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Atrazine contamination at the watershed scale and environmental factors affecting sampling rates of the polar organic chemical integrative sampler (POCIS)

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ABSTRACT

Polar organic chemical integrative samplers (POCIS) were used to estimate atrazine contamination at 24 stream/river sites located across a watershed with land use ranging from 6.7 to 97.4% annual crops and surface water nitrate concentrations ranging from 3 to 5404 μg/L. A gradient of atrazine contamination spanning two orders of magnitude was observed over two POCIS deployments of 28 d and was positively correlated with measures of agricultural intensity. The metabolite desisopropyl atrazine was used as a performance reference compound in field calibration studies. Sampling rates were similar between field sites but differed seasonally. Temperature had a significant effect on sampling rates while other environmental variables, including water velocity, appeared to have no effect on sampling rates. A performance reference compound approach showed potential in evaluating spatial and temporal differences in field sampling rates and as a tool for further understanding processes governing uptake of polar compounds by POCIS.

1. Introduction

Agricultural herbicides are a significant contributor of non-point source pollution to surface waters through run-off and leaching from agricultural fields (Pantone et al., 1992; Waite et al., 1992; Smith et al., 1993; McMahon et al., 1994) as well as dry deposition and spray drift (Grover et al., 1988; Asman et al., 2003). The triazine herbicide atrazine (ATR) (6-chloro-*N*-ethyl-*N*′-1-methylethyl-1,3,5-triazine-2,4-diamine) is commonly detected in North American surface and ground waters due to its widespread usage, primarily on corn crops, as well as its mobility and persistence (Solomon et al., 1996; Gilliom et al., 2006). Atrazine is the most heavily used herbicide in the United States (US EPA, 2012a) and the second most commonly used pesticide on corn crops in Ontario, Canada (McGee et al., 2010). In contrast, ATR has not been registered with the European Commission since 2003 (European Commission, 2003) but remains 1 of 33 priority substances posing a significant risk to the European aquatic environment (European Commission, 2008).

A risk assessment for ATR in surface waters concluded that inhibitory effects on the most sensitive organisms, phytoplankton and macrophytes, were likely followed by rapid recovery and ATR was unlikely to pose a significant risk at environmentally relevant concentrations (typically <5 μg/L) (Solomon et al., 1996). However, other studies found effects of ATR on phytoplankton photosynthesis (DeNoyelles et al., 1982), primary production and community structure (Pannard et al., 2009) at concentrations <5 μg/L. Atrazine has been shown to cause reductions in fish egg production due largely to decreased spawning events at concentrations as low as 0.5 μg/L (Tillitt et al., 2010). Additional research provided evidence that ATR feminizes male frogs (Hayes et al., 2003) and alters gonadal differentiation and metamorphosis (Langlois et al., 2010) at concentrations as low as 0.1 μg/L and 1.8 μg/L respectively. Of particular concern is the potential for ATR to demasculinize and feminize male gonads across vertebrate classes (Hayes et al., 2011). Furthermore, ATR is persistent in soil and has for example been detected 22 years following application (Jablonowski et al., 2009).

Assessment of the occurrence of ATR and other herbicides in surface waters, as well as their risk to aquatic organisms, is challenging because herbicide concentrations are often highly variable. Monitoring programs traditionally used point-in-time estimates, such as grab samples, that provide a snapshot of overall

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contamination. However, pulses in concentration are not integrated, resulting in an over- or underestimation of actual concentrations and a lack of understanding of actual exposures to biota. For example, Rabiet et al. (2010) found that grab sampling largely underestimated herbicide concentrations and fluxes, whereas Petersen et al. (2012) observed that grab sampling failed to account for the variability in the occurrence, duration and concentration of herbicide pulses following rain events. This issue is not unique to herbicides and a number of passive sampling technologies have been developed to provide time-weighted-average (TWA) concentrations of contaminants (reviewed in Vrana et al., 2005; Stuer-Lauridsen, 2005). The polar organic chemical integrative sampler (POCIS) was developed to integrate trace concentrations of hydrophilic compounds (log $K_{OW} < 4$) such as pesticides, pharmaceuticals, personal care products and industrial chemicals (Alvarez et al., 2004) and has been used to detect over 300 compounds (Harman et al., 2012).

