Chemosphere 83 (2011) 271–280

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

The effects of dissolved organic matter and pH on sampling rates for polar organic chemical integrative samplers (POCIS)

Hongxia Li [a], Paul A. Helm [b], Gordon Paterson [c], Chris D. Metcalfe [a,*]

[a] Worsfold Water Quality Centre, Trent University, 1600 West Bank Drive, Peterborough, ON, Canada K9J 7B8
[b] Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment, 125 Resources Road, Toronto, ON, Canada M9P 3V6
[c] Great Lakes Institute for Environmental Research, University of Windsor, 401 Sunset Avenue, Windsor, ON, Canada N9B 3P4

ARTICLE INFO

Article history:
Received 28 August 2010
Received in revised form 14 December 2010
Accepted 15 December 2010
Available online 17 January 2011

Keywords:
Pharmaceuticals
Personal care products
Endocrine disrupting substances
Passive sampling
Uptake

ABSTRACT

The effect of solution pH and levels of dissolved organic matter (DOM) on the sampling rates for model pharmaceuticals and personal care products (PPCPs) and endocrine disrupting substance (EDS) by polar organic chemical integrative samplers (POCIS) was investigated in laboratory experiments. A commercially available POCIS configuration containing neutral Oasis HLB (hydrophilic–lipophilic balance) resin (i.e. pharmaceutical POCIS) and two POCIS configurations prepared in-house containing MAX and MCX anion and cation exchange resins, respectively were tested for uptake of 21 model PPCPs and EDS, including acidic, phenolic, basic and neutral compounds. Laboratory experiments were conducted with dechlorinated tap water over a pH range of 3, 7 and 9. The effects of DOM were studied using natural water from an oligotrophic lake in Ontario, Canada (i.e. Plastic Lake) spiked with different amounts of DOM (the concentration of dissolved organic carbon ranged from 3 to 5 mg L^{-1} in uptake experiments). In experiments with the commercial (HLB) POCIS, the MCX-POCIS and the MAX-POCIS, the sampling rates generally increased with pH for basic compounds and declined with pH for acidic compounds. However, the sampling rates were relatively constant across the pH range for phenols with high p*Ka* values (i.e. bisphenol A, estrone, estradiol, triclosan) and for the neutral pharmaceutical, carbamazepine. Thus, uptake was greatest when the amount of the neutral species in solution was maximized relative to the ionized species. Although the solution pH affected the uptake of some model ionic compounds, the effect was by less than a factor of 3. There was no significant effect of DOM on sampling rates from Plastic Lake. However, uptake rates in different aqueous matrixes declined in the order of deionized water > Plastic Lake water > dechlorinated tap water, so other parameters must affect uptake into POCIS, although this influence will be minor. MAX-POCIS and MCX-POCIS showed little advantage over the commercial POCIS configuration for monitoring in natural waters.

1. Introduction

Passive sampling techniques have been developed for monitoring environmental contaminants in aquatic environments (Stuer-Lauridsen, 2005; Kot-Wasik et al., 2007; Arditsoglou and Voutsa, 2008; Söderström et al., 2009). These techniques can be used to determine the time-weighted average (TWA) concentrations of a wide range of environmental contaminants over extended sampling periods, and are capable of concentrating trace contaminants to detectable levels (Arditsoglou and Voutsa, 2008). One example is semipermeable membrane devices (SPMDs) which have been widely used to accumulate hydrophobic (lipophilic) organic chemicals (Huckins et al., 1993, 1999; Stuer-Lauridsen, 2005; O'Toole et al., 2006; Metcalfe et al., 2008).

Recently, the polar organic chemical integrative sampler (POCIS) has been developed for sampling of polar (i.e. hydrophilic) organic water contaminants (Alvarez, 1999; Alvarez et al., 2004). POCIS consists of a solid sequestration medium (sorbent) enclosed between two hydrophilic microporous membranes. Two configurations of POCIS are commercially available: pharmaceutical-POCIS and pesticide-POCIS. Pesticide-POCIS contains a triphasic sorbent admixture and shows good retention of pesticide and hormones and many other contaminants (Alvarez et al., 2004). Pharmaceutical-POCIS, which contains Oasis HLB (i.e. neutral) sorbent has been reported to be more suitable for pharmaceuticals and other compounds with multiple functional groups (Alvarez et al., 2004). Our previous studies have shown that there are some practical advantages to using the pharmaceutical-POCIS for monitoring polar organic contaminants (Li et al., 2010a).

* Corresponding author. Address: Environmental and Resource Studies, Trent University, 1600 West Bank Drive, Peterborough, ON, Canada K9J 7B8. Tel.: +1 705 748 1011x7272; fax: +1 705 748 1569.
E-mail address: cmetcalfe@trentu.ca (C.D. Metcalfe).

0045-6535/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2010.12.071

In order to estimate the ambient water concentrations of contaminants from accumulated amounts in POCIS, calibration data are required. This involves estimation of the sampling rates (R_S) in L d^{-1} for individual compounds. Several recent studies have demonstrated that POCIS can be used to monitor for trace levels of polar compounds in surface water and wastewater (Petty et al., 2004; Mills et al., 2007; Zhang et al., 2008; Martínez Bueno et al., 2009; Harman et al., 2009). Despite the wide application of POCIS, the R_S data are available for only a limited number of compounds, and over a limited range of ambient conditions (Macleod et al., 2007; Mazzella et al., 2007; Togola and Budzinski, 2007; Arditsoglou and Voutsa, 2008; Harman et al., 2008; Li et al., 2010b). The R_S for passive samplers depends on the physicochemical properties of the chemicals (such as molecular weight and hydrophobicity) and the environmental conditions, such as temperature, water flow rate/turbulence, pH, dissolved organic matter (DOM) and biofouling (Huckins et al., 1999; Alvarez et al., 2004; Macleod et al., 2007; Harman et al., 2008; Li et al., 2010b). Our previous studies have demonstrated that the water temperature and flow rate have minor effects on the POCIS sampling rates (Li et al., 2010a,b), but there have been few data on the influence of other factors such as solution pH and DOM concentration on R_S.

Pharmaceuticals and personal care products (PPCPs) and endocrine disrupting substances (EDS) have functional groups that can be ionized at various pHs. The chemical speciation of compounds is controlled by solution pH and the dissociation constants (p*K*a) of the chemical (Waite, 2004). Solution pH can affect other physicochemical properties, such as hydrophobicity and solubility (Avdeef et al., 2000). It has been reported that the hydrophobicity of several pharmaceuticals varies as a function of the solution pH (Avdeef et al., 2000). Because of changes in the physicochemical properties of the various species of PPCPs and EDS, their uptake into POCIS may differ significantly with the solution pH. However, Zhang et al. (2008) reported that the R_S for the EDS compounds, bisphenol A, estrone, 17-β-estradiol, 17-α-ethinylestradiol (p*K*a > 10) were not affected when pH varied from 4 to 10, or when the salinity changed from 0% to 3.5%.

Another important factor which may affect POCIS uptake is the levels of DOM in the aquatic environment. All natural waters contain dissolved organic matter. The simplest measure of the total concentration of DOM is the concentration of dissolved organic carbon (DOC) (Drever, 1997). The concentrations of DOC are typically 2–10 mg L^{-1} in rivers and lakes (Malcolm, 1985; Drever, 1997). Most of the DOC in natural waters is fulvic acids (major components, ~45%) and humic acid (~5%). The rest of DOC is from low-molecular-weight acids (25%), neutrals (15%), bases (5%), and contaminants (5%) (Malcolm, 1985). It has been reported that DOM reduces bioavailability and uptake into SPMDs of hydrophobic organic contaminants in the aquatic environment (Haitzer et al., 1998, 1999; Gourlay et al., 2005). Enhancement of bioconcentration by aquatic organisms at low levels of DOM has also been reported (Chiou et al., 1986; Mayer et al., 2005, 2007). Enhanced water solubility and mass transfer through aqueous boundary layers in the presence of DOM may be the reason for enhanced uptake (Chiou et al., 1986; Mayer et al., 2005, 2007).

The objectives of the present study were to: (1) evaluate the effect of solution pH and DOM on the sampling rates of model PPCP and EDS compounds for a commercial configuration of POCIS (i.e. pharmaceutical- POCIS); and (2) compare the uptake efficiency of the commercially available pharmaceutical-POCIS to two POCIS configurations prepared in-house with an anionic exchange sorbent (i.e. MAX) and a cation exchange sorbent (MCX), respectively. Laboratory studies with static systems were conducted to estimate uptake rates (R_S) under various conditions of pH and DOM. A total of 21 model PPCPs and EDS from basic, acidic, phenolic and neutral classes were studied. Extracts from POCIS were analyzed by liquid chromatography with tandem mass spectrometry (LC-MS/MS).

