent over-estimation of both pesticide and hormone concentrations (relative to water samples) suggests that underestimation of specific discharge of water through the PSFM may be responsible for at least part of the discrepancy since this would affect both compound classes equally. Figure 4.4 illustrates the range of PSFM darcy flux for all field samples (69 samples total). Given that tracer retardation factors were determined at PSFM darcy flux of 5-28 cm/d (Figure 2.6) and 9.1 cm/d (Figure 2.8), it is likely that a greater degree of non-equilibrium was experienced in some field samples relative to what occurred in tracer miscible displacement experiments.

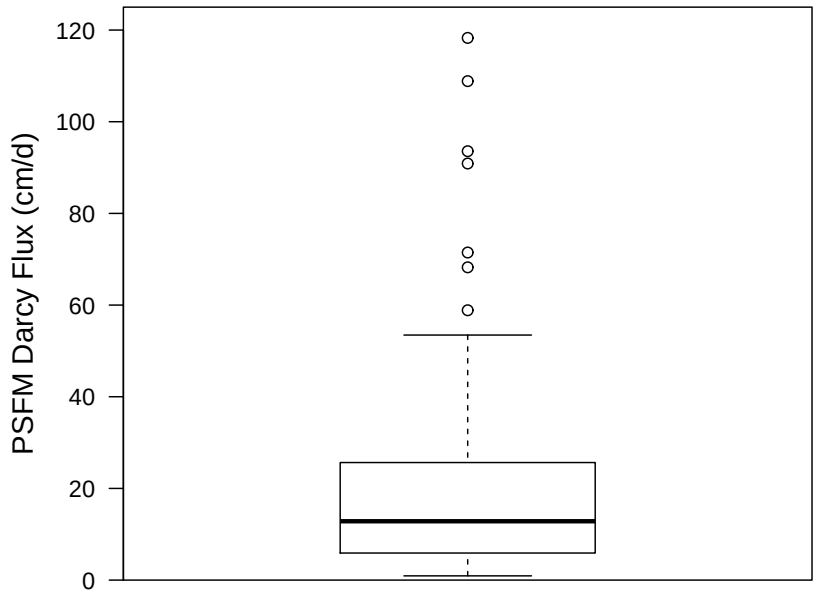


Figure 4.4.: Box Plot Illustrating the Range of Mean Darcy Flux for 69 Field Deployed PSFM Units. The box represents the 25th, 50th, and 75th percentiles while the whiskers extend to 1.5× the interquartile range. Outliers are signified by open points.

Although it seems logical that flux meters deployed in a flume should experience a similar degree of tracer non-equilibrium as those in the field under similar flow conditions, examination of ΔH as a function of external velocity in flume and field deployed flux meters reveals an inconsistency (figure 4.5). In the majority of cases, the time averaged ΔH for flux meters deployed in the stream is smaller than that of flux meters in a flume under similar averaged external flow conditions. The transient nature of stream flow may result in a high degree of tracer non-equilibrium during periods when the majority of discharge occurs. This may result in underestimation of PSFM flow even in cases where the time averaged stream discharge indicates that equilibrium conditions should prevail within the PSFM. Although transience of flow in field samples complicates the comparison, PSFM darcy flux was lower than predicted by the relationship between external flow and PSFM flow determined in the flume even for flux meters experiencing near constant flow conditions in the field.

Decreased permeability due to accumulation of suspended sediments may also contribute to the differences between PSFM flow in a flume and that in a stream under similar external flow conditions. Deposition of suspended particulates within porous media is a function of solution chemistry and hydrodynamic factors such as particle size and linear velocity [70]. In a study of particle deposition in glass beads, Silliman [106] found that greater numbers of particles were deposited at interfaces where particulates passed from regions of larger size beads into regions containing small beads than were deposited in more homogeneous media. This suggests that decreased permeability in the PSFM due to clogging may occur primarily at the interface between GAC and the flow restricting sand layer.

Likewise, blocking of the PSFM inlet by foreign matter would also decrease flow through the device. While only one out of 69 stream deployed flux meters was found with vegetative matter blocking the inlet upon retrieval, it is possible that transient blockage could have occurred in some cases and not been detected. However, it is unlikely that nearly all of the flux meters experienced temporary blockage that was subsequently cleared before retrieval of the device. Assuming tracer equilibrium and

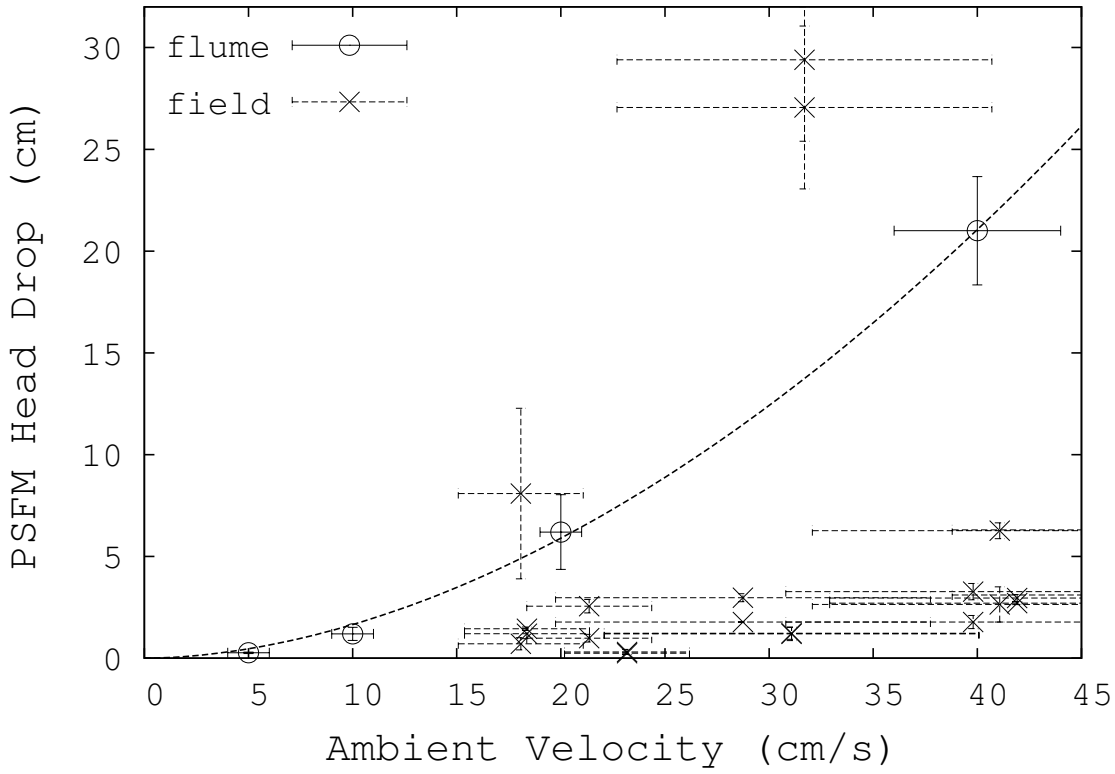


Figure 4.5.: PSFM head differential in flume and field samples

chemostatic behavior of contaminants, neither accumulation of sediments nor blocking of the inlet would explain differences in concentration estimates. However, they could explain lower PSFM flow than expected based on external stream velocity and the relationship between external velocity and PSFM flow measured in a flume.

The formation of preferential flow channels in the PSFM sorbent packing, if it occurs, would exacerbate the degree of non-equilibrium and hence underestimation of PSFM discharge, since extreme non-equilibrium would result in segments where channeling was occurring with decreased flow in other parts of the PSFM. Although channeling seems unlikely in the GAC and SMZ sorbents which have large particle size and uniform distribution relative to the 75/250 mesh sand mixture used for limiting PSFM flow, settling or loss of the fine mesh fraction of the sand mixture through the PSFM outlet resulting in the formation of preferential flow channels is possible. While

PSFM units were maintained in the upright position during packing and transport to avoid the formation of preferential flow channels, turbulence caused by the flowing stream during deployment could result in vibration and consequent settling or loss of material from the sand flow restricting layer.

When attempting to estimate stream discharge from PSFM darcy flux or when comparing PSFM darcy flux of field samples to flume samples, a distinction should be made between the stream velocity at 60% of stream depth (estimated from the rating curve) and stream velocity at the depth of the flux meter. Although PSFMs were initially deployed at a fixed depth corresponding to 60% of stream stage, their location relative to the depth of the stream changes as stream stage rises and falls. Therefore, a correction factor was applied to the stream velocity obtained using the rating curve to estimate the velocity at the depth of the PSFM unit. A logarithmic velocity profile was assumed ([57]):

$$\frac{v_s(z)}{v^*} = \frac{1}{\kappa} ln(\frac{z}{z_0}) \tag{4.6}$$

where $v_s(z)$ is the stream velocity (L/T) at depth z, κ is the von Karman constant (0.4, dimensionless), z_0 is the depth of zero velocity (0.033 * roughness height, L), and v^* is the friction velocity (L/T):

$$v^* = \sqrt{gH\lambda} \tag{4.7}$$

where g is the acceleration due to gravity (9.81 m/s^2), H is the stream stage (L), and λ is the stream slope (dimensionless). Initial calculations using the stream slope estimated from topographic data (see Figure 5.1) did not result in acceptable correlation with measured data of stream stage and velocity at 60% depth (v_{60}). Therefore, least squares minimization of error was used to adjust stream slope and depth of zero velocity within reasonable bounds to result in acceptable correlation of the predicted v_{60} with the measured values shown in Appendix N, Figure N.1B.

It was found that $z_0 = 0.36cm$ and $\lambda = 0.00037$ resulted in the best fit to experimental data while maintaining physically meaningful values of the constants. An example of the velocity profile predicted by equation 4.6 when stream stage = 0.7 ft is illustrated in Figure 4.6. To predict the velocity at the depth of the flux meter position, Equation 2 was used to calculate the ratio of the predicted stream velocity at the depth of the flux meter (v_{PSFM}) to v_{60} and this ratio multiplied by v_{60}, which was determined from periodic measurements of stream stage and the rating curve developed by measuring v_{60} at various levels of stream stage as outlined in Appendix N.

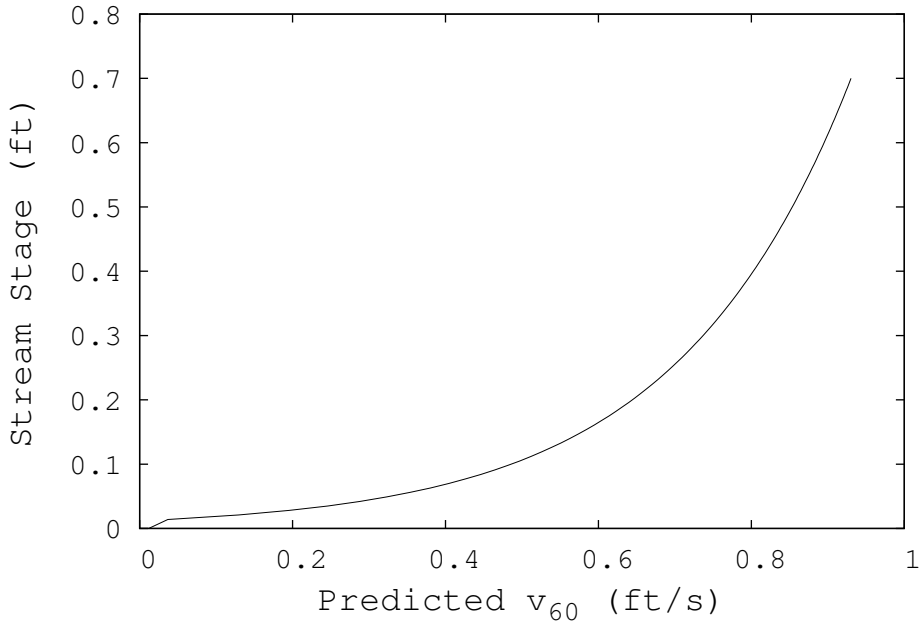


Figure 4.6.: Example of predicted logarithmic velocity profile when stream stage is 0.7 feet.

When comparing PSFM measured concentration to flow weighted average concentrations determined from ISCO water samples, it must be realized that because of the non-linear relationship between external stream velocity and PSFM flow illustrated in figure 2.12, the PSFM measured concentration is weighted more toward concentrations occurring in the stream during periods of high flow. By investigating the

relationships shown in figures 2.12 and 4.8, it is possible to estimate the magnitude and direction of bias incurred when concentration is measured using the PSFM.

The flow weighted average concentration of any dissolved or particulate bound contaminant in a flowing stream is defined as:

$$C_s^{FWA} = \frac{\int Q_s(t)C_s(t)dt}{\int Q_s(t)dt} \tag{4.8}$$

Typically, both Q_s and C_s are measured at discreet intervals and equation 4.8 is integrated numerically to estimate C_s^{FWA}. In case of the PSFM, the measured value represents an average over the deployment period. Hence, the time dependence of both Q_{PSFM} and C_{PSFM} are unknown and we are unable to make any inference about the time dependence of Q_s or C_s using the PSFM. Consequently, it is not possible to precisely determine the average contaminant concentration in the stream (C_s^{FWA}) from the PSFM measurement. One approach to estimate C_s^{FWA} from the PSFM measured value is to use an empirically derived relationship between contaminant concentration in the stream and specific discharge:

$$C(t) = mQ(t)^n \tag{4.9}$$

Substituting C(t) into equation 4.8, we obtain:

$$C_s^{FWA} = \frac{m\int Q_s(t)^{n+1}dt}{\int Q_s(t)dt} \tag{4.10}$$

Although Q_s is a complex function of time that can only be integrated numerically, we can simplify the problem by examination of a representative portion of the hydrograph. The recession curve of a single hydrograph can be approximated by an exponential function:

$$Q = Q_0e^{-kt} \tag{4.11}$$

Substituting into equation 4.10 and integrating, we obtain:

$$C_s^{FWA} = \frac{m}{n+1} \tag{4.12}$$

Assuming all the contaminant mass (M) that enters the PSFM during the deployment period (t) is captured by the sorbent, the flow weighted average contaminant concentration captured by the PSFM (C_{PSFM}^{FWA}) can be estimated from measurements of contaminant mass captured:

$$C_{PSFM}^{FWA} = \frac{\int Q_{PSFM}(t)C(t)dt}{\int Q_{PSFM}(t)dt} = \frac{M}{Q} \tag{4.13}$$

or, in terms of darcy flux rather than specific discharge:

$$C_{PSFM}^{FWA} = \frac{A\int q_{PFSM}(t)C(t)dt}{A\int q_{PSFM}(t)dt} \tag{4.14}$$

Now we can use the previously determined relationship between q_{PSFM} and v_s in figure 2.12 ($q_{PSFM}(t) = av_s(t)^b$) to transform equation 4.14 from PSFM darcy flux into stream velocity.

$$C_{PSFM}^{FWA} = \frac{\int v_s(t)^b C(t)dt}{\int v_s(t)^b dt} \tag{4.15}$$

For estimation of concentration in the stream, we need equation 4.15 in terms of stream flow instead of velocity. For this, we use an empirically derived relationship between stream velocity and specific discharge (Figure 4.7, $v_s(t) = cQ_s^d$) to transform the equation into terms of Q_s:

$$C_{PSFM}^{FWA} = \frac{\int Q_s(t)^{bd} C(t)dt}{\int Q_s(t)^{bd} dt} \tag{4.16}$$

Finally, we use the previously described empirical relationship between contaminant concentration in the stream and specific discharge (Figure 4.8, $C(t) = mQ(t)^n$) to remove the dependence on C(t):

$$C_{PSFM}^{FWA} = \frac{m\int Q_s(t)^{bd+n}}{\int Q_s(t)^{bd} dt} \tag{4.17}$$

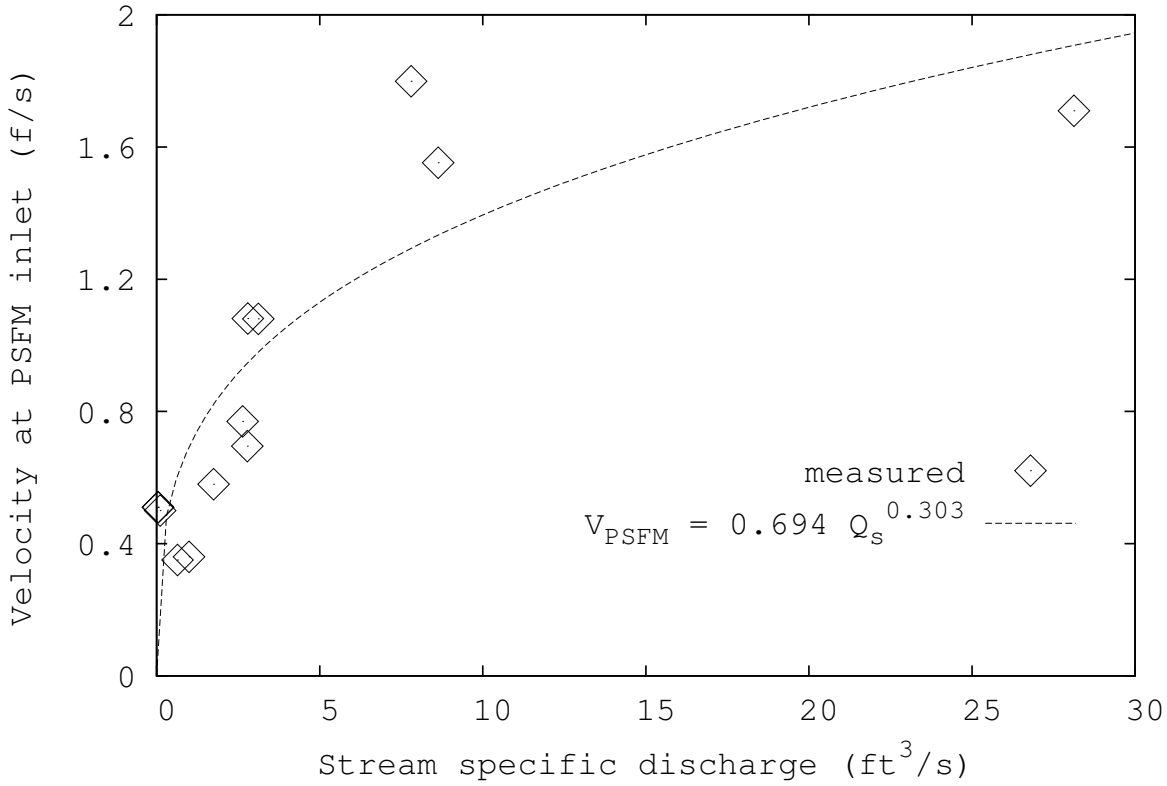


Figure 4.7.: Relationship between stream velocity at PFSM inlet and stream specific discharge.