Sampling rates (R_s) estimate the water volume cleared of chemical per unit time by POCIS and are typically derived from laboratory calibrations. However, experiments have also shown that R_s are affected by factors such temperature, water flow rates, biofouling and pH (reviewed in Harman et al., 2012). Therefore, under field conditions R_s are expected to vary from those established under laboratory conditions. This issue has been resolved for absorption based passive sampling of hydrophobic compounds (e.g. semi permeable membrane devices) by the addition of performance reference compounds (PRCs) to passive samplers. When both PRCs and target analytes follow isotropic exchange, dissipation of PRCs is equivalent to uptake of target analytes and can be used to correct analyte concentrations for *in situ* R_s (Booij et al., 1998, 2002; Huckins et al., 2002). In contrast, POCIS is an adsorption based sampler that tends to act as an infinite sink for analytes (Alvarez et al., 2004). However, Mazzella et al. (2007) provided evidence of isotropic exchange in POCIS for deuterated desisopropyl atrazine (DIA-D5), a high fugacity metabolite of ATR. Subsequently, Mazzella et al. (2010) used DIA-D5 as a PRC and successfully narrowed the differences in herbicide concentrations obtained with POCIS from those obtained with automatic samplers. Despite this success, it is unclear whether factors affecting the rate of desorption of poorly sorbed PRCs are equivalent to those affecting adsorption of strongly sorbed target analytes, resulting in a gap in knowledge as to whether PRCs can accurately correct R_s of target analytes (Harman et al., 2011). Currently, there is no consensus on suitable PRCs for broad ranges of target analytes or even if the PRC approach is suitable for POCIS (Harman et al., 2012).

In the present study, we used POCIS to determine ATR contamination throughout an agricultural watershed in Eastern Ontario, Canada (Fig. 1). Atrazine concentrations obtained with POCIS were compared with those obtained from grab samples and correlated with measures of agricultural intensity. The results represent a comprehensive study using POCIS at the watershed scale, across a gradient of physico-chemical and hydrological conditions. Despite its recent popularity, POCIS remains poorly characterized in terms of modeling uptake rates and environmental factors (Harman et al., 2012). A PRC approach using DIA-D5 was used to examine factors affecting R_s under complex field conditions at four field sites during two time periods.

2. Materials and methods

2.1. Chemicals and materials

Atrazine was purchased from ChemService Inc. (West Chester, USA), while deuterated atrazine (ATR-D5) and deuterated desisopropyl atrazine (DIA-D5) were from CDN Isotopes Inc. (Point-Claire, Canada). The measured chemical purity of each lot was 98.9%, >99% and 98.8% for ATR, ATR-D5 and DIA-D5 respectively. Stock solutions of each standard were prepared gravimetrically at 1 mg/mL in methanol, sonicated and stored in darkness at −30 °C. HPLC grade methanol and water were purchased from Sigma–Aldrich Canada (Oakville, Canada). LCMS grade acetonitrile, methanol and water were from Fisher Scientific (Ottawa, Canada). Oasis hydrophilic-lipophilic balanced (HLB) cartridges (6 mL, 500 mg) were purchased from Waters (Mississauga, Canada). Empty 3 mL polypropylene solid phase extraction (SPE) tubes and polyethylene frits (20 μm pore size) were from Sigma–Aldrich Canada. Oasis HLB bulk sorbent, polyethersulfone (PES) membranes and POCIS hardware were from Environmental Sampling Technologies Inc. (St. Joseph, USA).

2.2. Study area and measures of agricultural intensity

Atrazine contamination in the South Nation River watershed, Canada was assessed between 18 May and 22 July 2010. The South Nation River watershed comprises 3915 km^2 in Eastern Ontario, Canada (Fig. 1) and has a historical (1915–2011) average annual discharge of 44.3 m^3/s at its mouth (Environment Canada, 2013). The headwaters commence near the St. Lawrence River (44°40′41″N, 75°41′58″W) and the 177 km long river flows north-easterly across a flat landscape until its confluence with the Ottawa River (45°34′24″N, 75°06′00″W). The watershed is predominately agricultural with crops of corn (*Zea mays* L.) and soybean (*Glycine max* L. (Merr.)) planted in tile-drained fields. Usage of ATR is typical of agricultural watersheds in Ontario and peak concentrations are expected following pre-plant incorporated, pre-emergent and post-emergent use on corn crops (late April through to July). Atrazine was previously detected in the watershed from weekly continuous flow surface water samples (mid-April–late October 1991–1992) (Fischer et al., 1995) and more recently from integrated grab samples (June 2008) (Dalton et al., 2013).

Twenty-four sites located throughout the South Nation River watershed were selected for study. Sites were paired along a given tributary with sites surrounded by low levels of agriculture located upstream of sites surrounded by high levels of agriculture. Paired sites are subsequently referred to as low and high agriculture sites respectively. Sites were selected using land use data to identify areas of low and high agriculture (Statistics Canada, 2006), using Google Earth v.4.2.0198.2451 (Google Inc., Mountain View, USA) to verify physical aspects and through field reconnaissance of potential sites. Two pairs of sites were located along different tributaries due to a lack of accessible and suitable sites. All sites were matched as closely as possible in terms of visible features such as steam width, bank slope and canopy cover. Agricultural intensity was calculated as the percentage of annual cropland in a 500 m radius surrounding each site (ArcMap v.10, ESRI, Canada Ltd, Toronto, Canada) using data provided by Agriculture and Agri-Food Canada (2008).

Elevated nitrate concentrations indicate agricultural contamination from synthetic fertilizers and manure (Dubrovsky et al., 2010) and were used as an additional measure of agricultural intensity. Water samples (300 mL) were collected in polyethylene terephthalate bottles during May, June and July 2010, corresponding to POCIS deployment periods at each site. Nitrate was analyzed at the Robert O. Pickard Environmental Centre Laboratory (Ottawa, Canada) following established methods of the Ontario Ministry of the Environment (2007). The method detection limit for nitrate was 4 μg/L.