2. Material and methods

2.1. Materials, chemicals and POCIS samplers

The PPCP and EDS used as model compounds included analytes from several chemical classes (Table 1). Deuterated or ^{13}C-labelled surrogates of each model compound (Table 1) were spiked into samples prior to extraction to compensate for matrix effects. High performance liquid chromatography (HPLC) or distilled in glass grades of methanol, acetone and acetonitrile, and American Chemistry Society reagent grade dichloromethane, hydrochloride acid (37%), sulfuric acid (96%), formic acid (88%), and ammonium hydroxide (30%) were purchased from Fisher Scientific (Ottawa, ON, Canada). Stock solutions of individual compounds were prepared at a concentration of 1 mg mL^{-1} in methanol. Working solutions of individual compounds and mixtures were prepared by appropriate dilution of the stock solutions in methanol. All the standard solutions were stored at 4 °C. The Nordic Reservoir NOM (natural organic matter) (Cat. No. 1R108N, reverse osmosis), purchased from the International Humic Substance Society (IHSS) (St. Paul, MN, USA), is a mixture of aquatic humic and fulvic components (Christy et al., 1999; Christy and Egeberg, 2000; He et al., 2008) that consists of primarily carboxyl, aromatic, and aliphatic carbon constituents (IHSS data, http://ihss.gatech.edu/thorn-nmr.html). The detail information for Nordic Reservoir NOM is provided in Supplemental data.

The pharmaceutical-POCIS, consisting of 200 mg of Oasis HLB sorbent enclosed between two polyethersulfone membranes, as well as additional polyethersulfone membranes used for making POCIS were purchased from Environmental Sampling Technologies, Inc. (St. Joseph, MO, USA). The total exchanging surface area of the membrane is approximately 41 cm^2 and the surface area per mass of sorbent ratio is approximately 200 cm^2 g^{-1}. The MCX-POCIS and MAX-POCIS were assembled in-house using polyethersulfone membranes and 200 mg of Oasis MCX or Oasis MAX sorbents, respectively, using techniques described previously for assembly of pharmaceutical-POCIS (Alvarez et al., 2004). The sorbents used for pharmaceutical-, MAX- and MCX-POCIS are the same as the sorbents used in the commercially available SPE cartridges, Oasis HLB, Oasis MAX and Oasis MCX, respectively. Oasis HLB is a hydrophilic–lipophilic balanced, reversed-phase sorbent for acid, base and neutral compounds. Oasis MCX is a mixed-mode cation-exchange (negatively charged) and reversed-phase sorbent for bases. Oasis MAX is a mixed-mode anion-exchange (positively charged) and reversed-phase sorbent for acids.

The Waters Oasis MAX and MCX sorbents were removed from Oasis MAX (6 cc, 500 mg) and Oasis MCX (6 cc, 150 mg) solid phase extraction (SPE) cartridges that were purchased from Waters Corporation (Milford, MA, USA). The sorbents were pooled and washed with methanol before use.

2.2. POCIS sampling rates

The static method used to determine the sampling rates for the 21 model PPCPs and EDS was reported previously (Li et al., 2010b). Briefly, static experiments were conducted in triplicate in amber glass bottles containing 3 L of water placed in a temperature controlled environmental chamber at 25 °C. The water was spiked with a mixture of the 21 model compounds, with nominal concentrations ranging from 2 to 10 ng mL^{-1}, and a single POCIS was placed in the water for a period of 8 d. A magnetic stirrer was used to gently mix the water. All bottles were covered with aluminium

Table 1
Model pharmaceuticals and personal care products (PPCPs) and endocrine disrupting substances (EDS) under study, including CAS number, recovery of solid phase extraction (%), log octanol–water partition coefficient (log K_{OW}), effective log octanol–water distribution coefficient (log D) at pH of 3, 7 and 9, and the acid dissociation constants (pKa), and the instrumental limits of quantification (LOQ) (ng mL^{-1}).

Class/compound	CAS	MW (g mol^{-1})	Internal Standard	log K_{OW} [a]	log D at pH of 3,7,9[b]	pKa	Ref.
Sulfonamide antibiotics							
Sulfamethoxazole[c]	723-46-6	253.3	Sulfamethoxazole-$^{13}C_6$[d]	0.89	0.89, −0.53, −2.51	1.7/5.6	Nghiem et al. (2005)
Acidic pharmaceuticals							
Naproxen[c]	22204-53-1	230.3	Naproxen-$^{13}C_1$, d_3[d]	3.18	3.15, 0.33, −1.67	4.15	SRC PhysPro
Ibuprofen[c]	15687-27-1	206.3	Ibuprofen-$^{13}C_3$[d]	3.97	3.96, 1.88, −0.12	4.91	SRC PhysPro
Gemfibrozil[c]	025812-30-0	250.3	Gemfibrozil-d_6[d]	4.77	4.75, 2.19, 0.19	4.42	Amjadi et al. (2008)
Estrogens							
Bisphenol A[c]	80-05-7	228.3	Bisphenol A-$^{13}C_{12}$[d]	3.32	3.32, 3.32, 3.3	10.3	Lewis and Archer (1979)
Estrone (E1) [c]	53-16-7	270.4	Estradiol-$^{13}C_2$[d]	3.13	3.13, 3.13, 3.12	10.77	Lewis and Archer (1979)
17-β-Estradiol (E2) [c]	50-28-2	272.4	Estradiol-$^{13}C_2$[d]	4.01	4.01, 4.01, 4	10.71	Lewis and Archer (1979)
Bacteriocides							
Triclosan[f]	3380-34-5	289.5	Triclosan-$^{13}C_{12}$[d]	4.76	4.76, 4.73. 3.81	8.1	Tixier et al. (2002)
Anti-depressants							
N-desmethyl venlafaxine[g]		263.4	Venlafaxine-d_{10}[g]	NA	NA, NA, NA	NA	
Venlafaxine[g]	93413-69-5	277.4	Venlafaxine-d_{10}	3.28	−3.12, 0.88, 2.74	9.4	Cherkaoui et al. (2001)
Desmethyl citalopram[g]	144025-14-9	310.4	Citalopram-d_4[g]	NA	NA, NA, NA	NA	
Citalopram[h]	59729-33-8	324.4	Citalopram-d_4	3.74	−2.85, 1.15, 3.05	9.59	Vasskog et al. (2006)
Paroxetine[c]	61869-08-7	329.3	Paroxetine-d_6[h]	3.95	−3.37,0.63, 2.61	10.32	Vasskog et al. (2006)
Fluoxetine[c]	54910-89-3	309.3	Fluoxetine-d_5[e]	4.05	−3.01, 0.99, 2.95	10.06	Vasskog et al. (2006)
Desmethyl sertraline[g]		291.1	Sertraline-d_3[g]	NA	NA, NA, NA	NA	
Sertraline[g]	079617-96-2	306.2	Sertraline-d_3	5.29	−1.18, 2.82, 4.69	9.47	Vasskog et al. (2006)
Beta-blockers							
Nadolol[c]	42200-33-9	309.4	Sotalol-HCl-d_6[i]	0.81	−5.86, −1.86, 0.06	9.67	SRC PhysPro
Metoprolol[c]	37350-58-6	267.4	Propranolol-d_7[e]	1.88	−4.72, −0.72, 1.18	9.6	SRC PhysPro
Propranolol[c]	525-66-6	259.3	Propranolol-d_7	3.48	−2.94, 1.06, 2.92	9.42	SRC PhysPro
Neutral pharmaceuticals							
Carbamazepine[c]	298-46-4	236.3	Carbamazepine-d_{10}[e]	2.45	2.45, 2.45, 2.45	13.9	Tadkaew et al. (2010)
Trimethoprim[c]	738-70-5	290.3	Trimethoprim-$^{13}C_3$[d]	0.91	−3.21, 0.55, 0.9	7.12	SRC PhysPro

NA: data not available.
SRC PhysProp Database. http://www.srcinc.com/what-we-do/databaseforms.aspx?id=386. Accessed on June, 2010.
[a] log K_{OW} values from Lienert et al. (2007) and http://www.srcinc.com/what-we-do/databaseforms.aspx?id=386. Accessed on June, 2010.
[b] log D values calculated from Eqs. (6) and (7): $D_{Base} = K_{OW}/(1 + 10^{pKa-pH})$, $D_{Acid} = K_{OW}/(1 + 10^{pH-pKa})$.
[c] Sigma–Aldrich.
[d] Cambridge isotope laboratories.
[e] C/D/N.
[f] KIC.
[g] Synfine.
[h] Cerilliant.
[i] Dr. Ehrenstorfer GmbH.

foil to reduce exposure to light and minimize volatilization of the analytes. Aliquots of the exposure water (2 × 20 mL) were removed from the bottles every 24 h to monitor the decrease in water concentration over time. Control experiments containing only fortified water without the POCIS (i.e. positive control) were run along with the calibration to correct for sorption, volatilization or degradation during exposure. One pre-soaked POCIS was exposed to 3 L of water without spiking of pharmaceuticals as a negative control to assess contamination during the experiment.