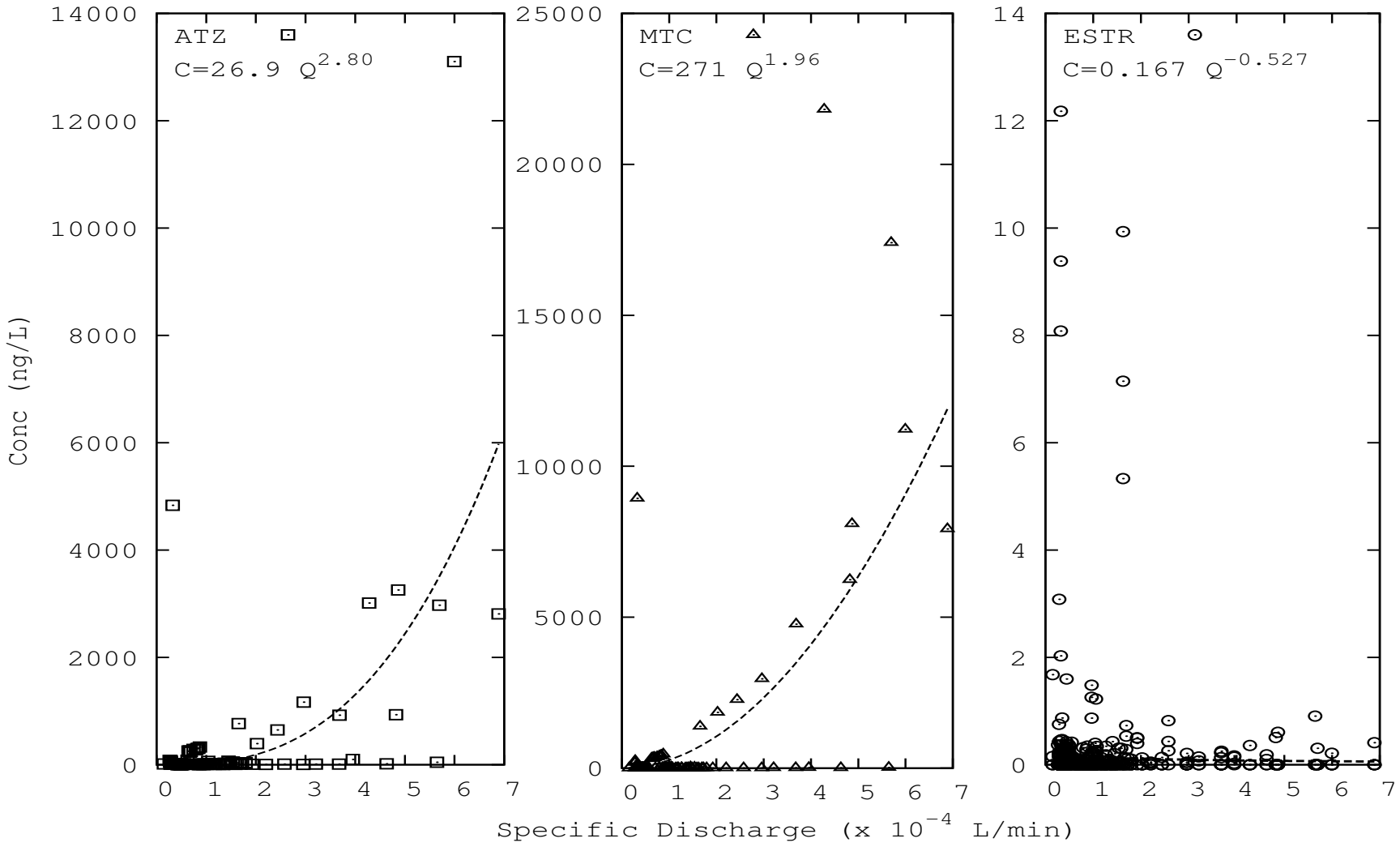


Figure 4.8.: Relationship between stream specific discharge and concentration of pesticides and total estrogens measured in ISCO water samples during 4/4 - 6/5.

Again focusing on the recession curve of a single hydrograph and substituting equation 4.11 for $Q_s(t)$ allows the explicit solution of equation 4.17:

$$C_{PSFM}^{FWA} = \frac{mbd}{bd+n} \tag{4.18}$$

Finally, the flow weighted average contaminant concentration in the stream is related to the concentration measured using the PSFM:

$$C_s^{FWA} = \frac{1+\frac{n}{bd}}{n+1} C_{PSFM}^{FWA} \tag{4.19}$$

When $n = 0$ (chemostatic), the contaminant concentration determined using the PSFM is equal to the concentration in the stream. Figure 4.8 illustrates the relationship between discharge and contaminant concentration of ATZ, MTC, and total estrogens (aE2 + bE2 + E1 + E3) measured in ISCO water samples at P1/S2 during the sampling periods under investigation. It is clear that while there is a positive correlation between discharge and concentration for ATZ and MTC, there seems to be a slight negative correlation for the estrogens. The result is that the concentration measured using the PSFM will be 138%, 134%, and 43% of the actual concentration in the stream for ATZ, MTC, and estrogens respectively. Obviously these estimates are based on empirical relationships and data that exhibit a high degree of variability, and as such, should be considered very rough estimates of the expected differences between contaminant concentrations measured in PSFM and actual concentrations. Furthermore, since the observed differences between estrogen concentrations estimated using the PSFM and those estimated from ISCO samples do not conform with the trends predicted by the flow weighting described herein, it does not appear that weighting of PSFM concentrations toward periods of high flow is responsible for the differences in estrogen concentration estimates. Finally, because the majority of contaminant loads are transported during periods of high stream flow [35], weighting of the PSFM measured concentration toward periods of high flow is unlikely to result in significant error in determination of contaminant flux or loading in streams and rivers.

In summary, comparison of concentrations measured using the PSFM and flow weighted average concentrations measured in ISCO water samples reveals that the PSFM generally yields higher values. It is probable that ISCO samples miss spikes in contaminant concentration resulting in underestimation of the actual flow weighted average concentration/flux of contaminants in the stream. Additionally, tracer non-equilibrium during periods of high flow may contribute to the observed disparity by causing underestimation of PSFM darcy flux of water. Limiting PSFM darcy flux and/or increasing deployment times may help to reduce the degree of tracer non-equilibrium allowing for more accurate measurement of trace level contaminants.

5 MEASUREMENT OF ESTROGENS AND PESTICIDES AT FIVE LOCATIONS IN A STREAM NETWORK NEAR ASREC

5.1 Field Site Description

Although the PSFM can potentially be used for measurement of many contaminant classes, we chose to focus field measurements on steroid hormones and the herbicides atrazine and metolachlor originating from the Purdue Animal Sciences Research and Education Center (ASREC), a confined animal feeding operation (CAFO) located on the Tipton Till Plain in North Central Indiana. The site is a working farm with 600 ha of cropland, and is an EPA-designated CAFO with beef, dairy, poultry, sheep, swine, and Ossabaw swine units. Animal wastes were stored on-site in an open lagoon system (effluent and slurries) or in piles (solids) and were applied to fields via pivot irrigation of lagoon effluent, broadcasting of solids, and subsurface injection of slurries. The dominant soil types, which are typical of poorly drained Midwestern soils, include Drummer silty clay loam (Typic Endoaquoll), Toronto silt loam (Udolloic Epiaqualfs), and Fincastle silt loam (Aeric Epiaqualfs). To improve drainage properties, subsurface tile drains ranging in diameter from 10 - 61 cm have been installed approximately 1 m below the soil surface and are spaced at 8 - 40 m intervals. A confining layer of glacial till exists approximately 1 m below the tile drains. A topographic map of ASREC and the surrounding area with tile drain and sampling site locations is shown in Figure 5.1.

Common agricultural contaminants, which may pose a risk to aquatic organisms if transported to nearby streams and rivers, include steroid hormones and pesticides. Hormones are naturally present in animal waste products which are commonly applied to fields for improvement of soil structure and as a nutrient source. Pesticides are typically surface applied by spraying for control of weeds (herbicides) or insects (insec-

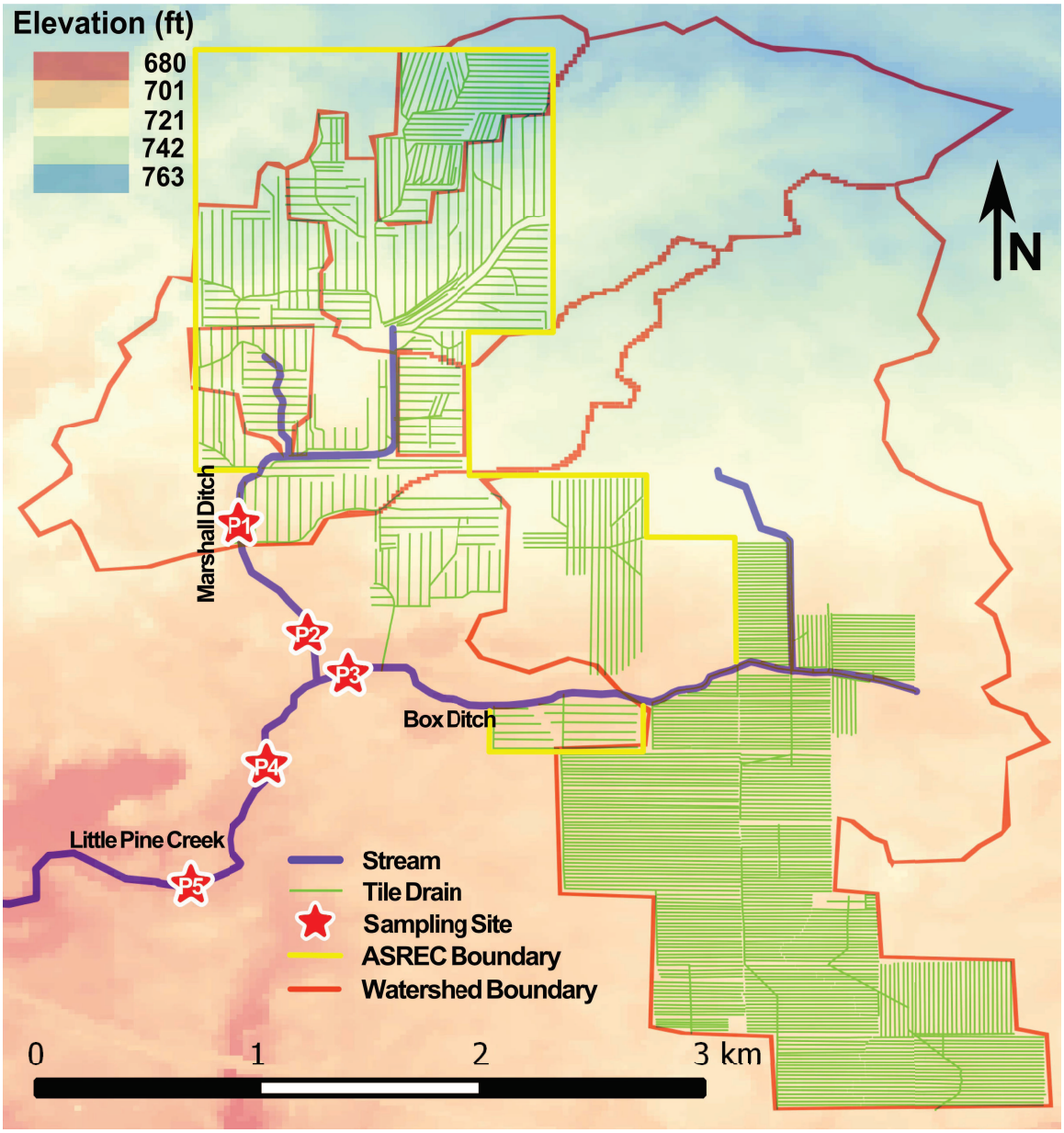


Figure 5.1.: Topographic Map of ASREC and Surrounding Area Showing Location of Tiledrains and Watershed Boundaries.

ticides). Both contaminant classes can be transported into nearby streams and rivers by over-land flow or leaching to groundwater. In fields where tile drains have been installed, sub-surface transport of contaminants is expedited resulting in increased possibility for negative ecological consequences. The magnitude of deleterious effects depends on the concentration and duration of exposure of non-target organisms. For this reason, it is important to develop monitoring strategies that are able to capture information about contaminant concentration/flux in affected areas resulting in an improved understanding of the processes affecting contaminant transport.

The PSFM is an attractive technology for contaminant monitoring in agricultural watersheds because of its ability to directly measure contaminant flux without independent measurement of discharge. Because of its long time scale relative to discreet sampling, the PSFM does not miss transient spikes in concentration or high flow events that may not be captured by more conventional sampling methods. Furthermore, the PSFM is less expensive and less labor intensive compared to automated discreet sampling. Steroid hormones and herbicides present a particular challenge for the PSFM given that the hormones are typically present at low ng/L while atrazine and metolachlor occur at μg/L concentrations in streams affected by agricultural activity [68, 113, 114, 118, 136]. Poor water quality due to manure application and runoff can further complicate analytical approach in an agricultural setting.

PSFM sampling was focused on contaminant loading in Box and Marshall ditches and transport further down the reach into Little Pine Creek. PSFM units were deployed at various locations along the stream starting at P1/S2 and ending in Little Pine Creek (Figure 5.1). Deployments occurred from 4/4/2013 - 6/5/2013 and lasted from 2 - 9 days each. Flux meters were attached to vertical poles in the center of the stream at a fixed point corresponding to 60% of the stream depth at the time of deployment. After deployment, flux meters were transported to the laboratory where they were extracted and analyzed using the protocols outlined in Appendices D, I, and M.

5.2 Measurement of Pesticide Concentrations

ATZ and MTC are routinely applied at ASREC prior to planting in the spring as a pre-emergent herbicide for control of grasses and broad leaf weeds. In 2013, both herbicides were applied during the time period from 5/9 - 5/16. Bicep II Magnum, which contains ATZ and MTC, was applied at a rate of 1.5 qt/acre (0.53 kg ATZ and 0.41 kg MTC per acre). Atrazine was applied on 5/14 without Metolachlor at a rate of 0.91 kg/acre. Dates, locations, and total amounts of pesticides applied are presented in figure 5.2. Prior to the 2013 applications, no herbicides had been applied since the previous spring.

Concentrations of ATZ, ATZ-DE, and MTC measured using the PSFM over the period 4/4/2013 - 6/5/2013 at the five sampling locations are presented in Figure 5.3. Prior to pesticide application, ATZ, ATZ-DE, and MTC concentrations averaged 78±18, 35±4, 52±13 ng/L (mean ± standard error) respectively over all sampling stations. No single station appeared to have higher concentration of any pesticide than the others. These levels correlate roughly with previously published data for atrazine and metolachlor in Midwestern streams and rivers during early spring [113, 114, 118]. In the pre-planting season, Thurman et al. [118] detected atrazine in 91% of samples from 149 sampling sites in the Midwestern United States with a median concentration of 230 ng/L while metolachlor was detected in only 34% of samples with a median concentration of less than 50 ng/L. Stoeckel et al. [114] measured atrazine concentrations in Upper Four Mile Creek, the main tributary feeding Acton Lake in southwestern Ohio, during April of 2005. Atrazine concentrations in the creek varied from 20-250 ng/L during this time period.

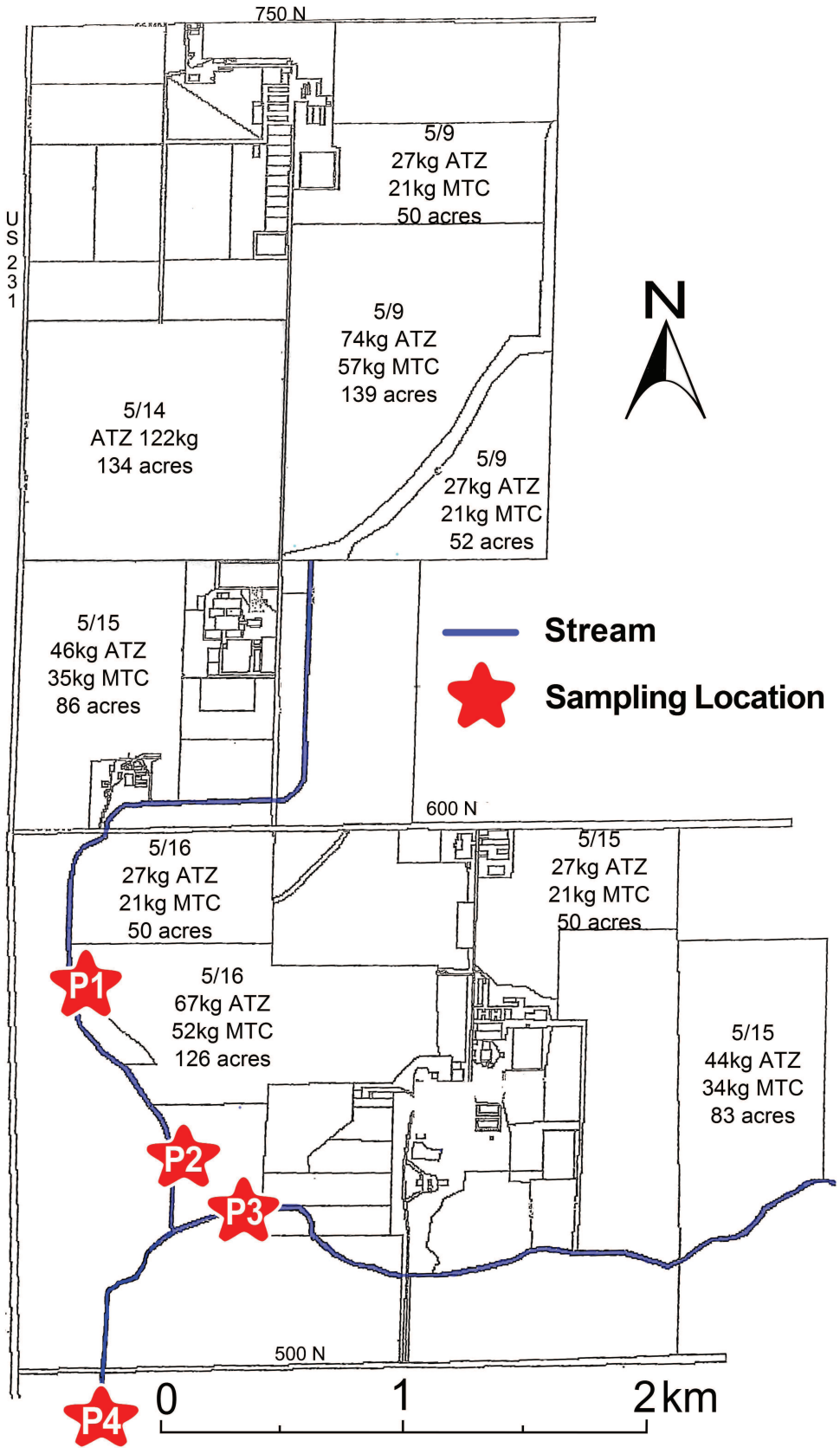


Figure 5.2.: Pesticide Application Locations, Dates and Total Amounts.

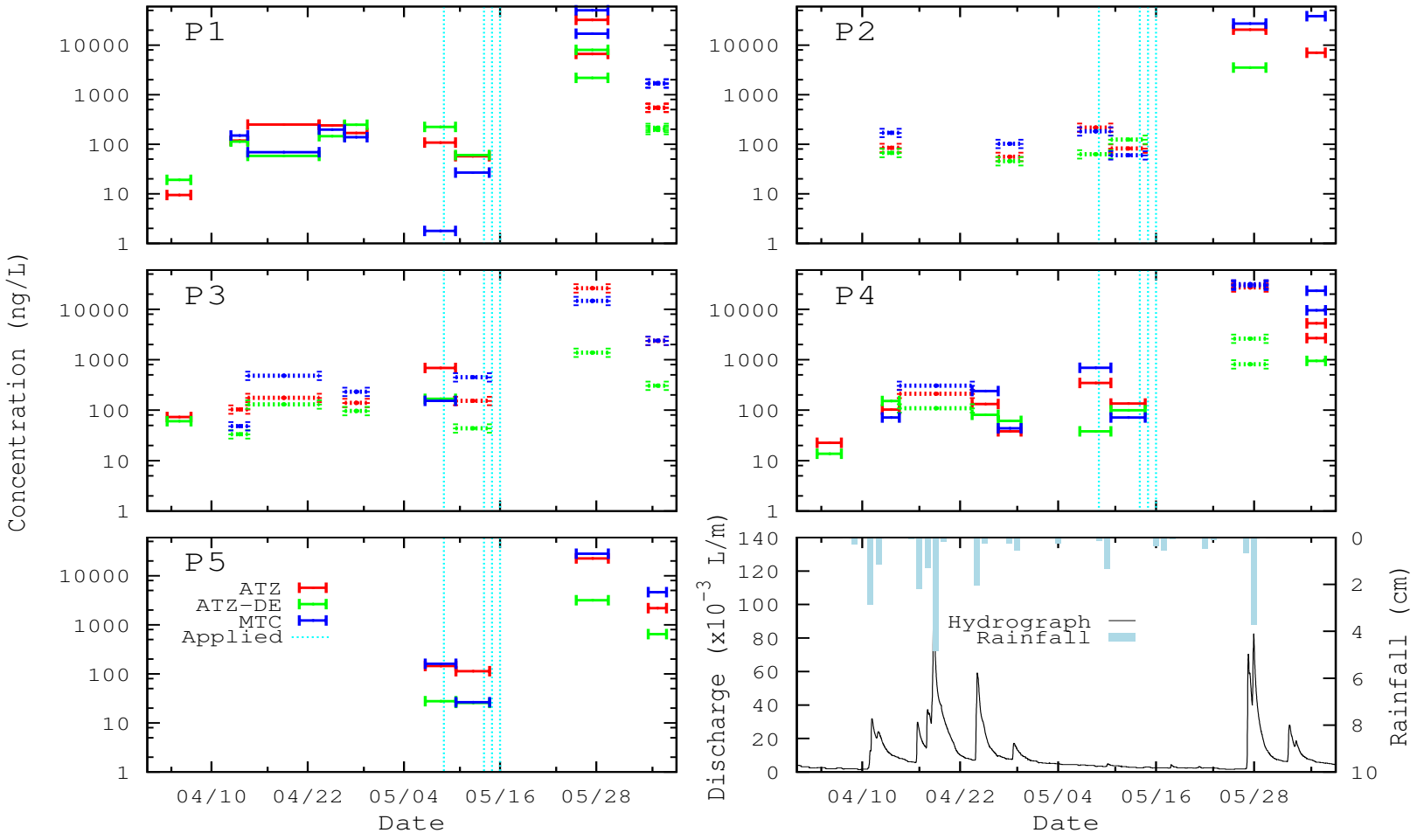


Figure 5.3.: Flow weighted average concentration of pesticides measured using the PSFM at five sampling locations near ASREC. Samples for which the cumulative water flux was beyond the linear range of all tracers are represented by dashed lines while those within the linear range of tracers are shown using solid lines. The hydrograph recorded at P1 is shown in the bottom right plot along with the hyetograph for the corresponding time period. Pesticide application dates are represented by vertical dotted lines.