2.3. Passive sampling with POCIS

POCIS contained 200 mg of Oasis HLB sorbent (poly(divinylbenzene-co-N-vinylpyrrolidone)) enclosed between two PES membranes and held together with compression between two stainless steel washers (Alvarez et al., 2004). POCIS had a standardized total sampling surface area of 41 cm^2. POCIS were assembled in the lab and transported to and from the field in methanol rinsed aluminum foil. High density polyethylene shields were designed to be easily assembled, durable, inexpensive and easy to clean (Fig. S1, Supplementary content). At each site, three replicate POCIS were secured within a shield and deployed mid-stream for two consecutive 28 d exposure periods (Fig. S1, Supplementary content). POCIS were deployed at a maximum depth of 40 cm below the water's surface and the depth reduced at shallow sites. Deployments were slightly staggered temporally to access field sites spread across the watershed.

Recovery of POCIS sorbent was modified from that described by Mazzella et al. (2010). POCIS were gently cleaned with distilled water and frozen at −30 °C. Each POCIS was dissembled and the sorbent transferred through a glass funnel into a 3 mL SPE cartridge with a Visiprep SPE Manifold (Sigma–Aldrich). The sorbent was rinsed into the cartridge with 40 mL HPLC grade water and packed with a polypropylene frit. The cartridges were washed with 15 mL of 5% HPLC grade methanol, dried for 20 min under vacuum and frozen at −30 °C for storage until elution. Cartridges were brought to room temperature prior to elution and analytes eluted with 5 mL methanol into 15 mL silanized (Surfacil, Fisher Scientific) glass centrifuge tubes. Extracts were evaporated to 0.5 mL at 30 °C (CentriVap Centrifugal Concentrator, Labconco, Kansas City, USA), filtered through 0.2 μm PTFE filters (Fisher Scientific), brought to a final volume of 1 mL and spiked with 250 ng/mL AT-D5 prior to analysis.

2.4. In situ field calibration with deuterated desisopropyl atrazine

Calibration studies, referring here to *in situ* correction of field R_s with a PRC, were conducted at four field sites representing a range of physico-chemical characteristics between 16 September and 14 October 2010 and between 12 July and 9 August 2011. DIA-D5 was used as a PRC and its desorption from POCIS sorbent used to calculate