The sampling rate was calculated by measuring the decrease in water concentration (C_W) over time, according to the equations:

$$C_W(t) = C_W(0)\exp[-(k_U + k_D)t] = C_W(0)\exp[-kt] \quad (1)$$

which rearranges to

$$\mathrm{Ln}[C_W(t)/C_W(0)] = -kt \quad (2)$$

where k_U, k_D are the uptake rate constant and the dissipation rate constant, respectively, in L d^{-1}, and $C_W(0)$ and $C_W(t)$ are the water concentrations at initiation of the experiment and at time t, respectively. The sampling rate, R_S, is thus:

$$R_S = k_U V_T \quad (3)$$

where V_T is the initial water volume in the tank (3 L in the present study). The value of k is estimated from the slope of the decrease of water concentration ($\mathrm{Ln}[C_W(t)/C_W(0)]$) over the exposure time. The uptake rate constant, k_U, was taken to equal k, as dissipation of the analytes was not observed in the positive blanks experiments.

Dechlorinated tap water from the City of Peterborough, ON, Canada was used in experiments to determine the effect of changes in pH on uptake. For dechlorination, air was bubbled through water for one week to volatilize the chlorine out of solution. The water was adjusted to pH 3, 7 and 9 using 0.1 M H_2SO_4 and 0.1 M NaOH. To determine the effect of DOM on uptake, water collected from Plastic Lake, an oligotrophic lake in south-central Ontario was used for the experiments. Volumes of 3 L of Plastic Lake water were spiked with 0, 6 and 18 mg of Nordic Reservoir NOM, corresponding to measured concentrations of DOC of 3.33, 3.86 and 4.92 mg L^{-1}, respectively. The DOC was measured using a Shimadzu (Japan) TOC-Vcph instrument with high temperature catalytic combustion at 680 °C. Before DOC analysis, the samples were filtered with Whatman Nylon syringe filters (25 mm × 0.45 μm) purchased from Mandel Scientific Company (Guelph, ON, Canada).

2.3. Extraction of water samples

The methods used to extract samples of water from the static tests have been described previously by Li et al. (2010a,b). Briefly,

the water samples (20 mL) were extracted by concentrating the analytes onto SPE cartridges. Two multi-residue extraction methods were used to extract all classes of PPCP and EDS analytes. The β-blocker and anti-depressant drugs, which are weak bases were extracted with Oasis MCX cation exchange cartridges. All other classes of PPCPs and EDS, including weakly acidic, phenolic and neutral compounds were enriched using Oasis MAX anion-exchange cartridges.

2.4. Extraction of POCIS samplers

The extraction procedures for POCIS were previously described by Li et al. (2010b). Briefly, the sorbent powder from the POCIS was carefully transferred into a glass chromatography column with methanol, then 100 µl internal standard mixture in methanol (500 ng mL^{-1} for each compound) was spiked directly onto the sorbent. After letting the column sit for one hour, the column was eluted with: (i) 50 mL of methanol for the pharmaceutical-POCIS, (ii) 100 mL of 5% ammonium hydroxide in methanol for MCX-POCIS, or (iii) 100 mL of 2% formic acid in methanol for the MAX-POCIS. The eluate volume was reduced to about 1 mL with a rotary evaporator and transferred into a conical centrifuge tube. The samples were evaporated to near-dryness under a stream of nitrogen and transferred into injection vials in 1 mL of methanol. The extracts were diluted with methanol/water (1:1) before LC-MS/MS analysis.

Table 2
Summary of tandem mass spectrometry parameters used for multiple reaction monitoring (MRM) for model compounds by atmosphere pressure chemical ionization (APCI) or electrospray (ESI). DP: declustering potential; CE: collision energy.

Compounds	*m/z*	APCI		
	MRM transition	Polarity	DP (V)	CE (V)
Carbamazepine	237.1 > 194.1	+	40	28
Trimethoprim	291.2 > 123.1	+	32	27
Sulfamethoxazole	254.2 > 156.1	+	30	20
Sertraline	306.2 > 158.8	+	24	35
Desmethyl sertraline	292.1 > 158.9	+	18	28
Venlafaxine	278.2 > 58	+	35	43
Citalopram	325.3 > 109	+	39	35
Fluoxetine	310.2 > 43.9	+	24	32
Paroxetine	330.3 > 70	+	41	49
Desmethyl citalopram	311.2 > 108.9	+	40	38
N-desmethyl venlafaxine	264.2 > 43.9	+	32	39
Labelled isotope				
Carbamazepine-d_{10}	247.1 > 204.1	+	25	30
Trimethoprim-$^{13}C_3$	294.2 > 126.1	+	42	32
Sulfamethoxazole-$^{13}C_6$	260.1 > 162	+	30	20
Sertraline-d_3	309.2 > 158.8	+	27	35
Venlafaxine-d_{10}	288.4 > 58	+	28	42
Citalopram-d_4	329.3 > 113	+	41	37
Fluoxetine-d_5	315.3 > 43.9	+	25	32
Paroxetine-d_6	336.3 > 76	+	40	50
	m/z	Electrospray		
	MRM transition	Polarity	Cone (V)	CE (electron-volts)
Naproxen	229 > 185	–	25	6
Ibuprofen	205 > 161	–	25	9
Gemfibrozil	249 > 121	–	25	12
Nadolol	310 > 254	+	35	20
Propranolol	260 > 115.9	+	35	20
Metoprolol	268 > 132.8	+	40	25
Bisphenol A	227 > 212.1	–	50	18
17-β-Estradiol	271.1 > 145	–	65	35
Estrone	269.1 > 145	–	65	38
Triclosan	286.9 > 35	–	30	8
Labelled isotope				
Naproxen-$^{13}C_1$,d_3	233 > 189	–	25	6
Ibuprofen-$^{13}C_3$	208 > 163	–	25	9
Gemfibrozil-d_6	255 > 121	–	25	12
Sotalol-d_6	279.1 > 261.1	+	22	13
Propranolol-d_7	267.3 > 117	+	35	20
Bisphenol A-$^{13}C_{12}$	239 > 224.2	–	40	25
17-β-Estradiol-$^{13}C_2$	273.1 > 147	–	65	45
Triclosan-$^{13}C_{12}$	298.9 > 35	–	25	8

2.5. Analysis

The analytical instrumentation and analytical techniques were previously described by Li et al. (2010a,b). Briefly, the analytes were separated by HPLC with a Genesis C18 column (150 × 2.1 mm i.d., 4 µm particle size) purchased from Chromatographic Specialties (Brockville, ON Canada), coupled with a guard column with the same packing material (4 mm × 2.0 mm) purchased from Phenomenex (Torrance, ON, Canada). The target analytes were analyzed by atmospheric pressure chemical ionization and tandem mass spectrometry (LC-APCI-MS/MS) or electrospray ionization and tandem mass spectrometry (LC-ESI-MS/MS). The analytes were identified by multiple reaction monitoring (MRM) of a precursor ion and a single product ion (one transition) as listed in Table 2. Six LC-MS/MS methods (Li et al., 2010b) were used for analysis of six classes of model compounds. Chromatographic and instrumental ionization parameters used for LC-MS/MS analysis are listed in Supplementary data (Table S1).

The quantification was performed using an internal standard method with a six point calibration curve generated for each compound. The stable isotope-labelled compound was used as an internal standard for each analyte. The curve was plotted by the peak area ratios of the target analyte and the internal standard against the concentration ratios of the analyte and the internal standard. The analyte concentration ranged from 2 to 1000 ng mL^{-1}, and the internal standard concentration was constant (50 ng mL^{-1}) in the calibration solutions. The stable isotope-labelled internal standards were spiked into the POCIS sorbents prior to extraction in order to compensate for the mass loss during the sample preparation and the matrix effects during LC-MS/MS analysis (Zhao and Metcalfe, 2008).

2.6. Limits of detection, quality control and statistical analysis

There were no target analytes detected in any of the aliquots of water or in the POCIS extracts from negative control (i.e. blank) treatments during POCIS experiments. The recovery of each analyte using the multi-residue solid phase extraction ranged from 71% to 118% (Li et al., 2010b). The instrumental detection limits (LODs) and instrumental quantification limits (LOQs), which were defined as the analyte concentration that produced a peak with a signal-to-noise ratio of 3 and 10, respectively, were determined using the lowest standards calibration solution. The LOQs of selected analytes ranged from 0.02 to 1.2 ng mL^{-1} (Table 1).