Pesticide concentrations rose to 10,000-50,000 ng/L for ATZ and MTC and 800-8000 ng/L for ATZ-DE during the first flow event (beginning 5/27) following pesticide applications. Concentrations of ATZ and MTC had decreased below 1300 ng/L at P1 and P3 by the beginning of the 6/3 - 6/5 deployment, but the concentration of ATZ and especially MTC remained very high at P2 and P4 during this time. Concentrations of ATZ and MTC at the P5 sampling station were 23% and 8% lower than at P4 during the 5/25-5/29 sampling period and 45% and 72% lower than at P4 during the 6/3-6/5 sampling period suggesting that some level of dissipation was occurring with transport downstream.

Although there is a wide disparity in laboratory measured degradation rates of ATZ, its persistence in soils with a history of exposure to the herbicide is considerably shorter relative to ATZ naive soils with half lives ranging from 1-3 days [12, 103]. Rapid degradation may explain previous findings that mobilization of ATZ shows a strong seasonal pattern with the majority of losses occurring during the first significant drainage event following application [61]. Degradation of metolachlor in agricultural soils is somewhat slower with reported half lives ranging from 9-11 days [12]. Vogel and Linard [132] found that peak ATZ concentrations in base flow samples of a primary stream affected by agricultural activity occurred within 3 weeks of pesticide application. They also found that during the first week following a storm event after application, 73% of the annual loads of ATZ were transported in the stream. The authors estimated that 2.34% of the annually applied ATZ was transported during this week. The peak loading for ATZ-DE occurred 3 weeks after application with 34% of the annual load occurring during this week. Using PSFM measured concentrations and estimated discharge, 0.5% - 2.1% of total applied ATZ and 1.9% - 5.5% of total applied MTC was transported into the stream during the first major flow event following application (5/27 - 6/1). During the second flow event following application, only 0.01% of ATZ and 0.08% of MTC were transported.

5.3 Measurement of Estrogen Concentrations

A map showing the fields where liquid (slurry) and solid animal wastes were applied is shown in Figure 5.4. Table 5.1 lists the application dates and total amounts applied for dairy bedding material broadcast in the fields on the south-east corner of ASREC. Dairy solids were applied to fields at the southeast corner of ASREC on multiple occasions during the previous winter as well as prior to and during the sampling period. Both of fields receiving dairy solids have tile drains which are connected to Box Ditch and affect the P3, P4, and P5 sampling stations.

Table 5.2 lists the amounts, manure source, application method and dates for manure slurry and lagoon effluent applications. Beef, Ossabaw, Swine, and Dairy manure slurries were sub-surface injected on multiple dates during the previous fall and winter. Pivot irrigation of Dairy slurry on fields affecting both legs of the ASREC stream network occurred during the previous winter and also during the weeks prior to the 5/25-5/29 sampling period.

Concentrations of aE2, bE2, E1, and E3 measured using the PSFM averaged 1.3±0.6, 1.2±0.5, 1.5±0.5, 2.3±1.5 ng/L respectively over the two month sampling period (Figure 5.5). Hormone concentrations did not appear to be correlated with manure/slurry applications suggesting that estrogen levels in streams and rivers affected by agricultural activity may be buffered by retarded transport and/or degradation of estrogens within the soil profile.

The maximum concentration of estrogens measured at the P1, P3 and P4 sampling locations occurred during the 4/23-4/26 sampling period following a prolonged rainfall event occurring 4/17-4/20. High concentrations of suspended sediments were also captured by the ISCO sampler at the P1 sampling station during this sampling period (Table 4.2) suggesting possible mobilization of particulate bound hormones by overland flow.

Maximum concentrations of aE2, bE2, E1, and E3 reached 19,18,19, and 62 ng/L at the P5 sampling station during the 5/6-5/10 deployment. Although dairy solids

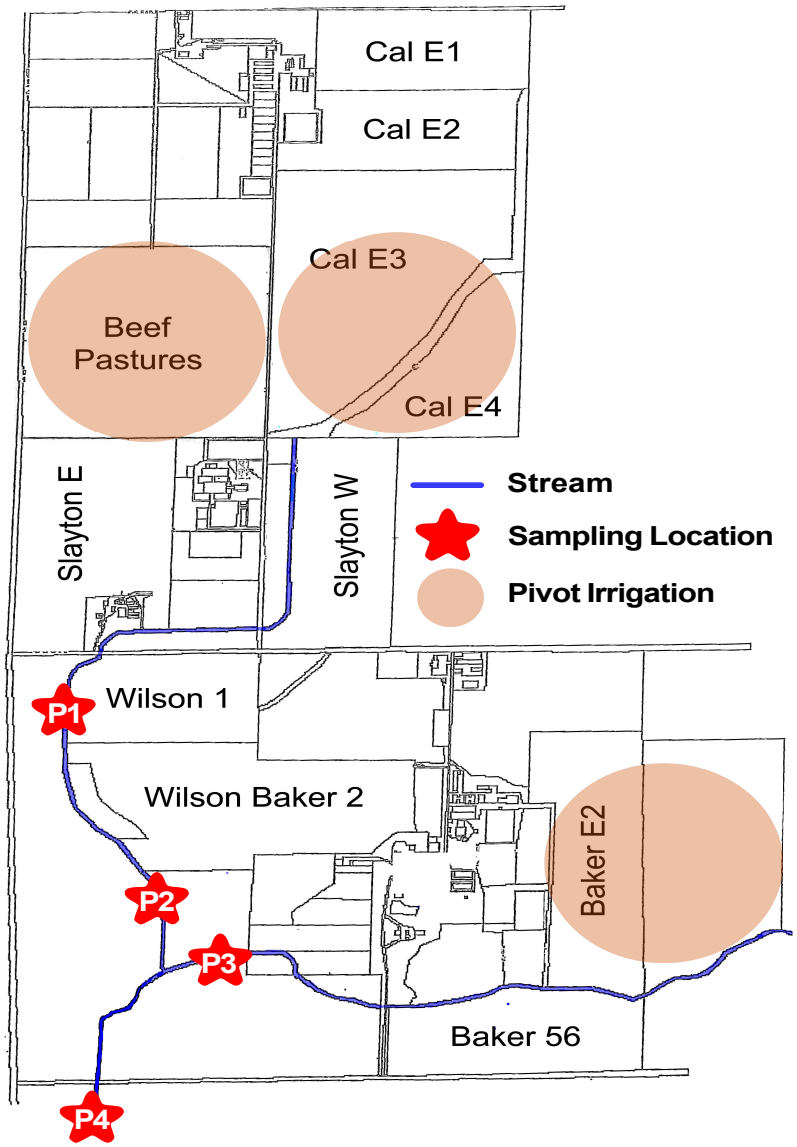


Figure 5.4.: Map of ASREC showing fields where manure was applied during the time period from July 2012 - June 2013.

were being broadcast on the Baker 56 field prior to and during this sampling period, elevated levels were not recorded at any of the other sampling stations and no significant discharge event occurred during this period. However, high antecedent moisture conditions and a rainfall event occurring 5/9-5/10 could have resulted in transport of hormones via over-land or sub-surface flow. Nonetheless, the particularly high

Table 5.1.: Dates, Location, and Amounts of Dairy Solids Broadcast Application at ASREC.

Date	Field	Total Tons
11/20/12	Baker 56	36
11/29/12	Baker 56	45
11/30/12	Baker 56	81
12/2/12	Baker 56	36
12/6/12	Baker 56	63
3/20/13	Baker 56	9
4/9/13	Baker 56	99
4/10/13	Baker 56	81
5/1/13	Baker 56	108
5/2/13	Baker 56	153
5/3/13	Baker 56	81
5/4/13	Baker 56	135
5/5/13	Baker 56	90
5/6/13	Baker E2	117
5/9/13	Baker E2	27
5/13/13	Baker E2	63
5/14/13	Baker E2	54
5/15/13	Baker E2	54
5/16/13	Baker E2	135
5/22/13	Baker E2	108
5/23/13	Baker E2	135
5/24/13	Baker E2	153
5/25/13	Baker E2	162
5/26/13	Baker E2	144

concentrations recorded at P5 during this time frame appear to be erroneous and laboratory contamination cannot be ruled out.

Table 5.2.: Dates, Location, and Amounts of Manure Slurry Applied at ASREC.

Date	Application Method	Source	Type	Field	Total Gallons
5/14/2013	Pivot Irrigation	Dairy	Lagoon Cell 2	Cal E3 & E4	189,000
5/15/2013	Pivot Irrigation	Dairy	Lagoon Cell 2	Cal E3 & E4	126,000
5/16/2013	Pivot Irrigation	Dairy	Lagoon Cell 2	Cal E3 & E4	493,500
11/8/2012	Pivot Irrigation	Dairy	Lagoon Cell 2	Beef Pastures	273,000
11/9/2012	Pivot Irrigation	Dairy	Lagoon Cell 2	Beef Pastures	388,500
11/10/2012	Pivot Irrigation	Dairy	Lagoon Cell 2	Beef Pastures	273,000
1016/2012	Pivot Irrigation	Dairy	Lagoon Cell 2	Cal E3 & E4	409,500
10/17/2012	Pivot Irrigation	Dairy	Lagoon Cell 2	Cal E3 & E4	399,000
11/8/2012	Pivot Irrigation	Dairy	Lagoon Cell 2	Cal E3 & E4	253,500
11/9/2012	Pivot Irrigation	Dairy	Lagoon Cell 2	Cal E3 & E4	388,500
11/10/2012	Pivot Irrigation	Dairy	Lagoon Cell 2	Cal E3 & E4	273,000
10/1/2012	Injected Slurry	Beef	Beef lagoon 1	Cal E2	341,032
10/1/2012	Injected Slurry	Beef	Beef lagoon 1	Cal E3	478,968
10/1/2012	Injected Slurry	Beef	Beef lagoon 1	Beef Pastures	432,000
10/1/2012	Injected Slurry	Beef	Beef lagoon 1	Beef Pastures	80,000
9/6/2012	Injected Slurry	Ossabaw	Ossabaw Site 2	Slayton W	100,650
9/7/2012	Injected Slurry	Ossabaw	Ossabaw Site 2	Slayton W	47,810
10/30/2012	Injected Slurry	Ossabaw	Ossabaw Site 2	Slayton W	89,110
11/11/2012	Injected Slurry	Ossabaw	Ossabaw Site 1	Cal E3	32,770
7/30/2012	Injected Slurry	Ossabaw	Ossabaw Site 1	Slayton W	35,810
11/2/2012	Injected Slurry	Swine	12 Room Slurrystore	Wilson 1	172,360
11/3/2012	Injected Slurry	Swine	12 Room Slurrystore	Wilson 1	131,740
11/5/2012	Injected Slurry	Swine	12 Room Slurrystore	Wilson 1	154,080
11/6/2012	Injected Slurry	Dairy	Dairy Slurrystore	Wilson Baker 2	58,520
11/6/2012	Injected Slurry	Dairy	Dairy Slurrystore	Slayton W	16,740
11/7/2012	Injected Slurry	Dairy	Dairy Slurrystore	Slayton W	66,440
11/8/2012	Injected Slurry	Dairy	Dairy Slurrystore	Slayton W	166,850
11/9/2012	Injected Slurry	Dairy	Dairy Slurrystore	Slayton W	28,400
11/9/2012	Injected Slurry	Dairy	Dairy Slurrystore	Baker 56	146,870
11/10/2012	Injected Slurry	Dairy	Dairy Slurrystore	Baker 56	147,840

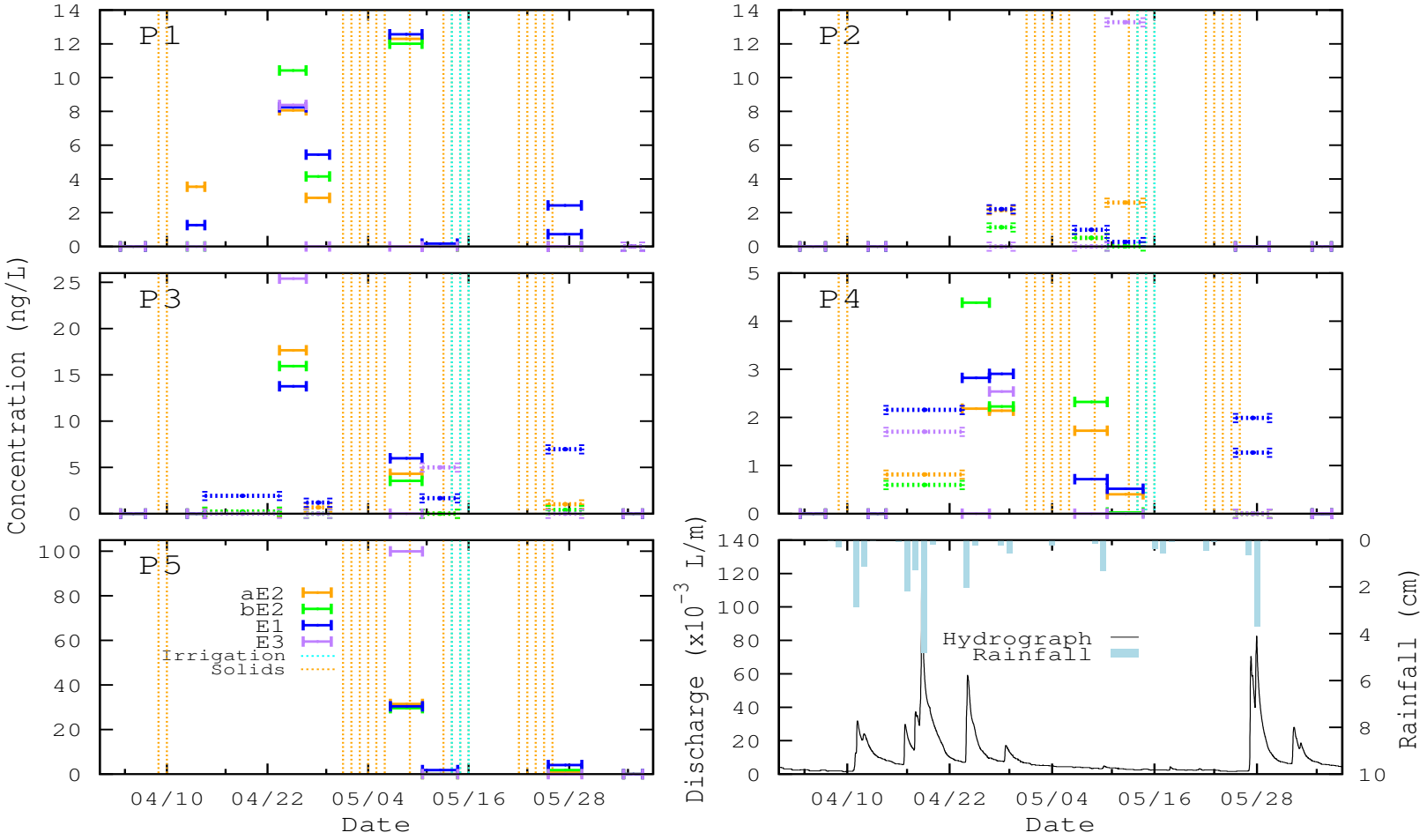


Figure 5.5.: Flow weighted average concentration of estrogens measured using the PSFM at five sampling locations near ASREC. Samples for which the cumulative water flux was beyond the linear range of all tracers are represented by dashed lines while those within the linear range of tracers are shown using solid lines. The hydrograph recorded at P1 is shown in the bottom right plot along with the hyetograph for the corresponding time period.

The amount and type of estrogens excreted by livestock varies greatly depending on species, age, sex, and reproductive status. Swine and poultry excrete estrogens mostly in urine (96% and 69% respectively) while cattle excrete them primarily in feces (58%) [3, 51, 84]. Estrogens are present in feces primarily in the unconjugated form while those in urine are mainly conjugated as glucuronides or sulfates [84]. Glucuronated estrogens readily deconjugated, presumably by β-glucuronidase enzyme produced by fecal bacteria, while sulfate forms are much more persistent [24]. In general cattle excrete larger amounts of aE2 whereas swine and poultry excrete primarily bE2 and E1 [30, 41, 42, 51, 91].

While swine manure slurry was subsurface injected in several fields during the previous fall/winter (7/30-11/11), only dairy and beef wastes were applied during 2013. Given that the dissipation half lives of estrogens measured in laboratory soil microcosms varies between < 1 d and 10 d with the formation of non-extractable residues [21, 59], it would seem that only hormones present in recently applied manures would be available for transport to nearby streams. However, if this is the case, aE2 might be expected to be present at significantly higher concentrations in PSFM samples since it is the dominant epimer in dairy and beef manures, which were the only manure types applied during 2013. This trend is not apparent in the data, however, where neither aE2 nor bE2 appears to be more prevalent. Microbial transformation of both aE2 and bE2 under aerobic conditions has been shown to result in the formation of E1. Under anaerobic conditions, E1 can be reduced back to estradiol with a preference for the bE2 isomer [67]. Therefore, it seems that transformation reactions favor the formation of E1 and bE2. The degree of degradation during transport, and hence the estrogen profile measured by the PSFM, will consequently depend upon environmental factors such as rainfall, soil moisture content, soil temperature, nutrient availability, and soil organic carbon content.

Estrogens sorb strongly to soil organic carbon with log K_{OC} values ranging from 2.94 - 3.34 [15, 31, 59, 65]. Lee et al. [59] found that sorption equilibrium for bE2 and E1 was attained within a few hours whereas Casey et al. [14] reported 48 hours

for bE2 to reach sorption equilibrium In river sediments, sorption was found to be even more rapid with near equilibrium achieved in the first 30 minutes [58]. In soils with high organic carbon content (as is common in agricultural fields), strong and rapid sorption may act to protect the hormones from degradation allowing them to accumulate within the soil profile [66]. Accumulation near the soil surface may result in transport via run-off with subsequent rain events. Build up of hormones in deeper soil horizons could result in increased persistence due to the lower microbial populations and decreased oxygen availability with depth [6, 67]. Following preservation for a prolonged period, colloid associated hormones may be mobilized during infiltration events. Freeze/thaw and wetting/drying events have been shown to increase mobilization of colloid associated materials [74]. Casey et al. [16] noted much more rapid movement of bE2 in a field lysimeter than predicted by its soil sorption coefficient suggesting probable colloidal transport.

Given the complex set of interactions between estrogens and the external environment along with interconversion between epimers and reduced/oxidized forms, it is not surprising that the observed concentrations are not easily correlated with manure applications or drainage. However, several general conclusions can be drawn from the PSFM data: (1) estrogen concentrations were generally lower at the sampling stations which were furthest from the source zone, (2) estrogen concentrations did not appear to be significantly correlated with manure applications, and (3) the highest estrogen concentrations were observed immediately following two large rainfall events occurring during early spring (4/17-4/20 and 4/24-4/25). Based on these conclusions, it can be inferred that strong sorption of estrogens within the soil profile and in benthic sediments results in accumulation with repeated manure application resulting in practically constant background levels of hormones in the dissolved phase of surface and ground water. Sorbed phase hormones can be mobilized with run-off or associated with soil particulates during rainfall events resulting in transport of the contaminants downstream from the source zone.