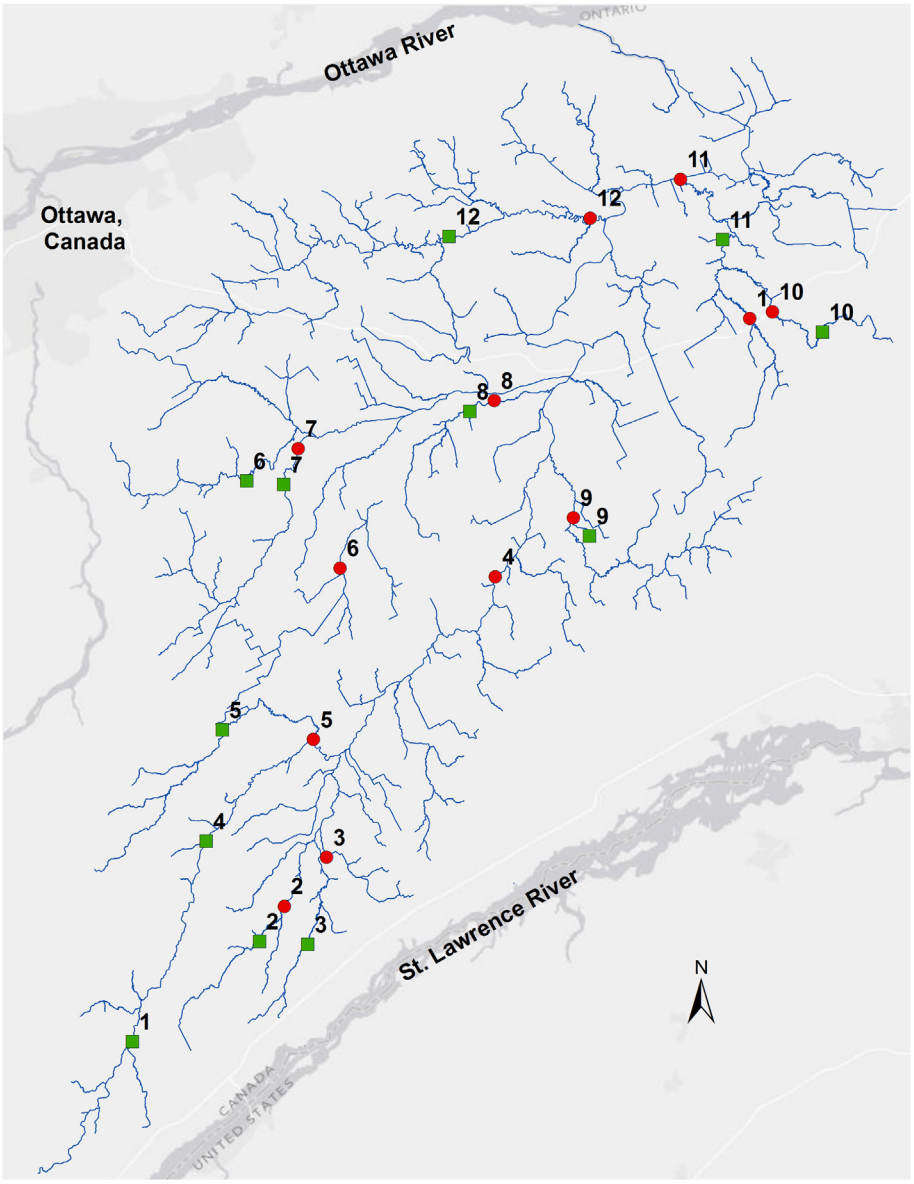

Fig. 1. Twelve paired field sites (total of 24) in the South Nation River watershed (3915 km^2), Canada. Sites were surrounded by low ■ or high ● levels of agriculture.

field corrected R_s. Each POCIS was spiked with 5000 ng DIA-D5. For each POCIS, Oasis HLB sorbent (200 mg) was placed on a PES membrane and 100 μL of 50,000 ng/mL DIA-D5 (dissolved in methanol) was added evenly throughout the sorbent by pipette. The methanol was allowed to evaporate before the second PES membrane was placed on top of the sorbent and the membranes secured with stainless steel washers. Six replicate Day 0 POCIS were prepared for both experimental periods to quantify initial DIA-D5 concentrations and account for any losses in recovery. For each experimental period and site, 12 POCIS were deployed on Day 0 and three POCIS removed every 7 d. DIA-D5 was recovered from POCIS as described above.

Environmental variables were measured weekly throughout the calibration experiments. Temperature, pH and conductivity were measured with a HydroLab 4a Sonde (Hach Hydromet, Loveland, USA). Surface water velocity was estimated by measuring the time for an orange wiffle golf ball to travel 1 m. Duplicate mid-channel, integrated water samples (1 L) were taken in polypropylene bottles for turbidity and chlorophyll *a* analysis. Planktonic chlorophyll *a* was a proxy of biofouling potential. Turbidity reflects factors affecting water clarity, such as phytoplankton, microbes, suspended sediments and dissolved organic carbon, and was a proxy of overall membrane fouling potential. Turbidity was measured with a turbidity meter (LaMotte, Chestertown, USA). Water samples (500 mL) were filtered through 1.5 μm Whatman glass fiber filters (type 934-AH, Whatman, Mississauga, Canada), algal pigments extracted from filters (Burnison, 1980) and chlorophyll *a* calculated using a trichromatic equation (Jeffrey and Humphrey, 1975). For each environmental variable, weekly data were averaged separately for each field site and deployment period (fall 2010 or summer 2011).

2.5. Solid phase extraction

Water samples (1 L) were collected in pre-cleaned amber borosilicate bottles at each field site at the beginning, middle and end of each POCIS deployment between 18 May and 22 July 2010 and every 7 d during the calibration experiments. Duplicate samples were taken for approximately 10% of the samples and matrix-blank samples (HPLC grade water) used to determine analyte recovery. Samples were filtered through 0.7 μm glass fiber filters (GF/F 47 mm diameter, Whatman) and spiked with 1000 ng/L ATR-D5. Samples for the calibration studies were also spiked with 5000 ng/L DIA-D5. Oasis HLB cartridges (6 mL, 500 mg) were conditioned with 15 mL methanol and equilibrated with 15 mL water. Samples were passed through the cartridges at 4 mL/min, washed with 15 mL 5% methanol, dried under vacuum for 20 min and frozen at −30 °C. Cartridges were brought to room temperature and analytes eluted with 5 mL methanol. Extracts were evaporated to 0.5 mL, filtered through 0.2 μm PTFE syringe filters (13 mm diameter, Fisher Scientific) and brought to a final volume of 1 mL.

2.6. LC–MS/MS analysis and validation

LC–MS/MS analyses were performed on a high performance liquid chromatograph hyphenated with a tandem mass spectrometer (3200 QTRAP, AB Sciex, Concord, Canada) at the Laboratory for the Analysis of Natural and Synthetic Environmental Toxins (LANSET) (University of Ottawa, Ottawa, Canada). An Agilent 1200 series HPLC was used to separate analytes using a Zorbax SB-C8 narrow-bore guard column (2.1 mm × 12.5 mm, average particle size 5 μm, Agilent Technologies) connected with

a Zorbax SB-C18 rapid resolution HT column (2.1 mm × 50 mm, average particle size 1.8 μm, pressure limit 600 bar, Agilent Technologies) at a column thermostat temperature of 45 °C, flow rate of 300 μL/min, mobile phase of A: water and B: acetonitrile and 1 μL injection volume. The mass spectrometer was operated in multiple reaction monitoring (MRM) mode with turbo ion spray in positive electrospray ionization. Quantitation and confirmation were based on the following MRM transitions: 217.96 > 176.10 and 217.96 > 68.10; 223.11 > 181.20 and 223.11 > 69.10; and 179.02 > 69.20 and 179.02 > 105.10, for ATR, ATR-D5 and DIA-D5 respectively.