The quality of fit for each regression describing the declines in compound concentrations over time was characterized by the regression correlation coefficients (r). The precision was estimated using the standard deviations from k_U estimates generated from the triplicate experiments. Analysis of variance (ANOVA) was used to test for differences in sampling rates across the pH treatments for each POCIS sorbent and for differences in sampling rates between the POCIS sorbents. ANOVAs were also completed to investigate the potential influence of DOM additions on pharmaceutical sampling rates by HLB-POCIS. Pair-wise comparisons were completed using a Tukey's post hoc test with a criterion of significance of $p < 0.05$. Prior to statistical analysis, all data were tested for normality using normal probability plots. Regression analyses were completed using Microsoft Excel software and all ANOVAs and

pair-wise comparison tests were completed using SYSTAT version 11.0 for Windows (SYSTAT, 2004).

3. Results and discussion

3.1. pH effects on sampling for pharmaceutical-POCIS

The uptake rates varied with pH for some classes of model compounds, but not for others (Table 3). The sampling rates for the acidic pharmaceuticals decreased as pH increased from 3 to 9, while the sampling rates for the basic compounds (such as β-blockers and anti-depressants) increased as the pH increased from 3 to 9. The sampling rates for the neutral drug, carbamazepine and the phenolic compounds with high pKa values (such as bisphenol A, estrone, etc.) were not affected by the ambient pH. The sampling rates for some pharmaceuticals at some pH levels could not be determined due to low sampling rates or poor linear relationships. The chemical structures of the model compounds are shown in Supplementary data (Fig. S1). The bases or acids were present in either neutral or ionized forms, depending upon the test pH. Bisphenol A and the natural steroids (estrone, estradiol) containing phenolic moieties with p*K*a > 10 (Lewis and Archer, 1979; Ivashechkin et al., 2004) and the neutral drug, carbamazepine with a p*K*a = 13.9 (Tadkaew et al., 2010) were present as neutral species at the test pHs. Because of differences in charge and physicochemical properties of the various species of a given model compound, their uptake into passive sampler may differ significantly. The speciation of chemicals can be determined by the Henderson–Hasselbalch equations (Harris, 2007).

For an acid, the Henderson–Hasselbalch equation is,

$$\mathrm{pH} = \mathrm{p}K_a + \log([A]^-/[HA]) \quad (4)$$

For a base, the equation is,

$$\mathrm{pH} = \mathrm{p}K_a + \log([B]/[BH^+]) \quad (5)$$

where pK_a is the acid dissociation constant of the weak acid BH^+.

The ratio of conjugated acid and base can be calculated using the solution pH and the p*K*a value for the compound. For acidic pharmaceuticals (naproxen, ibuprofen and gemfibrozil), where the p*K*a values are below 5, the chemicals are protonated (neutral species) at pH = 3, and deprotonated (ionized species) at pH = 7 and 9 (from Eq. (4)).

Sulfamethoxazole can exist in positive, neutral and negatively charged forms due to its two ionisable amine groups: one primary aromatic amine $-NH_2$ and one sulfonamide -NH group (Nghiem et al., 2005). The speciation of sulfamethoxazole over the entire pH range is shown in Supplementary data (Fig. S2). At the test pHs, sulfamethoxazole was present in the neutral form at pH 3, and as the negatively charged species at pHs 7 and 9. The sampling rates for acidic pharmaceuticals and sulfamethoxazole were highest at pH 3 for the HLB-POCIS configuration (Table 3), but not statistically different from the sampling rates of these compounds determined at pH 7 and 9 using this POCIS configuration (ANOVA; $p = 0.075$). For the phenolic compounds and the steroids (bisphenol A, estrone, 17-β-estradiol) with p*K*a values > 10, the sampling rates were not significantly different (ANOVA; $p = 0.594$) at pH = 3, 7 and 9 for the HLB-POCIS configuration. Although the pKa for triclosan has been reported as 8.1 (Tixier et al., 2002), sampling rates for this compound by the HLB-POCIS exhibited no trends with pH. In general, no significant pH effect (ANOVA; $p = 0.594$) was observed on the sampling rates of neutral compounds for the HLB-POCIS configuration. It is probable that the neutral form of the test compounds passes more easily through the POCIS membrane and/or the neutral form has higher retention factors on neutral HLB sorbents (i.e. pharmaceutical-POCIS) than the ionized species.

The sampling rates of most basic chemicals, including the antidepressants, β-blockers, and trimethoprim, were positively correlated with pH (Table 3). For these compounds, the sampling rates of all three POCIS configurations were significantly lower at pH 3 relative to the higher pH treatments (ANOVAs; $p \leqslant 0.002$). For most basic model compounds, the p*K*a values are > 9 (Vasskog et al., 2006), except for trimethoprim with a p*K*a = 7.12 (SRC PhysProp Database, 2010). The test pHs were below the p*K*a of the antidepressants and the β-blockers, although the proportion in the neutral species would be maximized at pH = 9. According to Eq. (5), trimethoprim was present in the cationic form, neutral form and as a cation-neutral mixture (about 1:1) at pH = 3, 9 and 7, respectively. Carbamazepine, with a p*K*a value of 13.9, has been reported to be present in the neutral form at all pHs that are typical of natural waters or wastewater (Tadkaew et al., 2010). However, the sampling rate of carbamazepine at pH = 3 was 61–64% of the

Table 3
Sampling rates (L d^{-1}) of model compounds for pharmaceutical-POCIS (HLB) as a function of solution pH and dissolved organic matter.

	pH 3	pH 7	pH 9	DOM 1[a]	DOM 2	DOM 3
N-desmethyl-venlafaxine	0.166 ± 0.003	0.237 ± 0.058	0.452 ± 0.048	0.262 ± 0.056	0.277 ± 0.027	0.460 ± 0.028
Venlafaxine	0.071 ± 0.020	0.287 ± 0.053	0.372 ± 0.085	0.377 ± 0.067	0.340 ± 0.003	0.442 ± 0.009
Desmethyl citalopram	0.377 ± 0.008	0.362 ± 0.028	0.471 ± 0.059	0.452 ± 0.055	0.516 ± 0.011	0.595 ± 0.017
Citalopram	0.120 ± 0.006	0.445 ± 0.041	0.561 ± 0.091	0.586 ± 0.059	0.548 ± 0.046	0.636 ± 0.034
Paroxetine	0.213 ± 0.025	0.573 ± 0.006	0.618 ± 0.025	0.718 ± 0.101	0.615 ± 0.017	0.578 ± 0.039
Fluoxetine	0.289 ± 0.032	0.502 ± 0.025	0.596 ± 0.074	0.553 ± 0.079	0.664 ± 0.025	0.658 ± 0.013
Desmethyl sertraline	0.343 ± 0.051	0.793 ± 0.061	0.686 ± 0.063	0.683 ± 0.056	0.578 ± 0.009	0.666 ± 0.001
Sertraline	0.321 ± 0.046	0.729 ± 0.048	0.748 ± 0.055	0.604 ± 0.046	0.618 ± 0.018	0.702 ± 0.059
Nadolol	NA	0.074 ± 0.018	0.275 ± 0.034	0.082 ± 0.030	0.176 ± 0.041	0.277 ± 0.006
Metaprolol	0.125 ± 0.023	0.321 ± 0.035	0.570 ± 0.063	0.323 ± 0.024	0.380 ± 0.012	0.406 ± 0.027
Propranolol	0.161 ± 0.028	0.478 ± 0.028	0.596 ± 0.064	0.506 ± 0.063	0.588 ± 0.019	0.536 ± 0.024
Carbamazepine	0.226 ± 0.028	0.354 ± 0.042	0.372 ± 0.003	0.360 ± 0.037	0.417 ± 0.075	0.404 ± 0.012
Trimethoprim	0.104 ± 0.006	0.209 ± 0.012	0.370 ± 0.059	0.260 ± 0.036	0.305 ± 0.062	0.393 ± 0.036
Sulfamethoxazole	0.220 ± 0.008	NA	NA	0.156 ± 0.001	0.186 ± 0.006	0.303 ± 0.010
Naproxen	1.18 ± 0.20	0.113 ± 0.034	0.117 ± 0.005	0.363 ± 0.022	0.348 ± 0.032	0.337 ± 0.014
Ibuprofen	1.02 ± 0.11	0.100 ± 0.008	0.214 ± 0.018	0.360 ± 0.041	0.413 ± 0.028	0.438 ± 0.020
Gemfibrozil	0.910 ± 0.020	0.344 ± 0.022	0.335 ± 0.058	0.412 ± 0.058	0.502 ± 0.026	0.473 ± 0.009
Bisphenol A	0.607 ± 0.011	0.634 ± 0.020	0.651 ± 0.050	0.620 ± 0.024	0.668 ± 0.029	0.709 ± 0.012
Estrone	0.793 ± 0.176	NA	NA	0.460 ± 0.023	0.583 ± 0.034	0.599 ± 0.036
Estradiol	0.702 ± 0.143	NA	NA	0.534 ± 0.019	0.586 ± 0.032	0.626 ± 0.015
Triclosan	1.06 ± 0.08	1.34 ± 0.01	1.01 ± 0.07	1.29 ± 0.05	1.27 ± 0.02	1.29 ± 0.01

NA: sampling rate can not be determined due to low sampling rates or poor linearity.
[a] DOM 1, 2, 3: concentrations of dissolved organic carbon are 3.33, 3.86 and 4.92 mg L^{-1}, respectively.

sampling rate determined at pH = 7 and 9 (Table 3), for reasons that are not clear.