6 SUMMARY

A passive surface water flux meter (PSFM) for measurement of contaminant concentration and/or flux in rivers and streams was described and tested. This is the first time that a passive flux meter has been used in a stream under transient flow conditions. Furthermore, the PSFM has never before been used for measurement of the herbicides atrazine and metolachlor or any of the steroid hormones. Water flow through the PSFM was estimated by measuring miscible displacement of alcohol tracers from a granular activated carbon (GAC) sorbent layer. For calibration of water flow, tracer retardation factors (R) on GAC were measured by miscible displacement from packed columns and by batch sorption experiemnts. PSFM water flux was measured as a function of external flow velocity in a flume under constant flow conditions at a range of velocities representative of those in streams and rivers. The relationship between PSFM water flux and external water velocity in a flume was non-linear as predicted by Bernoulli's equation for velocity potential flow. However, in samples deployed in a natural stream, the relationship between PSFM water flux and external flow was weak with less flow passing through the PSFM under field conditions than predicted by measurements in a flume. The sorption and degradation of the contaminants of interest on surfactant modified zeolite (SMZ), the sorbent used for contaminant capture, were evaluated in laboratory and field experiments. Although the contaminants of interest were found to sorb moderately (ATZ and ATZ-DE) or strongly (MTC and steroid estrogens) on SMZ, kinetic experiments indicated that sorption non-equilibrium may be possible resulting in breakthrough of contaminants under moderate to high flow conditions. PSFM performance was evaluated in a stream network at the Purdue Animal Sciences Research and Education Center (ASREC). Sampling was focused on the steroid hormones and pesticides, which are present at trace concentrations in the stream network as a result of agricultural activity. Esti-

mates of contaminant flow weighted average concentration obtained using the PSFM were compared to concentrations measured in water samples taken at regular intervals using automated sampling equipment. Concentrations of both estrogens and pesticides measured using the PSFM were generally higher than those measured in water samples. This difference was attributed primarily to the high temporal variability of contaminant concentration and flow in the stream resulting in large temporal inequality of transport which is not adequately sampled using discreet methods. Furthermore, it was hypothesized that non-equilbrium tracer desorption during periods of high stream velocity may cause underestimation of PSFM specific discharge and consequent overestimation of contaminant flux in some cases. The PSFM was used to measure contaminant concentration at five strategically located sampling stations over the course of two months. The flow weighted average concentrations of steroid estrogens measured using the PSFM were generally in the low ng/L range while that of the pesticides was in the $\mu g/L$ range. Estrogen concentrations were not correlated with manure application, precipitation, or stream discharge and were more highly variable relative to the pesticides. Conversely, the concentration of the pesticides atrazine, desethyl-atrazine, and metolachlor increased dramatically following the first precipiation event following pesticide application suggesting disparate transport mechanisms for the compound classes.

7 RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Increased Deployment Times

This is the first time that the passive surface water flux meter (PSFM) has been used for measurement of hormone and pesticide concentrations. Due to the extremely low concentrations of these contaminants in streams and rivers, this is a particularly challenging application for the PSFM. Even with significant concentration of the extracted samples by evaporation, a large volume of water must be sampled by the PSFM to allow for accurate measurement of steroid hormones with the instrumentation used for this work (Sciex API-3000 with tandem Shimadzu HT-A Liquid Chromatography System). In approximately 1/3 of the field deployed flux meters, the large volume of water sampled by the PSFM suggests that significatnt tracer non-equilibrium may have occurred (Figures 5.3 and 5.5) potentially resulting in underestimation of PSFM water flux and consequent overestimation of contaminant concentration. It may be possible to decrease the potential for tracer non-equilibrium while maintaining sufficient sampling volume for instrumental quantitation of contaminants by further limiting the hydraulic conductivity of the device *and* increasing deployment times. However, stability of the target contaminants over the entire deployment period under field conditions must be verified.

7.2 Alternate Means of Limiting Flow

In the current PSFM design, flow though the flux meter is limited by incorporating a layer of fine sand on the PSFM outlet side (Figure 2.2). The fine sand layer is composed of a mixture of 75 mesh and 250 mesh (2/1) silica sands. This mixture provides a resistance to hydraulic flow which effectively limits the amount of water

sampled to < 500 mL/day under high stream flow conditions (1.5 ft/sec). A potential problem, however, is that some portion of the fine fraction of the sand layer can be washed through the outlet side even with a 320 mesh screen installed. Furthermore, since there may be some room for settling of the PSFM packing during transport (in the vertical position) and during deployment (in the horizontal position), it is possible for preferential flow pathways to form within the flow restricting sand layer. If this occurs, the magnitude of PSFM flow, and hence potential for tracer non-equilibrium, will increase significantly resulting in underestimation of PSFM specific discharge.

Therefore, it is prudent to develop alternative means of restricting PSFM flow that are not subject to this problem. A possibility that requires minimal modification to the current design is the incorporation of a small pore filtration membrane in lieu of the fine sand layer. If the membrane is placed on the outlet side, its sole function would be to limit flow. If placed on the inlet side of the PSFM, the filtration membrane would serve to limit flow and to capture suspended sediments along with any contaminants that may be absorbed to them. After deployment, it would be possible to measure sediment loading as well as concentration of dissolved and particulate associated contaminants. While blocking of the membrane by suspended particulates could be a problem with this method, the potential for blocking is lower if the membrane is placed on the outlet side of the device since sedimentation of particulates will occur within the SMZ and GAC layers reducing the filtration load. Control of the magnitude of resistance to flow could be accomplished by using multiple, stacked membranes or using membranes with differing pore size. However, fine grained control of hydraulic conductivity may be difficult.

Placement of a small capillary at the inlet and/or outlet side(s) of the PSFM could also serve to limit flow through the device. Alternatively, changes could be made to the configuration of the inlet and/or outlet opening(s) of the PSFM to decrease the hydraulic pressure gradient resulting in decreased PSFM specific discharge. If the inlet/outlet configuration is modified so that PSFM darcy flux is not influenced by stream velocity but by pressure gradient alone, it is possible to allow for stream stage-

weighted measurements. Such a configuration would theoretically result in improved estimates of flow weighted average contaminant concentration in the stream due to increased linearity of the relationship between specific discharge of water passing through the flux meter and external water velocity in the stream.

7.3 Alternative Sorbents for Capturing a Variety of Contaminants

SMZ is a versatile sorbent capable of capturing contaminants with widely varying properties including cations, anions, polar organic and hydrophobic organic compounds (HOCs). Additionally, SMZ can be modified by loading with silver ions to impart antimicrobial properties so that degradation of contaminants is minimized. However, SMZ has a number of disadvantages. Extraction of contaminants from SMZ using accelerated solvent extraction (ASE) at elevated temperature likely results in co-extraction of surfactant, potentially causing problems such as ion suppression during analysis by electrospray mass spectrometry, fouling of gas chromatographic inlets and/or columns, and alteration of chromatographic separations by ion pairing interactions with the analytes of interest. Furthermore, laborious clean-up steps may be required to remove co-extracted compounds prior to analysis. Therefore, it may be advantageous to investigate alternative sorbents.

GAC is a highly effective sorbent for HOCs; however, as discussed in Chapter 3, estrogens were not extractable once sorbed. Furthermore, GAC is not an effective sorbent for ionic species or highly polar organic compounds. Organosilane based materials make very good sorbents for HOCs, and 'C18' based commercial sorbents are widely available. Although these are expensive relative to GAC or SMZ, it would be possible to regenerate the sorbent after each use. Furthermore, it is possible to produce custom, reverse phase sorbents for capture of HOCs by silylation of granular silica gel thereby reducing costs. Sorbent disks are also available that could be used in a flux meter by sandwiching the disk between the inlet and the tracer impregnated GAC layer. An advantage of sorbent disks is that a flux meter containing multiple

layers of disks with affinity for different classes of chemical compounds could be easily constructed without the need for careful layering as is necessary with granular sorbents. Ion exchange resins could be used for capture of electrically charged contaminants, nutrients, or ionizable organic compounds. In fact, a multitude of different sorbents could be used in the flux meter as long as the compounds of interest have high affinity for the material, are extractable, and the hydraulic conductivity of the material is within the required range.

7.4 Perform Field Calibration of Water Flux Estimation

Although tracer retardation factors in GAC have been measured in packed columns under controlled laboratory conditions, the accuracy of water flow estimation under the transient conditions experienced in the field have not been verified. Capture of water exiting the PSFM outlet would be an effective means of calibrating the estimation of water flux by means of resident tracer depletion. Water leaving the flux meter could be captured in an empty submerged container connected to the device outlet. The submerged container could then be connected to a hollow tube that extends above the surface of the stream. In this way, the outlet side of the flux meter would always be at atmospheric pressure while the inlet side would be at some positive pressure that would depend upon stream stage and the linear velocity of the stream. The submerged container would need to be made of a heavy material, or otherwise need to be secured to the stream bed. Although the dependence of the PSFM pressure differential on stream velocity would be altered, calibration of estimation of water flow by measurement of tracer depletion in-situ would be possible providing further confidence in the accuracy of measurements made using the device under normal operating conditions.

7.5 Flux Meter for Capture of Suspended Sediments

Knowledge of the dynamics of sediment transport in the fluvial environment is important to a complete understanding of the fate of many contaminants. A wide variety of contaminants, including the estrogens and the herbicides investigated in this study, are strongly associated with sediments and soils and can be transported in the sorbed phase during periods of high discharge or with run-off occurring during storm events [25, 33, 37, 50, 58, 75, 78, 112]. Furthermore, contaminants may remain protected from microbial degradation in the sorbed phase, resulting in accumulation within the sediment bed or soil profile [6, 66].

In constrast to sorbent materials designed to capture dissolved contaminants, a granular, non-sorbing material could be used in place of SMZ in the flux meter to capture only suspended sediments by sedimentation letting dissolved constituents pass through. For example, glass beads or sand which has been washed with acid and peroxide to remove carbonates and organic matter could be used as a sorbent for capture of sediments. Numerous models have been used to describe the accumulation of particulates within porous media [8, 43, 46, 70, 104]. Sedimentation depends on chemical and hydrodynamic properties of the system and typically proceeds exponentially with respect to depth within the media bed (so called "deep bed filtration") as larger particulates deposit more quickly and smaller ones travel deeper into the media. Particle size distribution of the packing media in a PSFM for sediment capture could be designed for fractionation of suspended particulates by size or simply for capture of all particulates greater than a certain diameter.

APPENDICES

A PREPARATION OF TRACER LOADED GRANULAR ACTIVATED CARBON

A.1 Background

The depletion of resident alcohol tracers from Granular activated carbon (GAC) in the PSFM was measured to provide an estimate of cumulative specific discharge of water through the device. GAC was washed with de-ionized water to remove fine particulates and equilibrated with an aqueous solution containing 1% each of methanol, ethanol, isopropanol, t-butanol, and 2,4-dimethyl-3-pentanol for 48 hours. Tracer loaded GAC was used immediately after preparation for construction of flux meters or stored at 4°C for up to 72 hours before use. If refrigerated, GAC was allowed to warm to room temperature before use. Duplicate or triplicate samples of tracer loaded GAC were taken at the time of flux meter construction for determination of initial tracer concentrations as outlined in Appendix D.

A.2 Procedure

1. Weigh a dry, empty 2 L plastic bottle.
2. Weigh a dry, empty 1000 mL graduated cylinder.
3. Add 1000 mL of dry GAC to the graduated cylinder.
4. Weigh the graduated cylinder containing dry GAC.
5. Pour the GAC into a 80 mesh sieve and wash with ultra-pure water until the wash water is clear.
6. Transfer the washed GAC into the plastic bottle.

7. Weigh the bottle containing GAC and water.
8. Calculate the amount of additional water needed to make 1 L of GAC and 1 L of water.
9. Add the required amount of water.
10. Weigh the plastic bottle containing GAC and water.
11. Using a 10 mL pipet, add 10 mL each of methanol, ethanol, isopropanol, t-butanol, and 2,4-dimethyl-3-pentanol (shake the mixture thoroughly after adding each alcohol).
12. Place container on a rotary end-over-end mixer for 48 hours.
13. Store in refrigerator at 4°C until ready to use.

B MEASUREMENT OF SORBENT BULK DENSITY, PARTICLE DENSITY, AND POROSITY

B.1 Background

Sorbent bulk density (ρ_b) and porosity (ϕ) are necessary parameters for estimating solute retardation factor (R) from the sorbent-solution partition coefficient (K_d).

$$R = 1 + \frac{\rho_b}{\phi} K_d$$

B.2 Approach

Bulk density, porosity, and particle density were determined gravimetrically.

B.3 Procedure

1. Weigh a clean, dry 25 mL volumetric flask.
2. Fill the flask to mark with sorbent, tapping the sides as you add it to fill as much empty space as possible.
3. Weigh the flask containing dry sorbent.
4. Measure room temperature.
5. Add room temperature distilled water to the flask until $\approx$ 80% full (care must be taken when adding water to GAC since the process is exothermic and foaming may result).
6. Place the flask in a vacuum desiccator connected to house vacuum ($\approx$ 25 in. Hg).

7. SLOWLY begin to apply vacuum to evacuate entrapped and dissolved air from sorbent/water.
8. When bubbling has nearly ceased, discontinue vacuum and fill flask with water to the mark.
9. SLOWLY begin to apply vacuum.
10. After bubbling begins to slow, increase vacuum slowly until vacuum is at full setting ($\approx$ 25 in. Hg).
11. When bubbling has completely ceased, remove from vacuum.
12. Adjust the water level to the mark.
13. Weigh the flask containing sorbent and water.
14. Remove all sorbent from the flask by washing with de-ionized water.
15. Fill the flask to the mark with de-ionized water.
16. Weigh the flask containing water.

B.4 Calculations

$$FlaskVolume = \frac{(Flask + Water) - (Flask)}{DensityWater}$$

$$BulkDensity = \frac{(Flask + Sorbent) - (Flask)}{FlaskVolume}$$

$$Porosity = \frac{\frac{(Flask + Sorbent + Water) - (Flask + Sorbent)}{DensityWater}}{FlaskVolume}$$

C DESORPTION OF ALCOHOL TRACERS FROM GRANULAR ACTIVATED CARBON

C.1 Hypotheses

- Methanol, ethanol, isopropanol, and t-butanol span a wide range of affinity for the GAC surface
- Larger tracers exhibit slower desorption kinetics resulting in potential non-equilibrium under field conditions

C.2 Approach

GAC was equilibrated with a sterile aqueous solution containing a mixture of 1% each of methanol (MeOH), ethanol (EtOH), isopropanol (IPA), and t-butanol (TBA). Tracer concentrations in the aqueous phase were measured by gas chromatography with flame ionization detector (GC/FID) using a DB-624 column as outlined in Appendix D at 12 hour intervals until the change in aqueous concentration was less than 5%. After near equilibrium was attained, the aqueous phase was decanted and fresh 0.005 M $CaCl_2$ solution added. Tracer concentrations were then measured at 0, 0.25, 0.5, 1, 2, 4, 8, 24, 48, and 72 hours. At each time point, a 1.5 mL aliquot of solution was transferred to a 2 mL HPLC vial and analyzed by GC/FID. After 72 h, the aqueous solution was decanted and fresh 0.005 M $CaCl_2$ solution added. The samples were allowed to equilibrate for 24 hours, and the tracer concentrations determined. The aqueous phase was decanted and fresh 0.005 M $CaCl_2$ solution added with equilibration two more times to obtain the desorption isotherm. All tracer mass lost from the aqueous solution was assumed to be sorbed, and the tracer sorption

coefficient calculated using the equation:

$$\frac{M_{aq}}{M_{tot}} = \frac{1}{K_d \frac{s}{l} + 1}$$

Table C.1.: Retardation factors for each tracer, measured in miscible displacement experiments, were used to estimate C_w at each step of the procedure given the initial concentration of 1%. Solid-liquid ratios were chosen to result in 20-80% of tracer mass in the aqueous phase for each tracer at one or more of the solid-liquid ratios.

Tracer	R	Kd (mL/g)	M_{aq}/M_t	C_i (mg/L)	GAC (g)	Solution (mL)	C_{w1}	C_{w2}	C_{w3} (mg/L)	C_{w4}	C_{w5}
meoh	1.8	1.2	0.67	10000	40	100	6687	4451	2963	1972	1313
etoh	6.7	8.8	0.22	10000	40	100	2207	1964	1747	1554	1383
ipa	31	46	0.05	10000	40	100	511	498	485	473	460
tba	71	108	0.02	10000	40	100	225	223	220	218	215
meoh	1.8	1.2	0.93	10000	6	100	9308	4976	2660	1422	760
etoh	6.7	8.8	0.65	10000	6	100	6538	4401	2962	1994	1342
ipa	31	46	0.26	10000	6	100	2640	2292	1989	1727	1499
tba	71	108	0.13	10000	6	100	1333	1244	1161	1084	1011
meoh	1.8	1.2	0.98	10000	1.5	100	9818	4998	2545	1296	660
etoh	6.7	8.8	0.88	10000	1.5	100	8831	4932	2754	1538	859
ipa	31	46	0.59	10000	1.5	100	5893	4157	2932	2068	1459
tba	71	108	0.38	10000	1.5	100	3808	3083	2496	2021	1636

C.3 Procedure

1. Weigh eight clean, dry 125 mL glass bottles with teflon-lined caps.

2. Sterilize bottles by dry autoclave for 30 min.

3. Prepare 0.005 M $CaCl_2$ solution by dissolving 0.735 g of $CaCl_2 * 2H_2O$ in 1 L of water.

4. Sterilize the $CaCl_2$ solution by boiling for 15 min, cover the solution, and cool to room temperature.

5. Add 10 mL each of methanol, ethanol, isopropanol, and t-butanol to the $CaCl_2$ solution, securely close the container, and mix well by shaking.
6. Add 1.5 g of GAC to 2 of the bottles, 6 g of GAC to 2 of the bottles, and 40 g of GAC to 2 of the bottles (the other 2 are controls and will not contain GAC).
7. Add 100 mL of sterile tracer solution to the samples and weigh bottles.
8. Equilibrate the samples at $23 \pm 3^{\circ}$ C for 12 hours.
9. After 12 h, centrifuge at 650 g for 20 min.
10. Transfer 1.8 mL of the aqueous phase to an HPLC vial.
11. Analyze for tracers by GC/FID.
12. If the concentration of tracers has changed from the previous value by more than 5%, equilibrate for another 12 h and repeat.
13. After equilibrium is reached, decant remaining aqueous solution carefully and weigh tubes.
14. Add 100 mL of fresh, sterile 0.005 M $CaCl_2$ solution (without tracers).
15. Equilibrate samples at 23°C for 0, 0.25, 0.5, 1, 2, 4, 8, 24, 48, and 72 hours, centrifuging and taking a 1.8 mL aliquot sample at each time point and placing the solution back on the mixer.
16. After all of these samples have been taken (72h), centrifuge, decant aqueous solution, and weigh samples.
17. Add another 100 mL of fresh, sterile $CaCl_2$ solution to the bottles.
18. Equilibrate samples on rotary mixer for 24 h.
19. Centrifuge, take 1.8 mL sample for GC analysis, decant aqueous solution, weigh sample, and repeat last 3 steps with fresh $CaCl_2$ solution two more times to obtain the desorption isotherm.

D EXTRACTION OF TRACERS FROM GAC AND ANALYSIS BY GAS CHROMATOGRAPHY

D.1 Background

GAC from flux meters and packed columns was extracted using 2-butanol:4-methyl-2-pentanone (1:1) and analyzed by gas chromatography with flame ionization detector (GC/FID) using a DB-624 column as outlined in Appendix D.