All samples, standards and blanks were injected in triplicate. A system blank (0 μL injection) and solvent blanks (acetonitrile, water and methanol) were run before the injection of the lowest concentration standard. A methanol blank was run approximately every six samples to evaluate and minimize carryover. Standard curves were updated and replaced every 12 h of analysis. External calibration was used for quantitation. Seven point (5–1250 ng/mL) and eight point (2–250 ng/mL) calibration curves were constructed for SPE and POCIS samples respectively. POCIS samples were diluted by a factor of 5 or more in methanol prior to analysis. Quantitation was performed using Analyst 1.4.2 (Applied Biosystems, Foster City, USA).

Calibration models were assessed by evaluating regression model fit (R^2), calculating the percent error at each concentration level (US EPA, 2003) and assessing overall model fit using relative standard error (RSE) (US EPA, 2012b). Calibration curves were fit with 1/× weighted quadratic models to emphasize precision at the lower end of the calibration range (US EPA, 2003, 2012b). The relative standard deviation (RSD) between triplicate injections was evaluated for both standards and samples. Concentrations were confirmed by evaluating percent differences between quantitation and confirmation transition values. Instrument limits of detection (LODs) and limits of quantitation (LOQs) were calculated as 3 and 10 times signal to noise respectively (where noise is 6× background signal standard deviation), averaged from triplicate injections of the lowest concentration standard for each calibration curve.

2.7. Statistics and modeling

Sampling rates were calculated according to the theory and models developed by Huckins et al. (2002, 2006) and Alvarez et al. (2004, 2007) using nomenclature outlined in Mazzella et al. (2010). TWA concentrations (C_w) (ng/L) of ATR at 24 field sites over 56 days were estimated by:

$$C_w = \frac{m}{R_{scal} \times t} \quad (1)$$

where m is the mass of ATR accumulated in each sampler (ng), R_{scal} is 0.239 L/d, a laboratory calibrated R_s for ATR (Mazzella et al., 2007) and t is the deployment time (d). A 56 d TWA concentration was calculated by summing m from two consecutive 28 d deployments.

For each calibration study site and time period, an *in situ* elimination rate constant ($k_{ePRCinsitu}$) (d^{-1}) for DIA-D5 was estimated:

$$C_{PRC(t)} = C_{PRC(0)} \times e^{-k_{ePRCinsitu} \times t} \quad (2)$$

where $C_{PRC(t)}$ and $C_{PRC(0)}$ are concentrations of DIA-D5 (ng) at time (t) and time (0) respectively.

Concentration data were ln-transformed to linearize the relationship and the slope k_e calculated using linear regression:

$$\ln C_{PRC(t)} = -k_{ePRCinsitu} \times t + \ln C_{PRC(0)} \quad (3)$$

Corrected sampling rates (R_{scorr}) (L/d) for ATR were calculated as:

$$R_{scorr} = R_{scal} \times \left(\frac{k_{ePRCinsitu}}{k_{ePRCcal}}\right) \quad (4)$$

where $k_{ePRCcal}$ is 0.057 d^{-1}, an elimination rate constant for DIA-D5 determined by Mazzella et al. (2010) in a laboratory calibration experiment.

Statistical analyses were performed using SPSS v.21 (IBM Corp., Armonk, USA). Three paired t-tests were conducted to compare 1) differences in POCIS ATR concentrations between 12 paired sites (24 sites total), 2) differences in SPE ATR concentrations between 12 paired sites (24 sites total) and 3) differences in ATR concentrations estimated with POCIS and SPE at 24 sites. Differences in ATR between time periods were assessed by calculating the percentage of total ATR at each period to normalize for differences in absolute ATR concentrations between sites and conducting a one-way analysis of variance (ANOVA). For each site and time period, k_e was calculated using linear regression as described above. Pearson's correlations quantified the relationship between ATR concentrations obtained from POCIS and SPE, ATR concentrations and measures of agricultural intensity, and between k_e values and environmental variables. Stepwise linear regression was used to further examine effects of environmental variables on k_e. Differences in k_e between field sites and time periods were modeled using a general linear model with percentage DIA-D5 as the dependent variable, field site and experimental period (fall 2010 or summer 2011) as fixed factors and day since deployment as a covariate. Model assumptions for all tests (normality and heterogeneity of variance) were assessed using Shapiro–Wilk's and Levene's tests respectively. Data were transformed if necessary to meet these assumptions.