The hydrophobicity and solubility of several of the model compounds vary significantly with pH (Avdeef et al., 2000). Changes in the hydrophobicity of some chemicals as a function of the solution pH can be illustrated by determining the effective log octanol–water distribution coefficient (log D), which adjusts for the pH of the medium and pKa of a given chemical. The log D expresses the distribution of both the neutral and the ionic fraction of the compound between octanol and water. The following equations (Magnér et al., 2009) have been used to calculate the D value for acidic and basic compounds:

$$D_{\text{Acid}} = K_{\text{OW}}/(1 + 10^{\text{pH}-\text{p}Ka}) \quad (6)$$

$$D_{\text{Base}} = K_{\text{OW}}/(1 + 10^{\text{p}Ka-\text{pH}}) \quad (7)$$

The calculated log D values are summarized in Table 1. Over the pH range of 3–9, the log D values of acidic pharmaceuticals (naproxen, ibuprofen, gemfibrozil) decrease with pH, while the log D values of the phenolic compounds (bisphenol A, estrone and estradiol) and carbamazepine are constant. For basic pharmaceuticals, the log D values increase with pH. From these data, it can be concluded that the sampling rates increase as the log D values increase. Fig. 1 indicates that a positive linear relationship

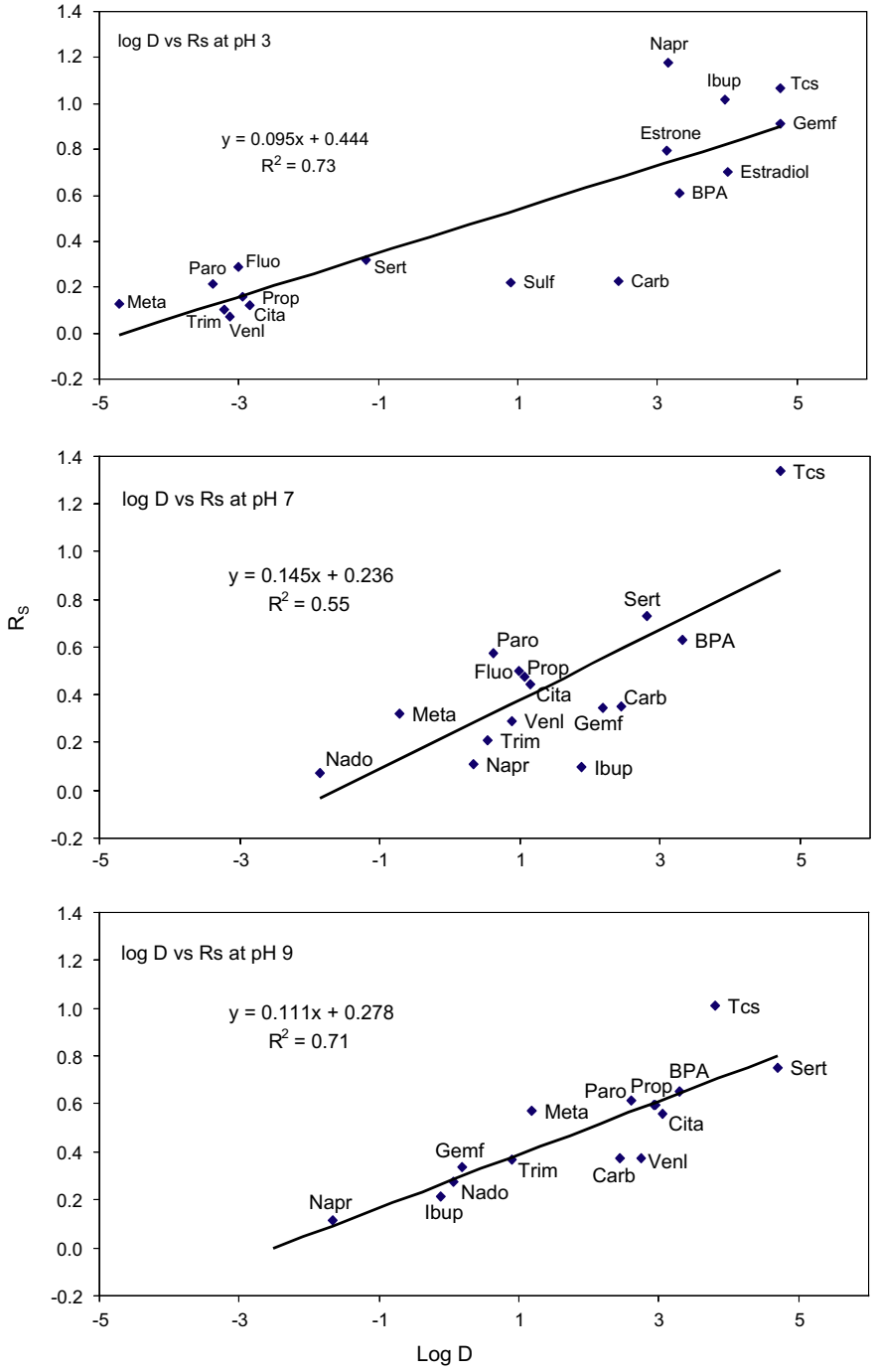

Fig. 1. Relationship between sampling rate (R_S) and the effective log octanol–water partition coefficients (log D) at three pHs (3, 7 and 9) for 17 selected model compounds. Napr - Naproxen, Ibup - Ibuprofen, Gemf - Gemfibrozil, Bisphenol A – BPA, Tcs – Triclosan, Venl – Venlafaxine, Citalopram – Cita, Paro – Paroxetine, Fluo - Fluoxetine, Sert – Sertraline. Nado – Nadolol, Meto – Metoprolol, Prop – Propranolol, Carb – Carbamazepine, Trim – Trimethoprim, Sulf – Sulfamethoxazole.

(R^2 = 0.55–0.73) exists between the sampling rate and log D at the three pHs studied. The influence of pH on the uptake rates of the acidic pharmaceuticals (Naproxen, Ibuprofen, Gemfibrozil) is apparent at pH 3. However, the slopes of the straight line were not significantly different at the three pHs tested (t-test, $p > 0.05$). Sampling rate-log D relationships may provide a means of estimating sampling rates. We previously reported that the sampling rates for POCIS increase with log K_{OW} for some PPCPs and EDS, excluding acidic pharmaceuticals and some phenolic compounds (Li et al., 2010b).

3.2. pH effects on sampling for MCX- and MAX-POCIS

The sampling rates of the target compounds by MCX- and MAX-POCIS at different solution pHs are summarized in Table 4. The pattern of uptake into MAX- and MCX-POCIS as a function of pH was the same as uptake into the pharmaceutical-POCIS, despite the fact that there were different sorbents used in the 3 POCIS configurations.

The MCX-POCIS are made from mixed-mode cation-exchange (negatively charged) and reversed-phase sorbents, which are appropriate for accumulation of neutrals and basic compounds at both low and high solution pHs. For the basic compounds (i.e. anti-depressants, β-blockers and trimethoprim), the sampling rate increased with pH, but by a factor of less than 2 (Table 4), though the sampling rate at pH of 3 is significantly lower than that at pH of 7 and 9 (ANOVA; $p = 0.001$). The sampling rates for phenols, estrogens, and neutral drugs were constant as the pH increased from 3 to 9. For acidic pharmaceuticals (i.e. sulfamethoxazole, naproxen, ibuprofen and gemfibrozil), the rate of sampling by MCX-POCIS decreased as the pH increased. The sampling rate at pH 3 was significantly higher than that at pH of 7 or 9 (~6-fold) (ANOVA, $p = 0.005$). Therefore, MCX-POCIS is not appropriate for accumulation of acidic compounds at high pHs.