D.2 Procedure

1. Homogenize GAC sample to be extracted by mixing with a spatula (work quickly so volatile tracers are not lost).
2. Transfer 2 g (wet mass) of GAC to a 35 mL glass centrifuge tube with teflon-lined closure (allow excess water to drain from the wet sorbent, but do not attempt to actively dry the sorbent).
3. Add 35 mL of 2-butanol:4-methyl-2-pentanone (50:50) containing 0.1% 2-ethyl-1-hexanol (EtHexOH, internal standard).
4. Equilibrate the mixture on rotary end-over-end mixer at 30 rpm overnight.
5. Transfer 1.5 mL of extract to an HPLC vial.
6. Analyze by GC/FID:
    - Column: J&W Scientific DB-624 60m X 0.53mm ID, 3μm film thickness
    - Carrier Gas = Helium at 38 cm/sec
    - Split Ratio = 15

- Injector temperature = $220°C$
- Detector temperature = $240°C$
- Column Temperature Program:
  - Initial temp = $60°C$
  - Ramp $5°C/min$ to $80°C$
  - Ramp $10°C/min$ to $170°C$
  - Ramp $20°C/min$ to $230°C$
  - Hold at $230°C$ for 1 minute

Table D.1.: Retention Time of Tracers and Internal Standard

Tracer	Retention Time (min)
MeOH	4.4
EtOH	5.1
IPA	5.6
TBA	6.0
DMP	13.2
EtHexOH	17.4

E MISCIBLE DISPLACEMENT OF TRACERS FROM GAC

E.1 Rationale

Estimation of PSFM water flux from fraction of tracer remaining is dependent upon the assumption that transport of tracers within the PSFM occurs under equilibrium conditions. If the velocity of water moving through the flux meter is fast relative to the rate of tracer sorption/desorption, dispersion and consequent underestimation of PSFM water flux will result. Because contaminants which are present at very low concentration require sufficient mass capture (and hence water flow) to allow for instrumental detection and quantitation, some degree of non-equilibrium may be unavoidable. Therefore, it is desirable to perform miscible displacement experiments to assess the potential for non-equilbrium and to estimate tracer retardation factors at flow rates similar to those experienced in the field.

E.2 Approach

GAC was equilibrated with tracers and initial tracer concentration determined using the protocols outlined in Appendices A and D. Column volume and sorbent porosity were determined gravimetrically as described Appendix B. The GAC column was wet packed keeping the sorbent submerged in water and gently tapping on the sides of the column to avoid dead space within the column.

Pump flow rate, measured gravimetrically, was adjusted prior to connecting to the column and monitored throughout the run. After the flow was adjusted to the desired rate, the pump was connected to the column and flow initiated. The concentration of tracers leaving the column outlet were determined by means of a flow-through cell attached to a gas chromatograph. The sampling rate for determination of tracer

conentration in column effluent by GC was initially fast to capture elution of smaller tracers and slower after methanol and ethanol have eluted.

E.3 Procedure

1. Measure column dimensions
2. Weigh empty column with end fittings.
3. Fill column with tracer loaded sorbent using the wet packing method (water level always just above sorbent, tap sides continuously while adding more sorbent and water).
4. Before connecting pump to column, check flow rate by pumping water.
5. Prepare standards containing tracer alcohols in sterilized water (boiled and cooled prior to adding alcohols in the desired amount). The highest standard should contain 6000 mg/L methanol, 2500 mg/L ethanol, 600 mg/L isopropanol, and 200 mg/L t-butanol. Four additional standards should be prepared by serial dilution of the highest standard to 50%, 25%, and 12.5% using sterilized water.
6. Connect pump to column.
7. Start pumping water through the column at the desired flow rate (record start time).
8. Connect column outlet to flow through cell on the gas chromatograph.
9. Measure flow rate gravimetrically by weighing effluent solution at periodic intervals.
10. Measure tracer alcohol concentration in column effluent by gas chromatography using the protocol outlined in Appendix. D. Tracer concentration should be measured at frequent intervals initially. After methanol and ethanol have eluted, the sampling frequency can be decreased.

F BATCH SORPTION OF HORMONES ON GAC

F.1 Background

A batch sorption experiment was conducted in 35 mL teflon-lined glass centrifuge tubes at $23°C$ to evaluate the affinity of steroid hormones for the GAC surface.

F.2 Procedure

1. Prepare a stock solution containing 10 mg/L hormones in acetonitrile.
2. Dilute the stock solution to 0.4 mg/L with acetonitrile to make the intermediate solution.
3. Prepare equilibration solutions of 25, 50, 100, 200, and 400 ng/L prepared by serial dilution of the intermediate solution in deionized water.
4. Add dry GAC (0.1g) to the centrifuge tubes.
5. Add equilibration solution (35 mL) to the centrifuge tubes.
6. Mix samples on a rotary end over end mixer for 24 hours.
7. After equilibration, centrifuge at 750 g for 20 min.
8. Transfer a 20 mL aliquot of clear supernatant to a clean 35 mL centrifuge tube.
9. Extract the 20 mL aliquot with dichloromethane (5 mL) for one hour.
10. Transfer a 4 mL aliquot of the DCM layer to a conical vial and evaporated to dryness under a gentle stream of nitrogen.
11. Reconstitute in 1 mL of methanol and analyze for hormones using LC/MS.

F.3 Calculation

Determine the sorbent/water sorption coefficient (K_d) assuming that all mass of hormone lost from solution is sorbed:

$$\frac{M_{aq}}{M_{tot}} = \frac{1}{K_d \frac{s}{l} + 1}$$

where M_{aq} is the mass of hormone in the aqueous phase and M_{tot} is the total mass of hormone in the initial equilibration solution.

G CEC/ECEC MEASUREMENT FOR SMZ

G.1 Background

Preparation of surfactant modified zeolite requires knowledge of the externally accessible cation exchange capacity (CEC) of the zeolite surface. It has been shown that nearly 100% of surfactant molecules are adsorbed up to the external CEC of zeolites resulting in monolayer coverage of the surface [40]. If additional surfactant is added, a partial or full bilayer can be formed resulting in a positively charged surface and changing the sorbent affinity for both ionic and neutral species in solution.

G.2 Approach

The determination of both total and external CEC of a natural granular clinoptilolite zeolite was determined by a compulsive exchange method [73]. Fines were removed from the granular zeolite using an 80 mesh seive and the zeolite was washed with 1 N NaOAc buffered to pH=5 to remove free carbonates and saturate cation exchange sites with Na^+. The excess Na^+ was removed by rinsing with DI water and ethanol. External exchange sites were then replaced for hexadecyltrimethylammonium bromide (HDTMA) and the external CEC determined by measurement of sodium in the washings. Excess HDTMA was removed by washing with ethanol, and the internal exchange sites were exchanged by washing with 1 N NH_4OAc. The internal CEC was then determined by measurement of sodium in the washings.

G.3 Preparation of Solutions

1. A solution of 1 N NaOAc was prepared by dissolving 20.5 g of NaOAc in 200 mL of de-ionized water, adjusting to pH=5 using 1M HCl or 1M NaOH, and diluting to 250 mL using de-ionized water
2. A solution of 1 N NH_4OAc was prepared by dissolving 19.25 g of NH_4OAc in 250 mL of de-ionized water
3. A solution of 0.5 N HDTMA was prepared by dissolving 45.6 g of HDTMA in 250 mL of de-ionized water

G.4 Procedure

1. Granular zeolite (100 g) was weighed into a beaker.
2. Fine particulates were removed by rinsing/shaking with de-ionized water over an 80 mesh seive.
3. The washed zeolite was returned to the beaker and dried in a vacuum oven (50° C and 25 in Hg).
4. Dried zeolite (5 g) was weighed into a clean 50 mL polypropylene centrifuge tube.
5. Another clean 50 mL polypropylene tube was processed as method blank.
6. NaOAc solution (20 mL) was added to the zeolite and the solution equilibrated for 1 hour on a rotary end-over-end mixer.
7. The mixture was centrifuged at 650 g for 20 min, and the supernatant discarded.
8. The zeolite was then washed with two 20 mL portions of NaOAc solution (1 hour first wash, overnight second wash, washes discarded).

9. Excess NaOAc was removed by rinsing for 15 min with one portion of de-ionized water (30 mL) and three portions of ethanol (20 mL each).

10. HDTMA solution (20 mL) was added to the sample and equilibrated at 50° C for 24 hours.

11. The sample was centrifuged at 650 g for 20 min, and the supernatant transfered to a clean 50 mL polypropylene centrifuge tube.

12. The sample was washed two more times with 20 mL HDTMA solution at 50° C for 24 hours each combining washings.

13. Combined washings were then diluted with de-ionized water to 100 mL in a clean (acid washed) polypropylene volumetric flask.

14. Combined washings were analyzed for sodium content by inductively coupled plasma/ mass spectrometry.

15. Excess HDTMA was removed by washing with one 20 mL of ethanol for 15 min, centrifuging, and discarding wash.

16. NH_4OAc solution (20 mL) was added to the sample and equilibrated for 24 hours on a rotary mixer.

17. The sample was centrifuged at 650 g for 20 min, and the supernatant transferred to a clean 50 mL polypropylene centrifuge tube.

18. The sample was washed two more times with 20 mL NH_4OAc solution for 24 hours each combining washings.

19. Combined washings were diluted to 100 mL in a clean 100 mL polypropylene volumetric flask.

20. Combined washings were analyzed for sodium content by inductively coupled plasma/ mass spectrometry.

G.5 Calculations

$$\text{CEC} = \frac{mgNa}{L} \times 0.1L \times \frac{1mmol}{23mg} \times \frac{1meq}{1mmol} \div 5g\ zeolite = \frac{meq}{g}$$

H PREPARATION OF SURFACTANT MODIFIED ZEOLITE

H.1 Background

The sorption capacity of natural clinoptilolite zeolite for hydrophobic organic compounds can be dramatically increased by replacement of surface exchangeable cations with cationic surfactants [28, 99, 100, 107]. Mono-layer surfactant coverage on the zeolite surface has been shown to maximize sorption kinetics for BTEX compounds [107]. Experiments were conducted to determine the external cation exchange capacity (ECEC) of the zeolite (Appendix G). Zeolite was equilibrated with cetyltrimethylammonium bromide (CTAB) at 40°C for 20 hours. The SMZ was washed with DI water and dried in a vacuum oven (25 in Hg, 50°C). Studies revealed that equilibration of zeolite with 1 eq. of CTAB surfactant (based on the measured ECEC) resulted in SMZ which required excessive washing with DI water to remove all excess surfactant as indicated by lack of foaming. When zeolite was equilibrated with 0.7 eq. of CTAB, however, the resulting sorbent was free of excess surfactant after 3 washes with DI water. Since excess surfactant may cause increased affinity of contaminants for the mobile phase, and hence decreased sorption, 0.7 eq. was chosen as the loading amount to avoid this possibility.

Recent studies have found that silver ions sorbed on montmorillonite reduced the number of bacterial colonies by 4-10 orders of magnitude within 24 hours [64]. They found the anti-bacterial activity to be due to desorption of Ag^+ into solution with a minimum inhibitory concentration (MIC) of both dissolved Ag^+ and montmorillonite-Ag^+ of $\approx$ 1 mg/L. Zeolites, which also have high cation exchange capacity, should have similar bactericidal properties if treated with Ag^+. As water flows through the PSFM, silver ions are released from the surface by cation exchange and function as

anti-bacterial agents in solution. SMZ for use as a sorbent in passsive surface water flux meters was loaded with silver ions at a rate of 15% (w/w).

H.2 Calculations

Surfactant Loading

Zeolite External CEC = $0.12\frac{meq}{g}$
Needed for 70% coverage = $0.12\frac{meq}{g} \times 1\frac{mmol}{meq} \times 0.7 \times 364\frac{mg}{mmol} \times 500g = 15.3g$

Silver Loading

Zeolite CEC = $0.5\frac{meq}{g}$
Ag needed for 15% of CEC = $0.5\frac{meq}{g} \times 1\frac{mmol}{meq}.15 \times 169.9\frac{mg}{mmol} \times 500g = 6.37g$

H.3 Procedure

1. Weigh 500g of granular zeolite and remove fine particulates by washing with deionized water through an 80 mesh sieve.
2. Transfer washed zeolite to a 1 L plastic container.
3. Prepare 2 L of 0.5 M sodium acetate:
   (a) Add 82 g of sodium acetate to a 2 L volumetric flask.
   (b) Fill the flask to 70% capacity with ultra pure water and swirl to completely dissolve sodium acetate.
   (c) Fill the flask to volume with ultrapure water.
   (d) Transfer the resulting solution to a 2 L plastic container.

4. Fill the plastic container containing washed zeolite to 90% capacity with sodium acetate solution.
5. Place the zeolite/ sodium acetate mixture on a rotary mixer for 1 hour.
6. Remove the zeolite/ sodium acetate mixture from the mixer and discard supernatant solution.
7. Wash the zeolite twice more to saturate all exchange sites with sodium ions.
8. Dissolve silver nitrate (6.37 g) in 200 mL of ultra pure water in a 250 mL beaker.
9. Transfer silver nitrate solution to the container with sodium exchanged zeolite.
10. Add ultra pure water to the zeolite/silver mixture to fill the container to 90% capacity.
11. Place the zeolite/ silver mixture on a rotary mixer for 1 hour.
12. Discard the excess supernatant and wash silver loaded zeolite once more with ultra pure water.
13. Add cetyltrimethylammonium bromide (CTAB, 15.3 g) to the container with zeolite.
14. Add ultra pure water to the zeolite-silver-CTAB mixture to fill the container to 90% capacity.
15. Place the zeolite/surfactant mixture on a mixer at $40°C$ for 20 hours.
16. Remove the mixture from the mixer and decant excess surfactant solution.
17. Wash surfactant modified zeolite with ultra pure water three times or until no foam forms upon shaking the wash solution.
18. Discard the excess water and dry SMZ in a vacuum oven at 50°C.

H.4 Comments

1. Surfactant loading can be determined by measuring the difference in initial and final surfactant concentration after equilibration with the zeolite. Washes should be combined with the equilibration solution before measurement of surfactant concentration in the "after" case.

2. A surfactant bilayer can allow the SMZ to absorb organics, anions, and cations.

3. Although cationic surfactants have antimicrobial activity in solution, their ability to disrupt microbial activity is greatly reduced when absorbed to mineral surfaces [64]. However, sorption of siver ions to montmorillonite exchange sites has been shown to be effective as a long term antimicrobial due to slow release upon exchange with other cations.

I EXTRACTION OF HORMONES AND PESTICIDES FROM SMZ

I.1 Background

Due to the very low concentrations of steroid hormones and pesticides present in stream water, all of the SMZ in the flux meter must be extracted so that the contaminants will be detectable in the final prepared sample. Accelerated Solvent Extraction (ASE) has the capability to extract large amounts of sorbent with minimal solvent using elevated temperature and pressure. Hormones and Pesticides were extracted from SMZ by ASE using methanol. The pesticides ATZ, ATZ-DE, and MTC were analyzed in the extracts without further sample preparation using the protocol outlined in Appendix M. Because of the extremely low concentration of hormones in ASE extracts, however, concentration of the extracts by evaporation was necessary to allow detection of the hormones by LC/MS using electrospray ionization.

I.2 Procedure

1. Loosen the PFM inlet side end cap using two pipe wrenches.
2. Weigh a clean, dry 100 mL beaker.
3. Carefully remove the inlet side end cap over the 100 mL beaker so that no SMZ was lost.
4. Use a spatula to transfer all of the SMZ from the PFM to the 100 mL beaker.
5. Weigh the 100 mL beaker containing wet SMZ.
6. Homogenize the wet SMZ using a spatula.
7. Weigh three clean, dry ASE extraction cells.

8. Affix an end cap to each extraction cell while leaving the other end open being careful not to mix up end caps since the cells have already been weighed.
9. Position the extraction cells with closed end down and a glass fiber filter placed into the extraction cell to cover the bottom frit.
10. Transfer a 1 cm layer of pelletized diatomacous earth into the extraction cell.
11. Transfer SMZ to fill the extraction cell.
12. Place a glass fiber filter on top of the SMZ sorbent.
13. Attach the ASE extraction cell top end cap.
14. Tighten both end caps.
15. Place the extraction cell into the ASE extractor.
16. Place a 250 mL clear narrow mouth collection bottle into the ASE extractor at the position matching the extraction cell.
17. Extract the sample using methanol:
    (a) Extraction temp = 75°C
    (b) Extraction cycles = 2
    (c) Extraction time = 5 min
    (d) Heating time = 5 min
    (e) Flush volume = 30%
18. Combine the extracts from the 3 samples for each flux meter resulting in one sample per flux meter.
19. Measure the combined volume of the extract using a 250 mL graduated cylinder.
20. Transfer a 1 mL aliquot of the extract to a 2 mL HPLC vial for analysis of ATZ, ATZ-DE, and MTC.

21. The remaining extract is concentrated for analysis of estrogens:

    (a) Add molecular sieves (2g, type 3a, dried at 150°C under 25 in. Hg vacuum for 24 hours) to the extract.

    (b) Mix the sample on a rotary end-over-end mixer for 5 minutes.

    (c) Decant the sample into a 200 mL round bottom flask.

    (d) Wash the molecular sieves with 15 mL of ethyl acetate/ ethanol (1:1).

    (e) Combine washes and extract in the 200 mL round bottom flask.

    (f) Evaporate the extract by rotary evaporation at 50°C with a gentle stream of nitrogen blowing into the round bottom flask to facilitate evaporation.

    (g) When the sample is concentrated to $\approx$ 4 mL, discontinue evaporation.

    (h) Pass the concentrated sample through a small column containing 3 g sodium sulfate on top of 1 g silica gel and collect the effluent in a 5 mL conical vial (sample passes through sodium sulfate first, both sodium sulfate and silica gel should be dried at 150°C under 25 in. Hg vacuum for 24 hours prior to use, a small amount of positive pressure is necessary to force the sample gently through the column).

    (i) Wash the sodium sulfate/silica column by passing 2 mL of ethyl acetate/ ethanol (1/1) through the column.

    (j) Combine washes with the clarified sample in the 5 mL conical vial.

    (k) Evaporate the sample to dryness under a gentle stream of nitrogen. For samples where the evaporation rate decreases markedly near the end indicating residual water, shake the sample with methyl-t-butyl ether (MTBE, 2 mL) and transfer the MTBE (upper) layer to a clean, dry 5 mL conical vial for evaporation to dryness under nitrogen.

22. Reconstiture the evaporated sample in 1 mL of methanol containing internal standard (26.5 ng bE2-16,16,17-d3) and analyze by LC/MS using the protocol outlined in M.

J SORPTION OF HORMONES AND PESTICIDES ON SMZ

J.1 Hypotheses

- The sorption of hormones and atrazine to Surfactant Modified Zeolite (SMZ) is sufficiently strong to ensure that breakthrough from the PSFM does not occur under near-equilibrium flow conditions.
- The kinetics of hormone and pesticide sorption on SMZ is sufficiently slow to allow for non-equilibrium transport of these contaminant within the PFM under field conditions.

J.2 Approach

SMZ was equilibrated with a sterile aqueous solution containing a mixture of aE2, bE2, E1, TST, AND, aTB, bTB, TND (17 ng/mL each), ATZ (100 ng/mL), ATZ-DE (250 ng/mL), ATZ-DIP (600ng/mL), ATZ-OH (1500ng/mL), MTC (110ng/mL), and CSF (2000ng/mL). SMZ-water partition coefficients (K_d) for pesticides were measured after equilibration for 0 (no SMZ controls), 4, 8, 12, 24, and 60 h while K_d for hormones were measured at 0, 8, 24, 60, and 120 h to evaluate sorption kinetics. After the prescribed time interval, samples were centrifuged, and 0.5 mL of the aqueous phase transferred to a 2 mL HPLC vial using a volumetric glass pipet, 0.5 mL of methanol was added and the aqueous phase analyzed by LC/MS with electrospray ionization. The remaining aqueous solution was decanted and the solid phase extracted with 35 mL of methanol. After centrifugation, methanol extracts were analyzed by LC/MS.

Table J.1.: Calculation of Ideal Solid-Liquid Ratio for Contaminant Sorption on SMZ

Analyte	K_{ow}	K_d (L/kg)	Optimum s/l	SMZ (g)	Solution (mL)	Fraction in Solution	C_i (ng/mL)	Predicted C_w (ng/mL)	LOQ (ng/mL)
E1	5012	2130	0.0005	0.1	38	0.15	17	2.6	0.2
aE2	10000	1520	0.0007	0.1	38	0.20	17	3.4	0.2
bE2	10000	3100	0.0003	0.1	38	0.11	17	1.9	0.2
E3	794	338	0.003	0.1	38	0.53	17	9.0	0.2
TST	2512	403	0.002	0.1	38	0.49	17	8.3	0.2
AND	794	1040	0.001	0.1	38	0.27	17	4.5	0.2
aTB	200	462	0.002	0.1	38	0.45	17	7.7	0.2
bTB	200	597	0.002	0.1	38	0.39	17	6.6	0.2
ATZ	562	4	0.27	8	33	0.53	29	15	0.04
ATZ-DE	35	<4	>0.27	8	33	>0.53	47	>25	0.15
ATZ-DIP	13	<4	>0.27	8	33	>0.53	76	>40	0.4
ATZ-OH	1	<2	>0.50	8	33	>0.53	155	>82	ND
MTC	794	545	0.002	0.1	38	0.41	110	45	0.1
CSF	0.1	587	0.002	0.1	38	0.39	25	10	0.5

Table J.1: SMZ-water partition coefficients (K_d) measured in a preliminary sorption test were used to calculate an ideal solid:liquid ratio. For compounds which SMZ-water K_d was not measured in the preliminary experiment (brown highlighted), K_{ow} was used to predict K_d based on a linear relationship fit to K_d-K_{ow} data for the other compounds. Solid/liquid ratios for sorption of contaminants on SMZ were proposed for equilibration experiments in 35mL tubes. C_w's were predicted based on C_i and K_d and compared to the limit of quantitation for analysis by LC/MS.