3. Results and discussion

3.1. Method validation

Analytical calibration curves met criteria of R^2 values >0.99, percent differences between nominal and calculated concentrations <20% and RSE <20% (EPA, 2003, 2012b). The average R^2 was 0.9980, the average percent difference between nominal and calculated concentrations was 2.9% and the average RSE was 4.6%. Average instrument LODs were 0.83, 0.87 and 0.25 pg on column and average instrument LOQs were 2.76, 2.89 and 0.82 pg on column for ATR, ATR-D5 and DIA-D5 respectively. Overall, RSD between triplicate injections were <15% (average 4.1%). Percent differences between quantitation and confirmation transitions were <20% for ATR and ATR-D5 (average 5.6%) but occasionally >20% for DIA-D5 (average 8.0%). Chromatographic interferences were observed in transition 179.02 > 105.10 and 179.02 > 69.20 was subsequently used for quantitation. No carry-over was observed in solvent blanks.

Recoveries of blank spikes (fortified HPLC water samples) were 100.5 ± 12.6% ($n = 7$) for ATR-D5 and 92.8 ± 8.7% ($n = 4$) for DIA-D5 and fell within the acceptable recovery range (70–130%) outlined by US EPA (2003). Recoveries of ATR-D5 and DIA-D5 from field-collected SPE samples were 89.3 ± 14.9% ($n = 130$) and 58.9 ± 7.0% ($n = 46$) respectively. The average difference in ATR concentrations between duplicate SPE samples was 10.6 ± 4.7% ($n = 11$). The average difference in DIA-D5 between duplicate SPE samples was similar but more variable (10.1 ± 11.1%; $n = 10$). Average recovery of ATR-D5 from POCIS samples was 56.7 ± 13.1% ($n = 239$), illustrating that matrix effects were much higher in POCIS samples compared to SPE samples.

3.2. Atrazine contamination in the South Nation River watershed

Accumulation of ATR in POCIS at 24 sites over a 56 d period ranged from 59 to 5510 ng/POCIS, demonstrating a clear gradient of ATR contamination across the watershed (Fig. 2). A gradient was also observed within tributaries and on average, high agriculture sites had higher concentrations of ATR (2393 ± 1707 ng/POCIS) compared to low agriculture sites (1311 ± 1349 ng/POCIS) (Fig. 2; $t = -4.9$; df = 1,33; $p < 0.001$). Significantly more ATR accumulated in POCIS in the first deployment period (average of 56.2% ATR for 18 May–24 June 2010) compared to the second deployment period

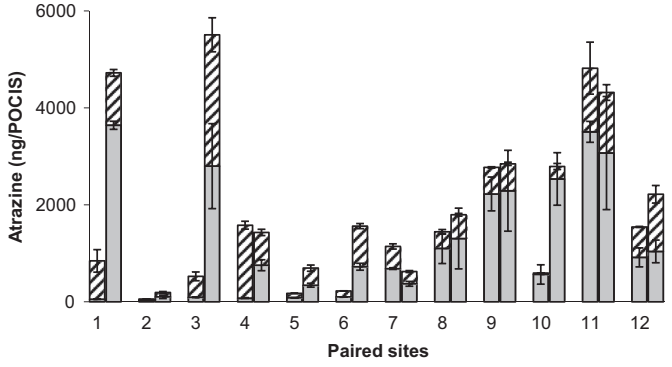

Fig. 2. Atrazine (ng) (±standard deviation) per polar organic chemical integrative sampler (POCIS) deployed over a 56 d period at 12 paired sites (total of 24) located throughout the South Nation River watershed. POCIS were deployed for 28 d between ▭ 18 May–24 June 2010 and ▨ 15 June–22 July 2010. Sites were paired along tributaries. Low agriculture sites (left column) were located upstream of high agriculture sites (right column).

(average of 43.8% ATR for 15 June–22 July 2010) (Fig. 2; $F = 10.0$; df = 1,138; $p = 0.002$; $R^2 = 0.067$).

Atrazine concentrations obtained from SPE-concentrated grab samples followed similar trends to POCIS samples (Fig. 3). High agriculture sites had higher average concentrations of ATR (97 ± 62 ng/L) compared to low agriculture sites (58 ± 58 ng/L) (Fig. 3; $t = -4.0$; df = 1,11; $p = 0.002$). A gradient of ATR contamination across the watershed was observed with average ATR concentrations ranging from 6 to 256 ng/L. Atrazine concentrations were higher in June compared to May or July (Fig. 3; $F = 34.2$; df = 2,69, $p < 0.001$; $R^2 = 0.498$), indicating POCIS deployment periods bracketed an appropriate timeframe to measure ATR.

ATR concentrations, integrated over a period of 56 d with POCIS, were strongly correlated with ATR concentrations averaged from SPE-concentrated water samples collected at the beginning, middle and end of the POCIS deployment period (Fig. 4). POCIS ATR concentrations were significantly higher than SPE ATR concentrations and ranged from 4 to 412 ng/L (Fig. 4; $t = 3.8$; df = 1,23; $p = 0.001$). The point-in-time estimates (SPE ATR) likely underestimated ATR contamination compared to the time-weighted-average estimates (POCIS ATR) because point-in-time estimates do not integrate pulses in concentrations that occur following rain events. ATR concentrations did not exceed Canadian water quality guidelines for the protection of aquatic life (1.8 μg/L) (Canadian Council of Ministers of the Environment, 1999). However, over half of the field sites (14/24) had 56 d average ATR concentrations >100 ng/L. Pulses in ATR concentrations may be almost 30× higher than post-pulse concentrations (Knight et al., 2013) suggesting potential for pulses above the guideline value.