The MAX-POCIS are constituted of a mixed-mode anion-exchange (positively charged) and reversed-phase sorbents, which are appropriate for accumulation of neutrals and acidic compounds at both low and high pHs (Table 4). For acidic pharmaceuticals (i.e. sulfamethoxazole, naproxen, ibuprofen and gemfibrozil), the sampling rate by MAX-POCIS decreased as the pH increased, but by a factor of less than 3, though the sampling rate at pH 3 was significantly higher than that at pH of 7 or 9 (ANOVA; $p = 0.004$). For the basic compounds (i.e. anti-depressants, β-blockers and trimethoprim), the sampling rate increased as the pH increased. The sampling rate for basic compounds at pH 3 was significantly lower than the sampling rates at pH of 7 or 9 (ANOVA; $p = 0.003$), but the sampling rates at pH 7 and 9 were not significantly different (Table 4) The sampling rates for phenols, estrogens, and neutral drugs were constant as the pH increased from 3 to 9. MAX-POCIS is not appropriate for accumulation of basic compounds at low pHs.

3.3. Comparison of three POCIS configurations

MCX-POCIS is an appropriate configuration for accumulation of basic compounds at high pH, but the uptake efficiency is lower than that of pharmaceutical (HLB)-POCIS The MAX-POCIS is an appropriate configuration for accumulation of acidic compounds at low pH (Table 4). However, the uptake efficiency is lower than that of pharmaceutical (HLB)-POCIS.

For basic compounds, sampling rates at pH 9 were significantly different (ANOVA; $p < 0.001$) among the three POCIS configurations and decreased in the order of HLB > MCX > MAX. No significant difference was determined for average sampling rates of basic compounds between the HLB- and MCX-POCIS configurations. However, the average sampling rate for basic compounds by the MAX POCIS was significantly lower than those determined for basic compounds by both the HLB and MCX-POCIS configurations (Tukey's post hoc; $p \leqslant 0.002$). For the acidic compounds at test pH 3, sampling rates did not differ significantly across the three POCIS configurations (ANOVA; $p = 0.652$). Similarly, for neutral compounds at test pH 7, no significant differences (ANOVA; $p = 0.855$) in sampling rates were determined among the three POCIS configurations. These results indicate that the pharmaceutical-POCIS (HLB) configuration exhibits the highest uptake efficiency for basic drugs and is equally efficient with the MCX and MAX sorbents for other chemical classes. For the MCX- and MAX-POCIS configurations, these sorbent materials were moderately efficient for sampling basic compounds at high pH and acidic drugs at low pH, respectively. These data demonstrate that there are limited advantages to using ion exchange sorbents in POCIS relative to the commercially available (HLB) sorbent. Additionally, these results

Table 4
Sampling rates (L d^{-1}) of model compounds for MCX- and MAX-POCIS as a function of solution pH.

	MCX-POCIS			MAX-POCIS		
	pH 3	pH 7	pH 9	pH 3	pH 7	pH 9
N-desmethyl-venlafaxine	NA	0.330 ± 0.013	0.411 ± 0.074	NA	NA	0.092 ± 0.011
Venlafaxine	0.266 ± 0.009	0.296 ± 0.019	0.392 ± 0.048	0.049 ± 0.003	0.174 ± 0.016	0.111 ± 0.001
Desmethyl citalopram	0.378 ± 0.036	0.286 ± 0.032	0.503 ± 0.003	NA	0.210 ± 0.033	0.347 ± 0.022
Citalopram	0.306 ± 0.015	0.396 ± 0.058	0.463 ± 0.013	NA	0.224 ± 0.026	0.223 ± 0.008
Paroxetine	0.292 ± 0.064	0.420 ± 0.019	0.536 ± 0.028	0.271 ± 0.090	0.386 ± 0.089	0.415 ± 0.037
Fluoxetine	0.217 ± 0.012	0.467 ± 0.034	0.569 ± 0.030	0.101 ± 0.009	0.246 ± 0.092	0.277 ± 0.049
Desmethyl sertraline	0.355 ± 0.056	0.699 ± 0.101	0.839 ± 0.049	0.223 ± 0.053	0.652 ± 0.043	0.548 ± 0.005
Sertraline	0.333 ± 0.064	0.565 ± 0.066	0.676 ± 0.062	0.235 ± 0.013	0.538 ± 0.054	0.446 ± 0.021
Nadolol	0.179 ± 0.046	0.276 ± 0.034	0.240 ± 0.012	NA	0.076 ± 0.008	0.101 ± 0.009
Metaprolol	0.271 ± 0.056	0.389 ± 0.028	0.621 ± 0.110	0.088 ± 0.011	0.278 ± 0.063	0.155 ± 0.004
Propranolol	0.299 ± 0.130	0.519 ± 0.022	0.437 ± 0.061	0.098 ± 0.013	0.390 ± 0.045	0.285 ± 0.019
Carbamazepine	0.242 ± 0.063	0.248 ± 0.038	0.228 ± 0.038	0.222 ± 0.029	0.164 ± 0.003	0.143 ± 0.011
Trimethoprim	0.205 ± 0.083	0.267 ± 0.054	0.278 ± 0.063	0.060 ± 0.002	0.190 ± 0.027	0.144 ± 0.005
Sulfamethoxazole	0.173 ± 0.054	NA	0.050 ± 0.010	0.246 ± 0.008	0.165 ± 0.001	0.168 ± 0.003
Naproxen	0.749 ± 0.061	0.071 ± 0.011	0.104 ± 0.014	0.812 ± 0.070	0.253 ± 0.074	NA
Ibuprofen	0.678 ± 0.074	0.142 ± 0.009	0.131 ± 0.019	0.731 ± 0.070	0.290 ± 0.070	0.189 ± 0.010
Gemfibrozil	0.680 ± 0.076	0.148 ± 0.033	0.166 ± 0.039	0.682 ± 0.054	0.260 ± 0.068	0.147 ± 0.038
Bisphenol A	0.380 ± 0.077	0.500 ± 0.036	0.526 ± 0.009	0.407 ± 0.023	0.498 ± 0.023	0.357 ± 0.034
Estrone	0.253 ± 0.075	0.569 ± 0.121	0.394 ± 0.024	0.432 ± 0.020	0.461 ± 0.023	0.332 ± 0.049
Estradiol	0.374 ± 0.024	0.334 ± 0.009	0.430 ± 0.013	0.316 ± 0.026	0.363 ± 0.042	0.221 ± 0.027
Triclosan	1.11 ± 0.03	1.14 ± 0.04	1.01 ± 0.04	1.07 ± 0.06	1.13 ± 0.05	1.11 ± 0.03

NA: sampling rate can not be determined due to low sampling rate or poor linearity.

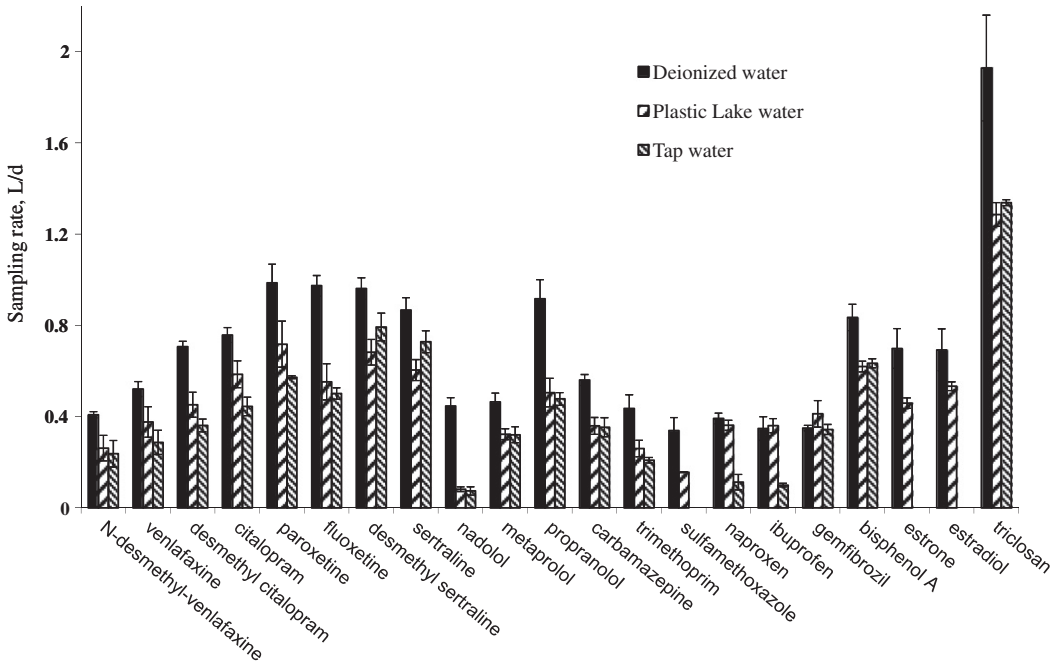

Fig. 2. The comparison of sampling rates of model compounds determined with Peterborough dechlorinated tap water and Plastic Lake water from the present study and with the deionized water cited from Li et al. (2010b). The pH of Plastic Lake water, dechlorinated tap water and deionized water were 6.13, 8.46 and 5.43, respectively. The concentration of dissolved organic carbon in Plastic Lake water, dechlorinated tap water and deionized water were 3.33,4.55, <1 mg L^{-1}, respectively. The pH of the dechlorianted tap water was adjusted to 7 for uptake experiments. The pH values of deionized water and Plastic Lake water were not adjusted for these experiments. The temperature of the chamber where the uptake experiments were conducted was set at 25 °C for all these three types of water.

indicate that the retention of pharmaceutical compounds on solid phase adsorbents is not the only factor governing sampling rate, as diffusion across the polyethersulfone (PES) membrane is maximized when the compounds are present in the neutral form.