Table J.2.: List of samples for batch sorption experiment

Equilibration Time (h)	Sorbent (g)	Solution (mL)	Replicates
0	0	38	3
4	8	33	3
8	8	33	3
8	0.1	38	3
12	8	33	3
24	8	33	3
24	0.1	38	3
60	8	33	3
60	0.1	38	3
120	0.1	38	3

Table J.2: Every sample was spiked with all of the contaminants at concentrations listed above (although hormones are expected to be $< LOQ$ in 5g SMZ samples and K_d unmeasureable for ATZ and degradates in 0.1g SMZ samples.

J.3 Procedure

1. Weigh thirty clean, dry centrifuge tubes with teflon-lined caps.

2. Sterilize centrifuge tubes by dry autoclave for 30 min.

3. Prepare 0.005 M $CaCl_2$ solution by dissolving 1.103 g of $CaCl_2 * 2H_2O$ in 1.5 L of water.

4. Sterilize the $CaCl_2$ solution by boiling for 15 min, then cool to room temperature.

5. Add SMZ (0.1 g) to 12 of the centrifuge tubes and 8 g of SMZ to another 15 tubes (an additional 3 were controls without SMZ).

6. Add 38 mL of sterile 0.005 M $CaCl_2$ solution to 0.1g samples and 33 mL of solution to 8g samples and record the weight of all tubes.

7. Add parent hormone/pesticide spiking solution (50 μL) to all tubes (contains 13 mg/L of each hormone, 17 mg/L of atrazine, 19.1 mg/L of chlorsulfuron, and 83 mg/L of metolachlor in 2-butanol).

8. Add degradate hormone/pesticide spiking solution (50 μL) to to all tubes (contains 13 mg/L androstenedione/estrone, 31.2 mg/L ATZ-DE, 50.4 mg/L ATZ-DIP in 2-butanol).

9. Add ATZ-OH spiking solution (50 μL) to all tubes (contains 102.5 mg/L ATZ-OH in DMF-water 70-30).

10. Equilibrate the samples at 23 ± 3°C covered with foil for the prescribed time interval.

11. After the prescribed time interval, centrifuge the tubes at 650 g for 20 min.

12. Transfer a 0.5 mL aliquot of the aqueous phase to a HPLC vial along with 0.5 mL of methanol.

13. Analyze samples for hormones and atrazine by LC/MS using the protocol outlined in Appendix M.

14. Decant the remaining aqueous solution carefully and weigh tubes.

15. Add methanol (35 mL) to the SMZ.

16. Extract samples on a rotary mixer for 20 hours.

17. Centrifuge samples at 650 g for 20 min.

18. For 0.1 g samples, transfer a 0.5 mL aliquot of methanol extract to a 2mL HPLC vial, dilute with 1 mL of methanol, and analyze by LC/MS using the protocol outlined in Appendix M.

19. For 8 g samples, transfer a 1 mL of methanol extract to a 2 mL HPLC vial and analyzed by LC/MS using the protocol outlined in Appendix M.

Note: The volume change upon mixing of methanol and water for preparation of final samples for LC/MS was determined by measuring the density of water/methanol solutions mixed in the same proportions.

K EXTRACTION OF HORMONES/ATRAZINE FROM WATER SAMPLES

Water samples were collected using ISCO auto-sampling equipment. Sulfuric acid (0.5 mL) was added to empty ISCO polyethylene bottles prior to collection of 1 L water samples with a target end point of pH=2 in the collected water sample for sample preservation. Water samples were refrigerated immediately upon receipt in the lab and processed within 36 h. Samples were weighed and filtered (VWR glass fiber filter, Grade 696, 1.2 m) through a Büchner funnel.

For determination of sediment bound contaminant concentration, filter papers were transfered to a weighed glass centrifuge tube with teflon lined closure and extracted with 25 mL of acetone for 20 h on a rotary mixer. The extract was transferred to a 35 mL glass vial and evaporated to $\approx$ 5 mL in a hood at room temperature. The extract was transferred to a 5 mL conical vial and evaporated to dryness under a gentle stream of nitrogen. For samples with high water content, evaporation can be expedited by addition of ethyl acetate/ ethanol (1/1) to remove the final traces of water by azeotropic evaporation.

Water samples with volume $<$ 1L were diluted with water to 1 L. Each filtered sample was amended with internal standard (6.25 ng of bE2-16,16,17-d_3 dissolved in 0.5 mL of methanol, purchased from CDN Isotopes), and extracted immediately or stored at 4° C in the dark for no longer than 72 h prior to further processing.

Water samples were pre-concentrated using solid phase extraction (SPE) on a 24 port Visiprep SPE vacuum manifold (Supelco, Bellefonte, PA) by passing through the cartridges (Phenomenex SDB-L, 200 mg in a 3-mL cartridge conditioned with 4 mL of isopropanol and 4 mL of water) at $<$ 10 mL/min. Loaded cartridges were stored at -20° C for up to four months. Cartridges were then washed sequentially with 3 mL of 90/10 (v/v) Tris buffer/methanol (pH 8.5), 3 mL of 85/15 (v/v) water/methanol and twice with 3 mL of water followed by drying for 5 min under vacuum to remove

bulk water. Analytes are then eluted with 4 mL of methanol, and the eluent was evaporated to dryness under a gentle stream of nitrogen. The residue was then reconstituted in methanol (0.5 mL) immediately prior to analysis by LC/MS using the protocol outlined in Appendix M.

L CONSTRUCTION OF PASSIVE SURFACE WATER FLUX METER

L.1 Background

Passive surface water flux meters (PSFMs) were assembled within 24 hours of PSFM deployment. The PSFM body was constructed of anodized aluminum (end caps) and stainless steel (pipe). Photographs of the individual PSFM components and an assembled PSFM unit are shown in Figures L.1 and L.2 respectively.

Sorbent and flow restricting layers were wet packed with screens of appropriate mesh size separating each layer. PSFMs were packed in a vertical position with the outlet side in the downward position. Initial tracer concentration in GAC was estimated for each day that flux meters were assembled by taking triplicate samples of GAC using the protocol outlined in Appendix D.

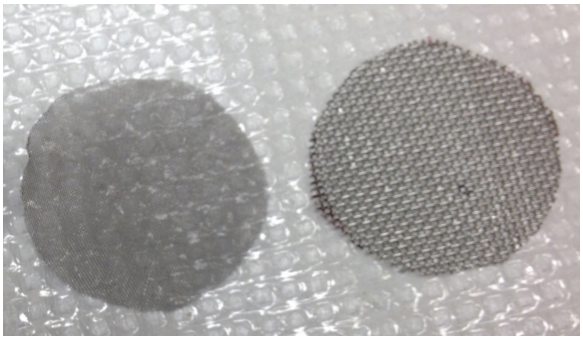
L.2 Procedure

1. Assemble PSFM outlet cap:
   (a) Wrap outlet cap threads with 2 rounds of PTFE tape.
   (b) Attach outlet cap to the 1.5 inch diameter stainless steel pipe and tighten using a wrench.
   (c) Place an aluminum spacer into the inside of the outlet cap.
   (d) Place a 12 mesh screen on top of the aluminum spacer.
   (e) Place a 320 mesh screen on top of the 80 mesh screen.
2. Wrap the threads on both sides of 1.5 inch diameter stainless steel pipe with 4-5 rounds of PTFE tape.

(a)

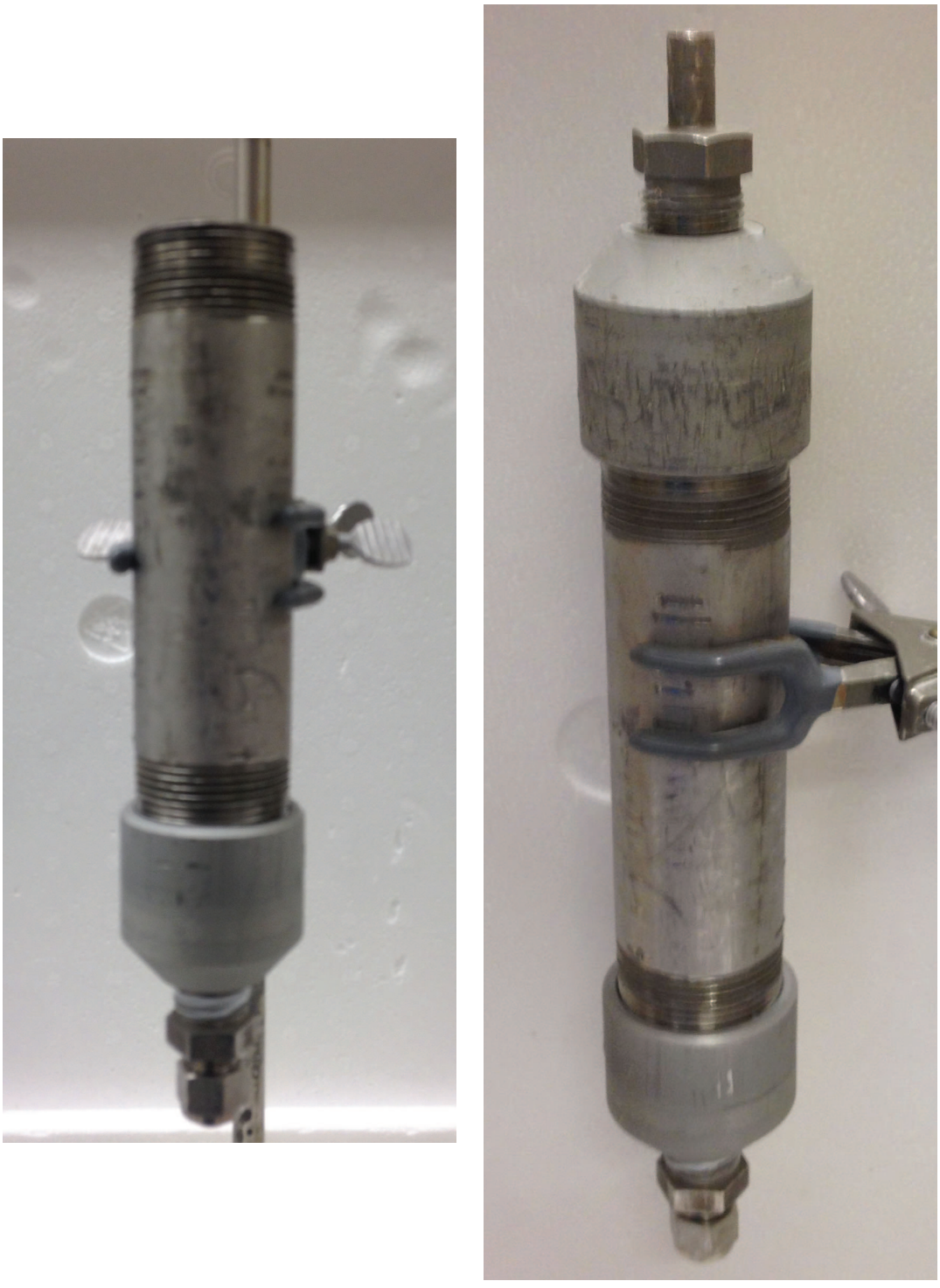
(b)

(c)



(d)

Figure L.1.: PSFM Componenets: a) Outlet (left) and inlet (right) end cap fittings, b) Assembled inlet end cap, c) Inside of outlet end cap, and d) Screens for containing sorbent and sand layers



(a) (b)

Figure L.2.: PSFM Assembly: a) Before packing with sorbent, b) Fully packed and assembled

3. Screw the 1.5 inch diameter stainless steel pipe into the outlet cap and tighten using two pipe wrenches (one wrench to hold pipe and the other to tighten cap, assembled unit must be water tight).

4. Transfer 50mL of 250 mesh silica sand and 100mL of 75 mesh silica sand into a 250mL beaker and mix thoroughly.

5. Attach the assembled PSFM outlet cap and pipe to a ring stand so that the outlet cap is at the bottom.

6. Transfer approximately 70mL of de-ionized water into the assembled PSFM.

7. Use a ruler to measure the distance from the screen at the bottom of the unit to the top of the 1.5 inch diameter pipe.

8. Add the 250/75 mesh sand mixture to the partially assembled PSFM unit.

9. Add the sand mixture to the unit while maintaining the water level just above the added sand level by addition of de-ionized water using a pasteur pipet. Tap the PSFM gently using a large rubber stopper as sand/water is added to avoid trapping air pockets in the sand.

10. Use a ruler to measure the distance from the top of the sand layer to the top of the 1.5 inch diameter pipe periodically as sand is added until the thickness of the sand layer is 4cm (the thickness of the sand layer can be adjusted to control the PSFM flow rate).

11. Measure the final distance from the top of the sand layer to the top of the 1.5 inch diameter pipe.

12. Place a 320 mesh screen on top of the sand layer.

13. Place a 80 mesh screen on top of the 320 mesh screen.

14. Add tracer loaded GAC to the partially assembled PSFM unit. As GAC is removed from the container in which it was equilibrated with tracers, allow excess solution to drain from the sorbent before adding to the PSFM unit working quickly to avoid evaporation of tracers.

15. Add tracer loaded GAC to the unit while maintaining the water level just above the added GAC by addition of de-ionized water using a pasteur pipet. Gently tap the sides of the PSFM with a large rubber stopper as GAC and water are added to avoid trapping air pockets in the GAC.

16. Use a ruler to measure the distance from the top of the GAC layer to the top of the 1.5 inch stainless steel pipe. Add GAC while tapping the sides of the PSFM unit until the thickness of the GAC layer is 5.5 cm.

17. Measure the final distance from the top of the GAC layer to the top of the 1.5 inch diameter pipe.

18. Place an 80 mesh screen on top of the GAC layer.

19. Add SMZ to the unit while maintaining the water level just above the added SMZ by addition of de-ionized water using a pasteur pipet. Use a large rubber stopper to tap the sides of the PSFM unit as SMZ and water are added to avoid trapping air pockets in the SMZ.

20. Fill the PSFM with SMZ to the top of the 1.5 inch diameter pipe.

21. Screw the inlet cap onto the partially assembled PSFM unit.

22. Tighten the inlet cap onto the 1.5 inch diameter pipe using two pipe wrenches (one wrench to hold 1.5 inch diameter pipe and the other wrench to tighten the cap).

23. Add SMZ through the opening in the inlet cap keeping the water level slightly above the top of the SMZ by addition of de-ionized water using a pasteur pipet.

24. Pack the SMZ as it is added to the inlet cap using a cylindrical tool so that the inlet cap is completely filled with sorbent.

25. When the inlet cap is completely filled with SMZ/water, wrap the threads of the inlet cap fitting with 2 rounds of PTFE tape.

26. Place an 80 mesh screen into the opening of the inlet cap.

27. Screw the inlet cap onto the inlet cap fitting and tightened using a wrench.

28. Fill the completely assembled PSFM unit with water.

29. Maintain the PSFM unit in the upright position until deployment so that water does not drain out of the inlet side.

M ANALYSIS OF HORMONES BY LC/MS

Analysis of hormones and pesticides was performed using high performance reverse-phase liquid chromatography tandem mass spectrometry (LC/MS) using a Shimadzu HPLC system (HTA autosampler with dual SCL-10ADvp pumps) coupled to a Sciex API-3000 with electrospray interface operated in multiple reaction monitoring mode. Chromatographic parameters for separation of estrogens and pesticides are outlined in tables M.1 and M.2 respectively. Mass spectrometric parameters for analysis of both compound classes are listed in table M.3.

Table M.1.: Chromatographic Conditions for Analysis of Estrogens

Column:	Phenomenex Gemini C18 (150 x 2.0 mm, dp = 5μm)
Mobile Phase	A: 90/10 H_2O/Methanol + 2mM ethanolamine
	B: Acetonitrile + 2mM ethanolamine
Injection Volume	25 μL
Flow Rate	0.35 mL/min

Time (min)	% A	% B
0.0	70	30
8.0	50	50
8.5	0	100
10.5	0	100
11.0	70	30
13.5	70	30

Table M.2.: Chromatographic Conditions for Analysis of Pesticides

Column:	Phenomenex Gemini C18 (150 x 2.0 mm, dp = 5μm)
Mobile Phase	A: 0.1% Formic Acid in H_2O
	B: 0.1% Formic Acid in ACN
Injection Volume	10 μL
Flow Rate	0.35 mL/min

Time (min)	% A	% B
0.00	85	15
1.75	85	15
2.50	40	60
8.00	10	90
10.00	10	90
10.50	85	15
12.50	85	15

Table M.3.: Parameters for Mass Spectrometric Analysis of Hormones and Pesticides

Compound	Precursor Ion (m/z)	Product Ion (m/z)
aE2	271	145
bE2	271	145
E1	269	145
E3	287	145
ATZ	216	174
ATZ-DE	188	146
ATZ-DIP	174	104
ATZ-OH	198	156
MTC	284	252
CSF	358	167
CPF	352	200

N MEASUREMENT OF DISCHARGE AT S2 STEAM SAMPLING LOCATION

Measurement of stream discharge at the S2 sampling station was accomplished by way of an engineered channel and rating curve developed using standard methods [123]. Briefly, the stream was divided into 1 ft segments with a segment division 6 in. to each side of the stream center. Stream velocity and depth were measured at the center of each segment (60% depth) and assumed to be constant over the entire width of the segment. The cross sectional area of each segment, calculated from the stream depth and known dimensions of the channel, was multiplied by the measured velocity to obtain the specific discharge for each segment. Finally, the specific discharge for the stream at the given stage was calculated by summing the discharge for all segments. Measurements were taken at varying levels of stream stage, and the streams stage-discharge relationship was determined. Similarly, the stream linear velocity at the location where flux meters were deployed (center of stream at 60% of stream depth) was measured at varying levels of stream stage and the stage-velocity relationship determined. Thereafter, only stream stage was measured to determine stream specific discharge and linear velocity at the point of the flux meter inlet. A Flo-Mate 2000 portable flow meter (Marsh-McBirney, Inc) was used for measurement of stream velocity and stage monitored at 15 minute intervals using a Campbell Scientific shaft encoder pulley system and datalogger.