The gradient in atrazine contamination across the watershed was associated with surrounding land use, specifically with measures of agricultural intensity. Atrazine concentrations were positively correlated with both the percentage of annual crops surrounding field sites and nitrate concentrations (Fig. 5). Annual crops in the South Nation River watershed often rotate annually between corn and soy crops and ATR is used on corn crops in Canada. Corn crops are typically treated with nitrogen-based fertilizers and in-stream nitrate concentrations >240 μg/L are indicative of anthropogenic nitrate contamination (Dubrovsky et al., 2010). Both percentage of surrounding annual crops and nitrate concentrations may be useful to identify areas of potential ATR contamination. However, a few sites had unexpectedly high ATR concentrations (Figs. 2 and 5). The discrepancies may be due to localized inputs of ATR or from groundwater which can also be a significant source of ATR during baseflow (Squillace et al., 1993; Fischer et al., 1995).

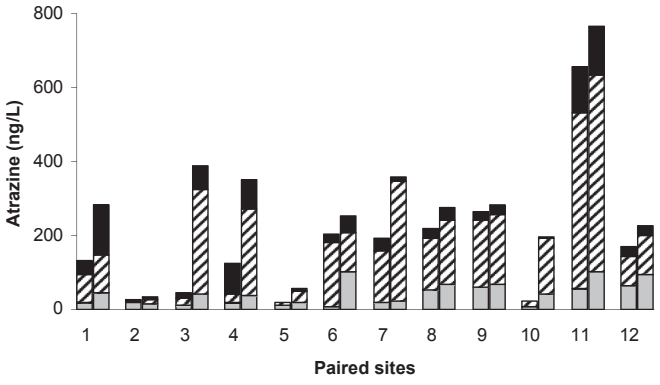

Fig. 3. Concentration of atrazine (ng/L) in grab samples (1 L) concentrated with solid phase extraction (SPE) and taken at 12 paired sites (total of 24) located throughout the South Nation River watershed. Samples were collected between ▭ 18–27 May, ▨ 15–24 June and ■ 13–22 July 2010. Sites were paired along tributaries. Low agriculture sites (left column) were located upstream of high agriculture sites (right column).

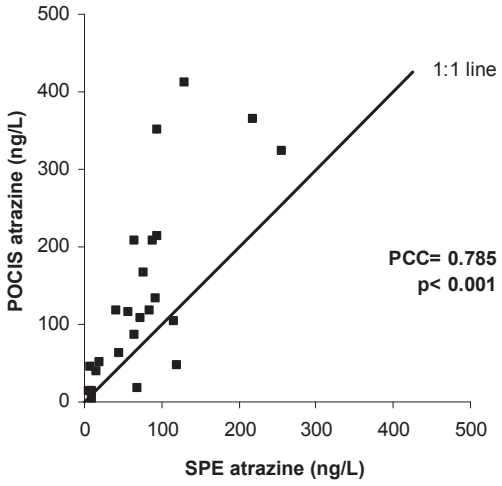

Fig. 4. Correlation between atrazine concentrations (ng/L) obtained from polar organic chemical integrative samplers (POCIS) and grab samples (1 L) concentrated with solid phase extraction (SPE). Time-weighted-average atrazine concentrations are shown for POCIS deployed for 56 d (two consecutive deployments of 28 d). Average SPE atrazine concentrations are shown for water samples taken on day 0, 28 and 56 of POCIS deployment. Pearson's correlation coefficient (PCC) and p value are shown.

3.3. *In situ field calibration with deuterated desisopropyl atrazine*

Desorption of DIA-D5 from spiked POCIS over 28 d was monitored at four sites in fall 2010 and again in summer 2011 (Fig. 6). Recoveries of ATR-D5 and DIA-D5 from SPE samples taken weekly at each field site during the two time periods were 99.3 ± 6.3% and 58.9 ± 7.0% respectively ($n = 46$), demonstrating that while extraction efficiency was high, there was substantial signal suppression of DIA-D5 due to matrix effects. Average recovery of DIA-D5 from Day 0 POCIS samples was 86.9 ± 10.7% ($n = 12$). Recoveries for Day 0 POCIS samples were further adjusted for estimated site specific matrix effects based on recovery of DIA-D5 from SPE samples. Direct assessment of matrix effects for DIA-D5 in POCIS samples was not possible as measured concentrations in field samples reflect both matrix effects and desorption of DIA-D5 over time. Desorption of ln(DIA-D5) was modeled using linear regression to calculate *in situ* rate elimination constants (k_e) from the slope of the regression line (Table 1). Mazzella et al. (2010) calibrated DIA-D5 desorption in a French stream and obtained a k_e of 0.022/d, comparable to the values observed in the fall experiment but lower than those observed in the summer experiment of this study (Table 1).