3.4. Effects of DOM on sampling rates

The concentrations of DOC in Plastic Lake water that was spiked and not spiked with DOM varied over a fairly narrow range, from 3 to 5 mg L^{-1}. Although there were trends for an increase in the sampling rates of the HLB-POCIS for the acidic, neutral and basic groups of compounds among the treatments for DOM additions (Table 3), these differences were not statistically significant (ANOVAs; $p \geqslant 0.476$). However, it must be noted that the DOM concentration in these experiments varied by less than a factor of 2.

DOM has been reported to reduce the accumulation of hydrophobic organic contaminants into SPMDs from the aquatic environment (Gourlay et al., 2005). It has been suggested that hydrophobic organic compounds may not be as available for accumulation in SPMDs due to the formation of complexes that are too large or too polar to cross the SPMD membrane (Haitzer et al., 1998, 1999; Gourlay et al., 2005). Enhancement of bioconcentration by aquatic organisms at low levels of DOM has been reported. Some research has indicated that diffusive mass transfer of hydrophobic organic compounds through aqueous boundary layers can be enhanced by the presence of DOM (Chiou et al., 1986; Mayer et al., 2005, 2007). The PES membrane has a pore size of 0.1 μm, which is much larger than the pore size of biological membranes and the SPMD membrane (Alvarez, 1999; Lam and Simpson, 2006). The DOM used in the present study is a mixture of natural dissolved organic matter prepared from the natural Nordic Lake water which was filtered through membranes with pore size of 0.45 μm. Although filtered through a 0.45 μm membrane filter, the colloidal nature of DOM may have permitted small (<0.1 μm) DOM-contaminant complexes to cross the PES membrane. The source of origin of DOM can influence the organic composition of these materials (He et al., 2008) and potentially the results of studies such as completed in the current research. Thus, additional research is required over a wider range of DOM concentrations and source materials to evaluate these responses.

3.5. The comparisons of sampling rates among water types

In the present study, the sampling rate varied with the source of the water. Li et al. (2010b) previously reported R_S values for these same model compounds in deionized water under circum-neutral conditions. Comparing the sampling rates determined in deionized water (Li et al., 2010b) to the data reported here for Plastic Lake water and dechlorinated tap water, the sampling rate of most model compounds at pH = 7 decreased in the order of deionized water > Plastic Lake water > dechlorinated Peterborough tap water. This consistent trend is illustrated in Fig. 2 whereby, with the exceptions of ibuprofen and gemfibrozil, POCIS sampling rates were consistently highest in experiments with deionized water and differed significantly among the other treatment media (ANOVAs; $p \leqslant 0.022$). For ibuprofen, the sampling rate in Plastic Lake water was not significantly different from the sampling rate determined in deionized water (ANOVA; $p = 0.961$), but was significantly higher (ANOVA; $p < 0.001$) than the sampling rate for this compound in tap water. There are major differences in these three kinds of water in the content of inorganic carbon and total dissolved organic carbon (Table 5). The inorganic and dissolved organic carbon contents decreased in the order of dechlorinated Peterborough tap water > Plastic Lake water > deionized water. However, there were many other differences among these three kinds of water, such as alkalinity, hardness, nitrate concentration, etc., which may also affect the uptake into POCIS. The salt concentration of water has been reported to affect the adsorption in the sequestering medium. Togola and Budzinski (2007) reported that changes in salinity either decreased or increased accumulation of

Table 5
The total dissolved organic carbon, total carbon and total inorganic carbon (mg L^{-1}) in Peterborough tap water and in Plastic Lake water used in the present study, and in the deionized water used in a previous study by Li et al. (2010b).

	pH	Alkalinity	NO_3^-	Dissolved organic carbon	Inorganic carbon	Total carbon
Deionized water	5.43	2	0.02	0.1–0.3	<0.4	<1
Plastic Lake water	6.13	32	0.32	3.33	0.40	3.73
Dechlorinated tap water	8.46	74	0.72	4.55	16.54	21.09

model pharmaceuticals by POCIS. More work is needed to better understand how the water matrix affects the uptake into POCIS.

4. Conclusions

The solution pH affected the uptake of some ionic compounds into pharmaceutical (HLB)-POCIS. For acidic compounds, accumulation is maximized under conditions of low pH when the compound is present primarily in the neutral form. For basic compounds, accumulation is maximized under conditions of high pH when the compound is present primarily in the neutral form. Uptake of neutral and phenolic compounds with high p*K*a values is unaffected by pH. However, the changes in sampling rate as a function of pH = 3–9 are less than 3-fold for most target compounds. Sampling rates for POCIS are governed by the hydrophobicity of the compound present in the aqueous phase. DOM does not appear to enhance sampling rates in POCIS, but once again, these differences were tested over a narrow range of DOM concentrations. The pattern of uptake into MCX- and MAX-POCIS as a function of pH was the same as uptake into the pharmaceutical-POCIS, despite the fact that there were different sorbents used in the 3 POCIS configurations. The pharmaceutical-POCIS (HLB) configuration exhibits the highest uptake efficiency for basic drugs and is equally efficient with the MCX and MAX sorbents for other chemical classes. MCX- and MAX-POCIS were moderately efficient for sampling basic compounds at high pH and acidic drugs at low pH, respectively. Overall, these data indicate that sampling rates for POCIS will vary only slightly over the range of conditions of pH and DOM observed in natural waters. There are limited advantages to using ion exchange sorbents in POCIS relative to the commercially available (HLB) sorbent.

Acknowledgements

Financial support was provided by the Ontario Ministry of the Environment. We thank Brenda McIlwain and Kayla Huycke for their technical assistance in sample preparation. We appreciate the help of Tracy Metcalfe for ordering the standards and reagents and for maintaining the lab facilities. We also appreciate Jules Carlson for sharing p*K*a values. All analyses were conducted at the Worsfold Water Quality Centre at Trent University.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.12.071.

References

Alvarez, D.A., 1999. Development of an Integrative Sampling Device for Hydrophilic Organic Contaminants in Aquatic Environments. PhD Thesis. University of Missouri, Columbia, MO, USA.

Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., Manahan, S.E., 2004. Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. Environ. Toxicol. Chem. 23, 1640–1648.

Amjadi, M., Manzoori, J.L., Farzampour, L., 2008. Development of a new analytical spectroscopic methodology based on the competitive aggregation in a dye–surfactant–drug system: application to the determination of gemfibrozil. Spectroscopy 22, 309–317.

Arditsoglou, A., Voutsa, D., 2008. Passive sampling of selected endocrine disrupting compounds using polar organic chemical integrative samplers. Environ. Pollut. 156, 316–324.

Avdeef, A., Berger, C.M., Brownell, C., 2000. PH Metric solubility. 2: correlation between the acid–base titration and the saturation shake-flask solubility pH methods. Pharm. Res. 17, 85–89.

Cherkaoui, S., Rudaz, S., Veuthey, J.L., 2001. Nonaqueous capillary electrophoresis-mass spectrometry for separation of venlafaxine and its phase I metabolites. Electrophoresis 22, 491–496.

Chiou, C.T., Malcolm, R.L., Brinton, T.I., Kile, D.E., 1986. Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and mlvic acids. Environ. Sci. Technol. 20, 502–508.

Christy, A.A., Bruchet, A., Dybacki, D., 1999. Characterization of natural organic matter by pyrolysis/GC–MS. Environ. Int. 25, 181–189.

Christy, A.A., Egeberg, P.K., 2000. Characterization of natural organic matter from the Nordic typing project water samples by chemometric analysis of their near infrared spectral profiles. Chemom. Intell. Lab. 50, 225–234.

Drever, J.I., 1997. The Geochemistry of Natural Waters-Surface and Groundwater Environments, third ed. Prentice Hall, Upper Saddle River, New Jersey.

Gourlay, C., Miege, C., Noir, A., Ravelet, C., Garric, J., Mouchel, J.M., 2005. How accurately do semi-permeable membrane devices measure the bioavailability of polycyclic aromatic hydrocarbons to Daphnia magna? Chemosphere 61, 1734–1739.

Haitzer, M., Hoss, S., Traunspurger, W., Steinberg, C., 1998. Effects of dissolved organic matter (DOM) on the bioconcentration of organic chemicals in aquatic organisms. Chemosphere 37, 1335–1362.