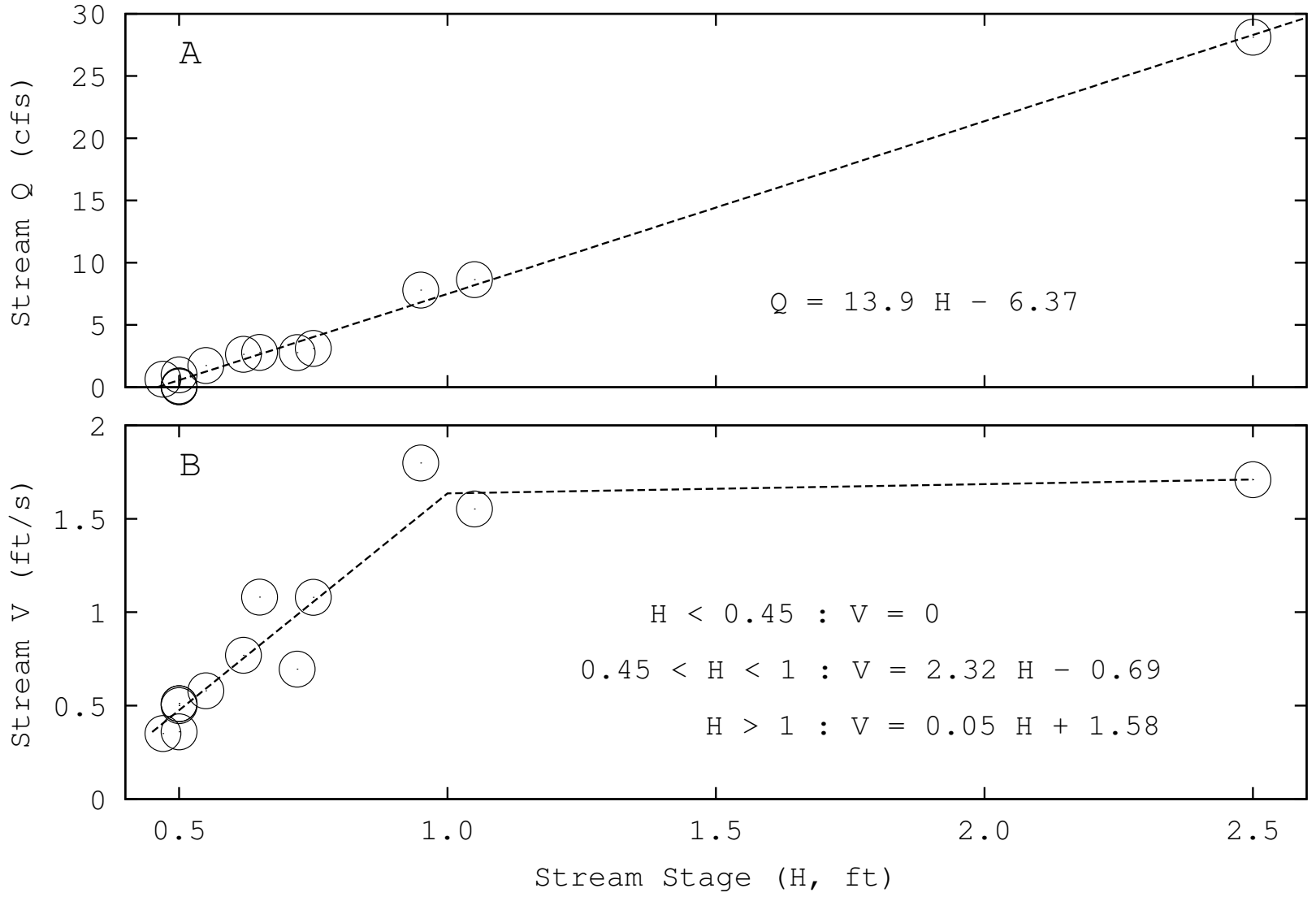


Figure N.1.: Relationship between (A) stream stage and specific discharge and (B) stream stage and linear velocity at sampling station S2/P1

REFERENCES

References

[1] A. J. Agopian, P. J. Lupo, M. A. Canfield, and P. H. Langlois. Case-control study of maternal residential atrazine exposure and male genital malformations. *American Journal of Medical Genetics Part A*, 161A(5):977–982, 2013.

[2] W. H. Ahrens, editor. *Herbicide Handbook*. Weed Science Society of America, 7th edition, 1994.

[3] L. Ainsworth, R. H. Common, and A. L. Carter. Chromatographic study of some conversion products of estrone-16-c14 in urine and feces of laying hen. *Canadian Journal of Biochemistry and Physiology*, 40(1):123–135, 1962.

[4] D. A. Alvarez, J. D. Petty, J. N. Huckins, T. L. Jones-Lepp, D. T. Getting, J. P. Goddard, and S. E. Manahan. Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. *Environmental Toxicology and Chemistry*, 23(7):1640–1648, 2004.

[5] M. D. Annable, K. Hatfield, J. Cho, H. Klammler, B. L. Parker, J. A. Cherry, and P. S. C. Rao. Field-scale evaluation of the passive flux meter for simultaneous measurement of groundwater and contaminant fluxes. *Environmental Science & Technology*, 39(18):7194–7201, 2005.

[6] S. Arnon, O. Dahan, S. Elhanany, K. Cohen, I. Pankratov, A. Gross, Z. Ronen, S. Baram, and L. S. Shore. Transport of testosterone and estrogen from dairy-farm waste lagoons to groundwater. *Environmental Science & Technology*, 42 (15):5521–5526, 2008.

[7] R. Bandyopadhyaya, M. V. Sivaiah, and P. A. Shankar. Silver-embedded granular activated carbon as an antibacterial medium for water purification. *Journal of Chemical Technology & Biotechnology*, 83(8):1177–1180, 2008.

[8] G. Boccardo, D. L. Marchisio, and R. Sethi. Microscale simulation of particle deposition in porous media. *Journal of Colloid and Interface Science*, 417: 227–237, 2014.

[9] K. Booij and B. L. van Drooge. Polychlorinated biphenyls and hexachlorobenzene in atmosphere, sea-surface microlayer, and water measured with semipermeable membrane devices (SPMDs). *Chemosphere*, 44(2):91–98, 2001.

[10] K. Booij, F. Smedes, and E. M. van Weerlee. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere*, 46(8):1157–1161, 2002.

[11] K. Booij, B. Vrana, and J. N. Huckins. Comprehensive analytical chemistry. In *Comprehensive Analytical Chemistry*, pages 141–164. Elsevier B.V., 2007.

[12] M. Bridges, W. B. Henry, D. L. Shaner, R. Khosla, P. Westra, and R. Reich. Spatial variability of atrazine and metolachlor dissipation on dryland no-tillage crop fields in colorado. *Journal of Environmental Quality*, 37(6):2212–2220, 2008.

[13] M. L. Brusseau and P. S. C. Rao. Sorption nonideality during organic contaminant transport in porous media. *Critical reviews in environmental control*, 19 (1):33–99, 1989.

[14] F. X. M. Casey, G. L. Larsen, H. Hakk, and J. Simunek. Fate and transport of 17b-estradiol in soil-water systems. *Environmental Science & Technology*, 37 (11):2400–2409, 2003.

[15] F. X. M. Casey, J. Simunek, J. Lee, G. L. Larsen, and H. Hakk. Sorption, mobility, and transformation of estrogenic hormones in natural soil. *Journal of Environmental Quality*, 34(4):1372–1379, 2005.

[16] F. X. M. Casey, P. G. Oduor, H. Hakk, G. L. Larsen, and T. M. DeSutter. Transport of 17b-estradiol and testosterone in a field lysimeter. *Soil Science*, 173(7):456–467, 2008.

[17] B. Cetin, S. Ozer, A. Sofuoglu, and M. Odabasi. Determination of Henry's law constants of organochlorine pesticides in deionized and saline water as a function of temperature. *Atmospheric Environment*, 40(24):4538–4546, 2006.

[18] T. Cheng, Y. Zhao, X. Li, F. Lin, Y. Xu, X. Zhang, Y. Li, R. Wang, and L. Lai. Computation of octanol-water partition coefficients by guiding an additive model with knowledge. *Journal of Chemical Information and Modeling*, 47:2140–2148, 2007.

[19] L. Chimuka and E. Cukrowska. The role of passive samplers in the monitoring of aquatic ecosystems and occupational hygiene pollution, 2006.

[20] J. Y. Cho, M. D. Annable, J. W. Jawitz, and K. Hatfield. Passive flux meter measurement of water and nutrient flux in saturated porous media: Bench-scale laboratory tests. *Journal of Environmental Quality*, 36(5):1266–1272, 2007.

[21] M. S. Colucci, H. Bork, and E. Topp. Persistence of estrogenic hormones in agricultural soils: I. 17 beta-estradiol and estrone. *Journal of Environmental Quality*, 30(6):2070–2076, 2001.

[22] ITRC Interstate Technology & Regulatory Council. Technology overview of passive sampler technologies. Technical report, Washington, D.C., 2005.

[23] R. L. Dalton, F. R. Pick, C. Boutin, and A. Saleem. Atrazine contamination at the watershed scale and environmental factors affecting sampling rates of the polar organic chemical integrative sampler (POCIS). *Environmental Pollution*, 189:134–142, 2014.

[24] G. D'Ascenzo, A. Di Corcia, A. Gentili, R. Mancini, R. Mastropasqua, M. Nazzari, and R. Samperi. Fate of natural estrogen conjugates in municipal sewage transport and treatment facilities. *Science of the Total Environment*, 302:199–209, 2003.

[25] H. De Jonge and G. Rothenberg. New device and method for flux-proportional sampling of mobile solutes in soil and groundwater. *Environmental Science & Technology*, 39:274–282, 2005.

[26] D. L. Denlinger, R. W. Brueggemeier, R. Mechoulam, N. Katlic, L. B. Yocum, and G. D. Yocum. Estrogens and androgens in insects. *Journal of Cellular Biochemistry*, 10C:61, 1986.

[27] S. I. Dodson, C. M. Merritt, J. P. Shannahan, and C. M. Shults. Low exposure concentrations of atrazine increase male production in daphnia pulicaria. *Environmental Toxicology and Chemistry*, 18(7):1568–1573, 1999.

[28] Y. Dong, D. Wu, X. Chen, and Y. Lin. Adsorption of bisphenol A from water by surfactant-modified zeolite. *Journal of Colloid and Interface Science*, 348 (2):585–590, 2010.

[29] V. V. Egorava, A. V. Zakharyc, and S. N. Ananchen. pKa of phenolic steroids. *Izvestiia Akademii Nauk SSSR. Seriya Khimcheskaya*, 3(3):726, 1972.

[30] R. E. Erb, B. P. Chew, and H. F. Keller. Relative concentrations of estrogen and progesterone in milk and blood, and excretion of estrogen in urine. *Journal of Animal Science*, 45(3):617–626, 1977.

[31] Z. Fan, F. X. M. Casey, H. Hakk, and G. L. Larsen. Persistence and fate of 17 beta-estradiol and testosterone in agricultural soils. *Chemosphere*, 67(5): 886–895, 2007.

[32] A. Finizio, A. Di Guardo, A. Arnoldi, M. Vighi, and R. Fanelli. Different approaches for the evaluation of kow for s-triazine herbicides. *Chemosphere*, 23 (6):801–812, 1991.

[33] O. Finlay-Moore, P. G. Hartel, and M. L. Cabrera. 17b-estradiol and testosterone in soil and runoff from grasslands amended with broiler litter. *Journal of Environmental Quality*, 29(5):1604–1611, 2000.

[34] H. E. Gall, C. T. Jafvert, and B. Jenkinson. Integrating hydrograph modeling with real-time flow monitoring to generate hydrograph-specific sampling schemes. *Journal of Hydrology*, 393(3-4):331–340, 2010.

[35] H. E. Gall, S. A. Sassman, B. Jenkinson, L. S. Lee, and C. T. Jafvert. Hormone loads exported by a tile-drained agroecosystem receiving animal wastes. *Hydrological Processes*, 28:1318–1328, 2014.

[36] A. P. Gamerdinger, R. S. Achin, and R. W. Traxler. Approximating the impact of sorption on biodegradation kinetics in soil-water systems. *Soil Science Society of America Journal*, 61(6):1618–1626, 1997.

[37] J. Gan, S. J. Lee, W. P. Liu, D. L. Haver, and J. N. Kabashima. Distribution and persistence of pyrethroids in runoff sediments. *Journal of Environmental Quality*, 34(3):836–841, 2005.

[38] W. R. Grace & Co. Zeolite molecular sieves, May 2012. URL `www.grace.com/EngineeredMaterials/MaterialSciences/Zeolites/Default.aspx`.

[39] L. Guo, W. A. Jury, R. J. Wagenet, and M. Flury. Dependence of pesticide degradation on sorption: nonequilibrium model and application to soil reactors. *Journal of Contaminant Hydrology*, 43(1):45–62, 2000.

[40] G. M. Haggerty and R. S. Bowman. Sorption of chromate and other inorganic anions by organo-zeolite. *Environmental Science & Technology*, 28(3):452–458, 1994.

[41] T. A. Hanselman, D. A. Graetz, and A. C. Wilkie. Manure-borne estrogens as potential environmental contaminants: A review. *Environmental Science & Technology*, 37(24):5471–5478, 2003.

[42] T. A. Hanselman, D. A. Graetz, A. C. Wilkie, N. J. Szabo, and C. S. Diaz. Determination of steroidal estrogens in flushed dairy manure wastewater by gas chromatography-mass spectrometry. *Journal of Environmental Quality*, 35: 695–700, 2006.

[43] J. Happel. Viscous flow in multiparticle systems - slow motion of fluids relative to beds of spherical particles. *A.I.Ch.E. Journal*, 4(2):197–201, 1958.

[44] K. Hatfield, M. Annable, J. H. Cho, P. S. C. Rao, and H. Klammler. A direct passive method for measuring water and contaminant fluxes in porous media. *Journal of Contaminant Hydrology*, 75(3-4):155–181, 2004.

[45] T. Hayes, K. Haston, M. Tsui, A. Hoang, C. Haeffele, and A. Vonk. Herbicides: Feminization of male frogs in the wild. *Nature*, 419(6910):895–896, 2002.

[46] J. P. Herzig, D. M. Leclerc, and P. Legoff. Flow of suspensions through porous media - application to deep filtration. *Industrial and Engineering Chemistry*, 62(5):8, 1970.

[47] http://sorbisense.com, accessed Aug 2014.

[48] J. N. Huckins, M. W. Tubergen, and G. K. Manuweera. Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavaiiability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere*, 20(5):533–552, 1990.

[49] A. R. Hurwitz and S. T. Liu. Determination of aqueous solubility and pKa values of estrogens. *Journal of Pharmaceutical Sciences*, 66(5):624–627, 1977.

[50] K. E. Hyer, G. M. Hornberger, and J. S. Herman. Processes controlling the episodic steamwater transport of atrazine and other agrichemicals in an agricultural watershed. *Journal of Hydrology*, 254(1-4):47–66, 2001.

[51] G. W. Ivie, R. J. Christopher, C. E. Munger, and C. E. Coppock. Fate and residues of 4-c-14-estradiol-17-beta after intramuscular injection into holstein steer calves. *Journal of Animal Science*, 62(3):681–690, 1986.

[52] A. A. Jennings and D. J. Kirkner. Instantaneous equilibrium approximation analysis. *Journal of Hydraulic Engineering-ASCE*, 110(12):1700–1717, 1984.

[53] J. K. Kingston, R. Greenwood, G. A. Mills, G. M. Morrison, and L. B. Persson. Development of a novel passive sampling system for the time-averaged measurement of a range of organic pollutants in aquatic environments. *Journal of Environmental Monitoring*, 2(5):487–495, 2000.

[54] R. Y. Kirdani and M. J. Burgett. pK of 5 estrogens in aqueous solutions. *Archives of Biochemistry and Biophysics*, 118(1):33, 1967.

[55] H. Klammler, M. A. Newman, E. Szilagyi, J. C. Padowski, K. Hatfield, J. W. Jawitz, and M. D. Annable. Initial test results for a passive surface water fluxmeter to measure cummulative water and solute mass fluxes. *Environmental Science & Technology*, 41(7):2485–2490, 2007.

[56] W. Kloas, I. Lutz, T. Springer, H. Krueger, J. Wolf, L. Holden, and A. Hosmer. Does atrazine influence larval development and sexual differentiation in xenopus laevis? *Toxicological Sciences*, 107(2):376–384, 2009.

[57] M. Kummu. Roughness characteristics and velocity profile in vegetated and nonvegetated channel. Master's thesis, Helsinki University of Technology, 2002.

[58] K. M. Lai, K. L. Johnson, M. D. Scrimshaw, and J. N. Lester. Binding of waterborne steroid estrogens to solid phases in river and estuarine systems. *Environmental Science & Technology*, 34(18):3890–3894, 2000.

[59] L. S. Lee, T. J. Strock, A. K. Sarmah, and P. S. C. Rao. Sorption and dissipation of testosterone, estrogens, and their primary transformation products in soils and sediment. *Environmental Science & Technology*, 37(18):4098–4105, 2003.

[60] J. K. Leet, L. S. Lee, H. E. Gall, R. R. Goforth, S. Sassman, D. A. Gordon, J. M. Lazorchak, M. E. Smith, C. T. Javfert, and M. S. Sepulveda. Assessing impacts of land-applied manure from concentrated animal feeding operations on fish populations and communities. *Environmental Science & Technology*, 46 (24):13440–13447, 2012.

[61] C. Leu, H. Singer, S. R. Muller, R. P. Schwarzenbach, and C. Stamm. Comparison of atrazine losses in three small headwater catchments. *Journal of Environmental Quality*, 34(5):1873–1882, 2005.

[62] K. M. Lewis and R. D. Archer. pKa values of estrone, 17b-estradiol and 2-methoxyestrone. *Steroids*, 34(5):485–499, 1979.

[63] S. L. Macleod, E. L. Mcclure, and C. S. Wong. Laboratory calibration and field deployment of the polar organic chemical integrative sampler for pharmaceuticals and personal care products in wastewater and surface water. *Environmental Toxicology and Chemistry*, 26(12):2517–2529, 2007.

[64] K. Malachova, P. Praus, Z. Pavlickova, and M. Turicova. Activity of antibacterial compounds immobilised on montmorillonite. *Applied Clay Science*, 43(3-4): 364–368, 2009.

[65] M. L. Mashtare, B. Khan, and L. S. Lee. Evaluating stereoselective sorption by soils of 17 alpha-estradiol and 17 beta-estradiol. *Chemosphere*, 82(6):847–852, 2011.

[66] M. L. Mashtare, D. A. Green, and L. S. Lee. Biotransformation of 17 alpha- and 17 beta-estradiol in aerobic soils. *Chemosphere*, 90(2):647–652, 2013.

[67] M. L. Mashtare, L. S. Lee, L. F. Nies, and R. F. Turco. Transformation of 17 alpha-estradiol, 17 beta-estradiol, and estrone in sediments under nitrate- and sulfate-reducing conditions. *Environmental Science & Technology*, 47(13): 7178–7185, 2013.

[68] P. Matthiessen, D. Arnold, A. C. Johnson, T. J. Pepper, T. G. Pottinger, and K. G. T. Pulman. Contamination of headwater streams in the United Kingdom by oestrogenic hormones from livestock farms. *Science of the Total Environment*, 367(2-3):616–630, 2006.

[69] K. D. Mattix, P. D. Winchester, and L. R. Scherer. Incidence of abdominal wait defects is related to surface water atrazine and nitrate levels. *Journal of Pediatric Surgery*, 42(6):947–949, 2007.

[70] D. C. Mays and J. R. Hunt. Hydrodynamic aspects of particle clogging in porous media. *Environmental Science & Technology*, 39(2):577–584, 2005.

[71] R. Mechoulam, R. W. Brueggemeier, and D. L. Denlinger. Estrogens in insects. *Experientia*, 40(9):942–944, 1984.

[72] J. L. Meyer, S. Rogers-Burch, J. K. Leet, D. L. Villeneuve, G. T. Ankley, and M. S. Sepulveda. Reproductive physiology in eastern snapping turtles (chelydra serpentine) exposed to runoff from a concentrated animal feeding operation. *Journal of Wildlife Diseases*, 49(4):996–999, 2013.

[73] D. W. Ming and J. B. Dixon. Quantitative determination of clinoptilolite in soils by a cation-exchange capacity method. *Clays and Clay Minerals*, 35(6): 463–468, 1987.

[74] S. K. Mohanty, J. E. Saiers, and J. N. Ryan. Colloid-facilitated mobilization of metals by freeze-thaw cycles. *Environmental Science & Technology*, 48(2): 977–984, 2014.

[75] J. F. Muller, S. Duquesne, J. Ng, G. R. Shaw, K. Krrishnamohan, K. Manonmanii, M. Hodge, and G. K. Eaglesham. Pesticides in sediments from queensland irrigation channels and drains. *Morine Pollution Bulletin*, 41(7-12):294–301, 2000.

[76] D. M. Nevskaia and A. Guerrero-Ruiz. Comparative study of the adsorption from aqueous solutions and the desorption of phenol and nonylphenol substrates on activated carbons. *Journal of Colloid and Interface Science*, 234(2):316–321, 2001.

[77] D. M. Nevskaia, A. Santianes, V. Munoz, and A. Guerrero-Ruiz. Interaction of aqueous solutions of phenol with commercial activated carbons: an adsorption and kinetic study. *Carbon*, 37(7):1065–1074, 1999.

[78] W. J. Ntow, P. Drechsel, B. O. Botwe, P. Kelderman, and H. J. Gijzen. The impact of agricultural runoff on the quality of two streams in vegetable farm areas in Ghana. *Journal of Environmental Quality*, 37(2):696–703, 2008.