Haitzer, M., Hoss, S., Traunspurger, W., Steinberg, C., 1999. Relationship between concentration of dissolved organic matter (DOM) and the effect of DOM on the bioconcentration of benzo[*a*]pyrene. Aquat. Toxicol. 45, 147–158.

Harman, C., Tollefsen, K.E., Boyum, O., Thomas, K., Grung, M., 2008. Uptake rates of alkylphenols, PAHs and carbazoles in semipermeable membrane devices (SPMDs) and polar organic chemical integrative samplers (POCIS). Chemosphere 72, 1510–1516.

Harman, C., Thomas, K.V., Tollefsen, K.E., Meier, S., Bøyum, O., Grung, M., 2009. Monitoring the freely dissolved concentrations of polycyclic aromatic hydrocarbons (PAH) and alkylphenols (AP) around a Norwegian oil platform by holistic passive sampling. Mar. Pollut. Bull. 58, 1671–1679.

Harris, D.C., 2007. Quantitative Chemical Analysis, seventh ed. WH Freeman and Company, New York, USA.

He, Z., Ohno, T., Wu, F., Olk, D.C., Honeycutt, C.W., Olanya, M., 2008. Capillary electrophoresis and fluorescence excitation–emission matrix spectroscopy for characterization of humic substances. Soil Sci. Soc. Am. J. 72, 1248–1255.

Huckins, J.N., Manuweera, G.K., Petty, J.D., Mackay, D., Lebo, J.A., 1993. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. Environ. Sci. Technol. 27, 2489–2496.

Huckins, J.N., Petty, J.D., Orazio, C.E., Lebo, J.A., Clark, R.C., Gibson, V.L., Gala, W.R., Echols, K.R., 1999. Determination of uptake kinetics (Sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. Environ. Sci. Technol. 33, 3918–3923.

Ivashechkin, P., Corvini, P.F.X., Dohmann, M., 2004. Behaviour of endocrine disrupting chemicals during the treatment of municipal sewage sludge. Water Sci. Technol. 50, 133–140.

Kot-Wasik, A., Zabiegała, B., Urbanowicz, M., Dominiak, E., Wasik, A., Namiesnik, J., 2007. Advances in passive sampling in environmental studies. Anal. Chim. Acta 602, 141–163.

Lam, B., Simpson, A.J., 2006. Passive sampler for dissolved organic matter in freshwater environments. Anal. Chem. 78, 8194–8199.

Lewis, K.M., Archer, R.D., 1979. PKa values of estrone, 17 beta-estradiol and 2-methoxyestrone. Steroids 34, 485–499.

Li, H., Vermeirssen, E.L.M., Helm, P.A., Metcalfe, C.D., 2010a. A controlled field evaluation of water flow rate effects on sampling polar organic compounds using polar organic chemical integrative samplers (POCIS). Environ. Toxicol. Chem. 29, 2461–2469.

Li, H., Helm, P.A., Metcalfe, C.D., 2010b. Sampling in the Great Lakes for pharmaceuticals, personal care products and endocrine disrupting substance using the passive polar organic chemical integrative sampler. Environ. Toxicol. Chem. 29, 751–762.

Lienert, J., Gudel, K., Escher, B.I., 2007. Screening method for ecotoxicological hazard assessment of 42 pharmaceuticals considering human metabolism and excretory routes. Environ. Sci. Technol. 41, 4471–4478.

Macleod, S.L., McClure, E.L., Wong, C.S., 2007. Laboratory calibration and field deployment of the polar organic chemical integrative sampler for

pharmaceuticals and personal care products in wastewater and surface water. Environ. Toxicol. Chem. 26, 2517–2529.
Magnér, J.A., Alsberg, T.E., Broman, D., 2009. The ability of a novel sorptive polymer to determine the freely dissolved fraction of polar organic compounds in the presence of fulvic acid or sediment. Anal. Bioanal. Chem. 95, 1525–1532.
Malcolm, R.L., 1985. Geochemistry of stream fulvic and humic substances. In: Aiken, G.R. et al. (Eds.), Humic Substances in Soil, Sediments and Water. Wiley-Interscience, New York, pp. 181–209.
Martínez Bueno, M.J., Hernando, M.D., Agüera, A., Fernández-Alba, A.R., 2009. Application of passive sampling devices for screening of micro-pollutants in marine aquaculture using LC–MS/MS. Talanta 77, 1518–1527.
Mayer, P., Karlson, U., Christensen, P.S., Johnsen, A.R., Trapp, S., 2005. Quantifying the effect of medium composition on the diffusive mass transfer of hydrophobic organic chemicals through unstirred boundary layers. Environ. Sci. Technol. 39, 6123–6129.
Mayer, P., Fernqvist, M.M., Christensen, P.S., Karlson, U., Trapp, S., 2007. Enhanced diffusion of polycyclic aromatic hydrocarbons in artificial and natural aqueous solutions. Environ. Sci. Technol. 41, 6148–6155.
Mazzella, N., Dubernet, J.F., Delmas, F., 2007. Determination of kinetic and equilibrium regimes in the operation of polar organic chemical integrative samplers – application to the passive sampling of the polar herbicides in aquatic environments. J. Chromatogr. A 1154, 42–51.
Metcalfe, T.L., Dillon, P.J., Metcalfe, C.D., 2008. Transport of toxic substances from golf courses into watersheds in the Precambrian Shield region of Ontario, Canada. Environ. Toxicol. Chem. 27, 811–818.
Mills, G.A., Vrana, B., Allan, I., Alvarez, D.A., Huckins, J.N., Greenwood, R., 2007. Trends in monitoring pharmaceuticals and personal care products in the aquatic environment by use of passive sampling devices. Anal. Bioanal. Chem. 387, 1153–1157.
Nghiem, L., Schäfer, A.I., Elimelech, M., 2005. Pharmaceutical retention mechanisms by nanofiltration membranes. Environ. Sci. Technol. 39, 7698–7705.
O'Toole, S., Metcalfe, C.D., Crane, I., Gross, M., 2006. Release of persistent organic contaminants from carcasses of Lake Ontario Chinook salmon (*Oncorhynchus tshawytscha*). Environ. Pollut. 140, 99–110.
Petty, J.D., Huckins, J.N., Alvares, D.A., Brumbaugh, W.G., Cranor, W.L., Gale, R.W., Rastall, A.C., Jones-Lepp, T.L., Leiker, T.J., Rostad, C.E., Furlong, E.T., 2004. A holistic passive integrative sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants. Chemosphere 54, 695–705.
Söderström, H., Lindberg, R.H., Fick, J., 2009. Strategies for monitoring the emerging polar organic contaminants in water with emphasis on integrative passive sampling. J. Chromatogr. A 1216, 623–630.
SRC PhysProp Database, 2010. <http://www.srcinc.com/what-we-do/database-forms.aspx?id=386> (accessed June, 2010).
Stuer-Lauridsen, F., 2005. Review of passive accumulation devices for monitoring organic micropollutants in the aquatic environment. Environ. Pollut. 136, 503–524.
SYSTAT, 2004. SYSTAT for Windows Version 11.0. SYSTAT Software Inc., Richmond, CA.
Tadkaew, N., Sivakumar, M., Khan, S.J., McDonald, J.A., Nghiem, L.D., 2010. Effect of mixed liquor pH on the removal of trace organic contaminants in a membrane bioreactor. Bioresour. Technol. 101, 1494–1500.
Tixier, C.S.H., Canonica, S., Muller, S.R., 2002. Phototransformation of triclosan in surface waters: a relevant elimination process for this widely used biocide – laboratory studies, field measurements, and modelling. Environ. Sci. Technol. 36, 3482–3489.
Togola, A., Budzinski, H., 2007. Development of polar organic integrative samplers for analysis of pharmaceuticals in aquatic systems. Anal. Chem. 79, 6734–6741.
Vasskog, T., Berger, U., Samuelsen, P.J., Kallenborn, R., Jensen, E., 2006. Selective serotonin reuptake inhibitors in sewage influents and effluents from Tromsø, Norway. J. Chromatogr. A 1115, 187–195.
Waite, D., 2004. Chemical speciation effects in nanofiltration separation. In: Schäfer, A.I., Fane, A., Waite, D. (Eds.), Nanofiltrations Principles and Applications. Elsevier, New York, pp. 147–168.
Zhang, Z.L., Hibberd, A., Zhou, J.L., 2008. Analysis of emerging contaminants in sewage effluent and river water: comparison between spot and passive sampling. Anal. Chim. Acta 607, 37–44.
Zhao, X., Metcalfe, C.D., 2008. Characterizing and compensating for matrix effects using atmospheric pressure chemical ionization liquid chromatography–tandem mass spectrometry: analysis of neutral pharmaceuticals in municipal wastewater. Anal. Chem. 80, 2010–2017.