[79] A. V. Ogram, R. E. Jessup, L. T. Ou, and P. S. C. Rao. Effect of sorption on biological degradation rates of (2,3-dichlorophenoxy)acetic acid in soils. *Applied and Environmental Microbiology*, 49:582–587, 1985.

[80] A. W. Olmstead and G. A. LeBlanc. Insecticidal juvenile hormone analogs stimulate the production of male offspring in the crustacean daphnia magna. *Environmental Health Perspectives*, 111(7):919–924, 2003.

[81] E. F. Orlando, A. S. Kolok, G. A. Binzcik, J. L. Gates, M. K. Horton, C. S. Lambright, L. E. Gray, A. M. Soto, and L. J. Guillette. Endocrine-disrupting effects of cattle feedlot effluent on an aquatic sentinel species, the fathead minnow. *Environmental Health Perspectives*, 112(3):353–358, 2004.

[82] J. C. Padowski, E. A. Rothfus, J. W. Jawitz, H. Klammler, K. Hatfield, and M. D. Annable. Effect of passive surface water flux meter design on water and solute mass flux estimates. *Journal of Hydrologic Engineering*, 14(12):1334–1342, 2009.

[83] P. Palma, V. L. Palma, C. Matos, R. M. Fernandes, A. Bohn, A. Soares, and I. R. Barbosa. Assessment of the pesticides atrazine, endosulfan sulphate and chlorpyrifos for juvenoid-related endocrine activity using daphnia magna. *Chemosphere*, 76(3):335–340, 2009.

[84] R. Palme, P. Fischer, H. Schildorfer, and M. N. Ismail. Excretion of infused (14)c-steroid hormones via faeces and urine in domestic livestock. *Animal Reproduction Science*, 43:43–63, 1996.

[85] A. Panacek, L. Kvitek, R. Prucek, M. Kolar, R. Vecerova, N. Pizurova, V. K. Sharma, T. Nevecna, and R. Zboril. Silver colloid nanoparticles: Synthesis, characterization, and their antibacterial activity. *Journal of Physical Chemistry B*, 110(33):16248–16253, 2006.

[86] A. Paschke, P. L. Neitzel, W. Walther, and G. Schuurmann. Octanol/water partition coefficient of selected herbicides: Determination using shake-flask method and reversed-phase high-performance liquid chromatography. *Journal of Chemical and Engineering Data*, 49(6):1639–1642, 2004.

[87] J. J. Perez, M. K. Williams, G. Weerasekera, K. Smith, R. M. Whyatt, L. L. Needham, and D. B. Barr. Measurement of pyrethroid, organophosphorus, and carbamate insecticides in human plasma using isotope dilution gas chromatography-high resolution mass spectrometry. *Journal of Chromatography B- Analytical Technologies in the Biomedical and Life Sciences*, 878(27, SI): 2554–2562, 2010.

[88] J. D. Petty, J. N. Huckins, D. A. Alvarez, W. G. Brumbaugh, W. L. Cranor, R. W. Gale, A. C. Rastall, T. L. Jones-Lepp, T. J. Leiker, C. E. Rostad, and E. T. Furlong. A holistic passive integrative sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants. *Chemosphere*, 54(6):695–705, 2004.

[89] D. Pickering. Performance of silverized gac vs. silver zeolite treated gac, http://www.watertechonline.com/filtration/article/performance-of-silverized-gac-vs-silver-zeolite-treated-gac, July 2011.

[90] X. Qiao, N. Carmosini, F. Li, and L. S. Lee. Probing the primary mechanisms affecting the environmental distribution of estrogen and androgen isomers. *Environmental Science & Technology*, 45(9):3989–3995, 2011.

[91] D. R. Raman, E. L. Williams, A. C. Layton, R. T. Burns, J. P. Easter, A. S. Daugherty, M. D. Mullen, and G. S. Sayler. Estrogen content of dairy and swine wastes. *Environmental Science & Technology*, 38:3567–3573, 2004.

[92] J. M. Ribo. The octanol water partition-coefficient of the herbicide chlorsulfuron as a function of ph. *Chemosphere*, 17(4):709–715, 1988.

[93] C. P. Rice, S. M. Chernyak, and L. L. McConnell. Henry's law constants for pesticides measured as a function of temperature and salinity. *Journal of Agricultural and Food Chemistry*, 45(6):2291–2298, 1997.

[94] B. J. Richardson, P. K. S. Lam, G. J. Zheng, K. E. McClellan, and S. B. De Luca-Abbott. Biofouling confounds the uptake of trace organic contaminants by semi-permeable membrane devices (spmds). *Mar. Pollut. Bull.*, 44(12):1372–1379, 2002.

[95] J. Rozemeijer, Y. van der Velde, H. de Jonge, F. van Geer, H. P. Broers, and M. Bierkens. Application and evaluation of a new passive sampler for measuring average solute concentrations in a catchment scale water quality monitoring study. *Environmental Science & Technology*, 44(4):1353–1359, 2010.

[96] K. J. Ryan. Biochemistry of aromatase - significance to female reproductive physiology. *Cancer Research*, 42(8):3342–3344, 1982.

[97] A. Saha, A. T. P. Shabeer, V. T. Gajbhiye, S. Gupta, and R. Kumar. Removal of mixed pesticides from aqueous solutions using organoclays: Evaluation of equilibrium and kinetic model. *Bulletin of Environmental Contamination and Toxicology*, 91(1):111–116, 2013.

[98] W. Sangchan, C. Hugenschmidt, J. Ingwersen, K. Schwadorf, P. Thavornyutikarn, K. Pansombat, and T. Streck. Short-term dynamics of pesticide concentrations and loads in a river of an agricultural watershed in the outer tropics. *Agriculture Ecosystems & Environment*, 158:1–14, 2012.

[99] L. Seifi, A. Torabian, H. Kazemian, G. N. Bidhendi, A. A. Azimi, F. Farhadi, and S. Nazmara. Kinetic study of btex removal using granulated surfactant-modified natural zeolites nanoparticles. *Water Air and Soil Pollution*, 219(1-4): 443–457, 2011.

[100] L. Seifi, A. Torabian, H. Kazemian, G. N. Bidhendi, A. A. Azimi, S. Nazmara, and M. AliMohammadi. Adsorption of btex on surfactant modified granulated natural zeolite nanoparticles: parameters optimizing by applying taguchi experimental design method. *Clean Soil Air Water*, 39(10):939–948, 2011.

[101] M. K. Sellin, D. D. Snow, M. Schwarz, B. J. Carter, and A. S. Kolok. Agrichemicals in Nebraska, USA, watersheds: Occurrence and endocrine effects. *Environmental Toxicology and Chemistry*, 28(11):2443–2448, 2009.

[102] D. Shaner, G. Brunk, S. Nissen, P. Westra, and W. Chen. Role of soil sorption and microbial degradation on dissipation of mesotrione in plant-available soil water. *Journal of Environmental Quality*, 41(1):170–178, 2012.

[103] D. L. Shaner and W. B. Henry. Field history and dissipation of atrazine and metolachlor in Colorado. *Journal of Environmental Quality*, 36(1):128–134, 2007.

[104] A. A. Shapiro and P. G. Bedrikovetsky. A stochastic theory for deep bed filtration accounting for dispersion and size distributions. *Physica A-Statistical Statistical Mechanics and its Applications*, 389(13):2473–2494, 2010.

[105] P. J. Shea. Chlorsulfuron dissociation and adsorption on selected adsorbents and soils. *Weed Science*, 34(3):474–478, 1986.

[106] S. E. Silliman. Paricle transport through 2-dimensional, saturated porous media - influence of physical structure of the medium. *Journal of Hydrology*, 167(1-4): 79–98, 1995.

[107] J. A. Simpson and R. S. Bowman. Nonequilibrium sorption and transport of volatile petroleum hydrocarbons in surfactant-modified zeolites. *Journal of Contaminant Hydrology*, 108(1-2):1–11, 2009.

[108] H. Singh, S. Usher, D. Johnson, and A. Poulos. A comparative study of straight chain and branched chain fatty acid oxidation in skin fibroblasts from patients with peroxisomal disorders. *Journal of Lipid Research*, 31(2):217–225, 1990.

[109] H. Singh, K. Beckman, and A. Poulos. Peroxisomal beta-oxidation of branched-chain fatty acids in rat liver - evidence that carnitine palmitoyltransferase-l prevents transport of branched-chain fatty acids into mitocondria. *Journal of Biological Chemistry*, 269(13):9514–9520, 1994.

[110] A. Sodergren. Solvent-filled dialysis membranes simulate uptake of pollutants by aquatic organisms. *Environmental Science & Technology*, 21(9):855–859, 1987.

[111] G. A. Sorial, M. T. Suidan, R. D. Vidic, R. C. Brenner, G. A. Sorial, M. T. Suidan, R. D. Vidic, and S. W. Maloney. Competitive adsorption of phenols on gac .2. adsorption dynamics under anoxic conditions. *Water Environment Research*, 119(6):1044–1058, 1993.

[112] R. F. Spalding and D. D. Snow. Stream levels of agrichemicals during a spring discharge event. *Chemosphere*, 19(8-9):1129–1140, 1989.

[113] P. J. Squillace and E. M. Thurman. Herbicide transport in rivers - importance of hydrology and geochemistry in nonpoint source contamination. *Environmental Science & Technolgy*, 26(3):538–545, 1992.

[114] J. A. Stoeckel, J. Morris, E. Ames, D. C. Glover, M. J. Vanni, W. Renwick, and M. J. Gonzalez. Exposure times to the spring atrazine flush along a stream-reservoir system. *Journal of the American Water Resources Association*, 48(3): 616–634, 2012.

[115] F. Stuer-Lauridsen. Review of passive accumulation devices for monitoring organic micropollutants in the aquatic environment. *Environmetal Pollution*, 136(3):503–524, 2005.

[116] A. P. Terzyk. Further insights into the role of carbon surface functionalities in the mechanism of phenol adsorption. *Journal of Colloid and Interface Science*, 268(2):301–329, 2003.

[117] A. P. Terzyk. Adsorption of biologically active compounds from aqueous solutions on to commercial unmodified activated carbons. part v. the mechanism of the physical and chemical adsorption of phenol. *Adsorption Science & Technology*, 21(6):539–585, 2003.

[118] E. M. Thurman, D. A. Goolsby, M. T. Meyer, M. S. Mills, M. L. Pomes, and D. W. Kolpin. A reconnaissance study of herbicides and their metabolites in surface water of the midwestern United States using immunoassay and gas chromatography mass/spectrometry. *Environmental Science & Technolgy*, 26 (12):2440–2447, 1992.

[119] Clive Tomlin and British Crop Protection Council, editors. *The pesticide manual : a world compendium.* Farnham : British Crop Protection Council, Farnham, 2000.

[120] USEPA. Finalization of atrazine interim reregistration eligibility decision, and completion of tolerance reassessment and reregistration, 2006. URL `http://www.epa.gov/oppsrrd1/REDs/atrazine_combined_docs.pdf`.

[121] USEPA. EPA atrazine summary, October 2006. URL `http://www.epa.gov/teach/chem_summ/Atrazine_summary.pdf`.

[122] USEPA. Atrazine updates, Jan 2013. URL `http://www.epa.gov/oppsrrd1/reregistration/atrazine/atrazine_update.htm`.

[123] USGS. United States Geological Survey, rating tables and curves, 2012. URL `www.nws.noaa.gov/os/hod/SHManual/SHMan040_rating.htm`.

[124] L. F. Velasco and C. O. Ania. Understanding phenol adsorption mechanisms on activated carbons. *Adsorption-Journal of the International Adsorption Society*, 17(1):247–254, 2011.

[125] N. M. J. Vermeulen, Z. Apostolides, D. J. J. Potgieter, P. C. Nel, and N. S. H. Smit. Separation of atrazine and some of its degradation products by high-performance liquid-chromatography. *Journal of Chromatography*, 240(1):247–253, 1982.

[126] G. Verreydt, J. Bronders, I. Van Keer, L. Diels, and P. Vanderauwera. Passive samplers for monitoring vocs in groundwater and the prospects related to mass flux measurements. *Ground Water Monitoring and Remediation*, 30(2):114–126, 2010.

[127] F. Verweij, K. Booij, K. Satumalay, N. van der Molen, and R. van der Oost. Assessment of bioavailable PAH, PCB and OCP concentrations in water, using semipermeable membrane devices (SPMDs), sediments and caged carp. *Chemosphere*, 54(11):1675–1689, 2004.

[128] R. D. Vidic and M. T. Suidan. Role of dissolved oxygen on the adsorptive capacity of activated carbon for synthetic and natural organic matter. *Environmental Science & Technology*, 25(9):1612–1618, 1991.

[129] R. D. Vidic, M. T. Suidan, G. A. Sorial, and R. C. Brenner. Molecular-oxygen and the adsorption of phenols - effect of functional-groups. *Water Environment Research*, 65(2):156–161, 1993.

[130] R. D. Vidic, M. T. Suldan, and R. C. Brenner. Oxidative coupling of phenols on activated carbon - impact on adsorption equilibrium. *Environmental Science & Technology*, 27(10):2079–2085, 1993.

[131] C. M. Villanueva, G. Durand, M. B. Coutte, C. Chevrier, and S. Cordier. Atrazine in municipal drinking water and risk of low birth weight, preterm delivery, and small-for-gestational-age status. *Occupational and Environmental Medicine*, 62(6):400–405, 2005.

[132] J. R. Vogel and J. I. Linard. Agricultural herbicide transport in a first-order intermittent stream, Nebraska, USA. *Applied Engineering in Agriculture*, 27 (1):63–74, 2011.

[133] B. Vrana, G. Mills, R. Greenwood, J. Knutsson, K. Svenssone, and G. Morrison. Performance optimisation of a passive sampler for monitoring hydrophobic organic pollutants in water. *Journal of Environmental Monitoring*, 7(6):612–620, 2005.

[134] B. Vrana, G. A. Mills, I. J. Allan, E. Dominiak, K. Svensson, J. Knutsson, G. Morrison, and R. Greenwood. Passive sampling techniques for monitoring pollutants in water. *Trends in Analytical Chemistry*, 24(10):845–868, 2005.

[135] G. G. Ying and R. S. Kookana. Sorption and degradation of estrogen-like-endocrine disrupting chemicals in soil. *Environmental Toxicology and Chemistry*, 24(10):2640–2645, 2005.

[136] S. Zhao, P. Zhang, M. E. Melcer, and J. F. Molina. Estrogens in streams associated with a concentrated animal feeding operation in upstate New York, USA. *Chemosphere*, 79(4):420–425, 2010.

[137] S. Q. Zheng and J. F. Cooper. Adsorption, desorption, and degradation of three pesticides in different soils. *Archives of Environmental Contamination and Toxicology*, 30(1):15–20, 1996.

VITA

VITA

Stephen A. Sassman

Objectives

The implementation of analytical methodology and computer modeling for investigating the fate and transport of environmental contaminants. Development of technologies for efficient use of natural resources in agricultural and industrial production.

Education

Bachelor of Science, Chemistry 1995
Texas State University, San Marcos, TX
Analytical Chemistry / Physics 3.18/4.0

Master of Science, Analytical Chemistry 1999
Texas State University, San Marcos, TX
Analytical Chemistry 3.63/4.0

Doctor of Philosophy, Environmental Chemistry 2014
Purdue University, West Lafayette, IN
Contaminant Fate and Transport 3.97/4.0

Experience

QC Chemist III Sovereign Pharmaceuticals 2014-Present

- Method development, validation, and transfer in a GMP environemnt.
- Implementation of analytical methodology using HPLC, GC, LC/MS, TLC, FT-IR, UV/Vis, Titrimetry, and Karl Fischer.
- Preparation of validation protocols, technical reports, and test methods.

Experience

Senior Analytical Chemist Purdue University 2000-2013

- Development and implementation of methods for measuring the concentration of legacy and emerging contaminants in the environment using HPLC, LC/MS, GC, GC/MS, ICP-OES, ICP/MS, and AA.
- Design and implementation of a novel passive sampling device for measuring contaminant concentration/flux in streams and rivers.
- Computer modeling for predicting contaminant fate and transport.
- Preparation of proposals, technical reports, and scholarly articles.

Analytical Chemist Texas State University 1998-2000

- Fractionation and characterization of crude oil using HPLC, LC/MS, NMR, and IR spectroscopy.
- Analysis of sulfur containing aromatic compounds in crude oil fractions using LC/ESI-MS with palladium as a sensitivity enhancing reagent.

Project Management

Senior Analytical Chemist Purdue University 2000-2013

- Coordinate laboratory activities involving multiple projects in the Department of Agronomy and the Department of Civil Engineering.
- Management of research laboratory operations including instrument troubleshooting and repair, ordering of supplies, and disposal of chemical and radioactive wastes.
- Training of research assistants and post-doctoral researchers to ensure lab safety and proper experimental protocol.

Teaching

Analytical Chemistry Purdue University 2000-2013

- Develop experiments for environmental chemistry lab sessions.
- Lecture on liquid and gas chromatographic theory and techniques, and atomic absorption theory.
- Train students in the proper use of analytical instrumentation.

Teaching Assistant Texas State University 1998-2000

- Teaching Assistant for CHEM 1142 (general chemistry lab) and CHEM 1430 (chemistry for non-science majors)

Information Technology

Operating Systems:	Windows & Linux
Software:	Word, Excel, Powerpoint, Access, Analyst, Empower, R, Empower, Class VP, Xcalibur, SigmaPlot, Gnuplot, LaTeX
Languages:	Matlab, Python, Perl, PHP, FORTRAN, BASIC, MySQL

Publications

Gall HE, Sassman SA, Jenkinson B, Lee LS, Jafvert CT. Hormone Loads Exported by a Tile-drained Agroecosystem Receiving Animal Wastes. 2013. Hydrological Processes 28(3), 1318-1328.

Leet JK, Lee LS, Gall HE, Goforth RR, Sassman S, Gordon DA, Lazorchak JM, Smith ME, Jafvert CT, Sepulveda MS. Assessing Impacts of Land-Applied Manure from Concentrated Animal Feeding Operations on Fish Populations and Communities. 2012. Environ Sci Tech 46(24), 13440-13447.

Gall HE, Sassman SA, Lee LS, Jafvert CT. Hormone Discharges from a Midwest Tile-Drained Agroecosystem Receiving Animal Wastes. 2011. Environ Sci Tech 45(20), 8755-8764.

Khan B, Lee LS, Sassman SA. Degradation of Synthetic Androgens 17 alpha- and 17 beta-Trenbolone and Trendione in Agricultural Soils. 2008. Environ Sci Tech 42(10), 3570-3574.

Sassman SA and Lee LS. Sorption and Degradation in Soils of Veterinary Ionophore Antibiotics: Monensin and Lasalocid. 2007. Environ Toxicol Chem 26(8), 1614-1621.

Sassman SA, Sarmah AK, and Lee LS. Sorption of Tylosin A, D, and A-Aldol and Degradation of Tylosin A in Soils. 2007. Environ Toxicol Chem 26(8), 1629-1635.

Lee LS, Carmosini N, Sassman SA, and Dion HM. Agricultural Contributions of Antimicrobials and Hormones on Soil and Water Quality. 2007. Advances in Agronomy 93, 1-68.

Strock TJ, Sassman SA, and Lee LS. Sorption and Related Properties of the Swine Antibiotic Carbadox and Associated N-Oxide Reduced Metabolites. 2005. Environ Sci Tech 39(9), 3134-3142.

Sassman SA and Lee LS. Sorption of three tetracyclines by several soils: Assessing the role of pH and cation exchange. 2005. Environ Sci Tech 39(19), 7452-7459.

Sassman SA, Lee LS, Bischoff M and Turco RF. Assessing N,N'-dibutylurea (DBU) formation in soils after application of n-butylisocyanate and benlate fungicides. 2004. J Agr Food Chem 52, 747-754.

Lee LS, Sassman SA, Bischoff B and Turco RF. Degradation of N,N'-dibutylurea (DBU) in soils treated with only DBU and DBU-fortified benlate fungicides. 2004. J Environ Qual 33(5), 1771-1778.

Rudzinski WE, Aminabhavi TM, Sassman S and Watkins LM. Isolation and characterization of the saturate and aromatic fractions of a Maya crude oil. 2000. Energ Fuel 14, 839-844.

Turner DR and Sassman SA. Approaches to sorption modeling for high-level waste performance assessment. 1996. J Contam Hydrol 21 (1-4), 311-332.

References Available Upon Request