A general linear model was used to assess effects of field site, experimental period (fall 2010 or summer 2011) and the number of days following deployment on the percentage of DIA-D5 remaining at sampler retrieval as a function of Day 0 concentrations. Significant effects of day ($F = 192.0$; $p < 0.001$), experimental period ($F = 21.6$; $p < 0.001$) and an interaction between day and experimental period ($F = 32.1$; $p < 0.001$) were observed. Desorption of DIA-D5 over time was greater and faster in summer 2011 compared to fall 2010 (Fig. 6). Desorption of DIA-D5 from POCIS did not differ significantly between field sites (Fig. 6; $F = 1.4$; $p = 0.247$). The corresponding k_e and R_{scorr} values illustrated that desorption of DIA-D5 and uptake of ATR was higher in summer 2011 compared to fall 2010 (Table 1). A recent review found R_s for ATR were similar between six studies, averaging 0.25 ± 0.03 L/d (Harman et al., 2012). The average field corrected R_s obtained in the present

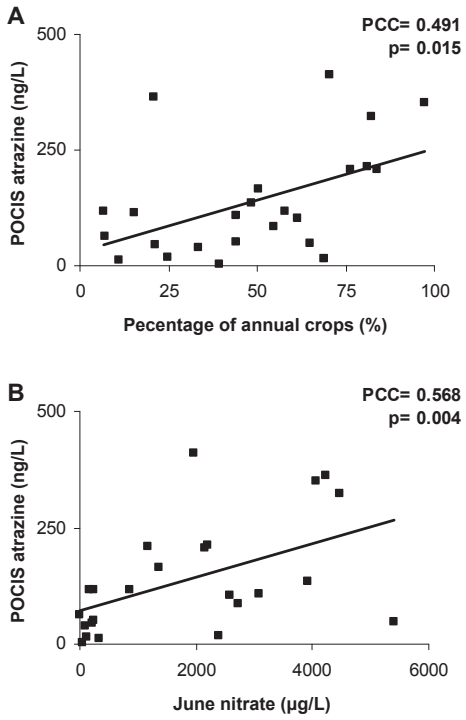

Fig. 5. Correlations between atrazine and A) the percentage of annual crops in a 500 m radius surrounding each site and B) June in-stream nitrate concentrations. Pearson's correlation coefficients (PCCs) and *p* values are shown. The line of best fit was illustrated using linear regression.

study was 0.23 ± 0.12 L/d (Table 1), suggesting that laboratory derived R_s and *in situ* PRC corrected R_s were comparable. However, the larger standard deviation observed in the present study compared to the six calibration studies and the differences observed between deployment periods (Table 1), highlighted that factors affecting R_s under field conditions warranted further investigation.

3.4. Effect of environmental variables on POCIS sampling rates

POCIS remains poorly characterized in terms of modeling uptake rates and environmental factors (Harman et al., 2012). Only three studies have published *in situ* R_s (Zhang et al., 2008; Mazzella et al., 2010; Jacquet et al., 2012) and none have related variability in *in situ* R_s with environmental parameters (reviewed in Morin et al., 2012). We examined the effect of environmental variables on R_s under field conditions. Gradients in a number of environmental variables were observed between field sites and experimental periods (Table 2). However, only temperature was significantly correlated with DIA-D5 k_e values, with desorption of DIA-D5 increasing with increasing temperature (Table 2). Desorption of DIA-D5 increased by an average of 2.7 ± 0.3 fold between the cooler fall and warmer summer experimental periods (Table 1). Previous studies found R_s to increase by <2 fold over a similar temperature range (reviewed in Harman et al., 2012).

Maximum analyte uptake occurs when the rate-limiting barrier to solute transport is the external aqueous boundary (i.e. the thin layer of water between the POCIS membrane and surrounding water) (Huckins et al., 2002). POCIS was under boundary layer control in previous laboratory studies (Alvarez et al., 2004; Mazzella et al., 2010). The observed increase in R_s with increasing temperature was in agreement with theoretical models that predict analyte diffusion across the aqueous boundary to be directly proportional to temperature (Alvarez et al., 2004 and references therein). Under boundary layer control, increases in flow velocity are expected to reduce the thickness of the boundary layer and increase *Rs* (Huckins et al., 2002; Alvarez et al., 2004). Previous studies found increases in R_s from <2 to 9 fold in turbulent conditions, with most studies comparing static versus stirred conditions and flow rates ranging from 2.6 to 37 cm/s for the studies that did measure flow rates (Harman et al., 2012). In the present study, R_s did not increase with increasing stream velocity, despite a range in velocity from 0.6 to 59 cm/s (Table 2). Harman et al. (2012) noted that measured flow rates may poorly represent actual flow rates at the sampler surface. Despite the limitation in accurately measuring flow rates at the sampler surface, the present study found that R_s did not appear to be affected by flow rates across a range of surface velocities measured in actual field deployment conditions.

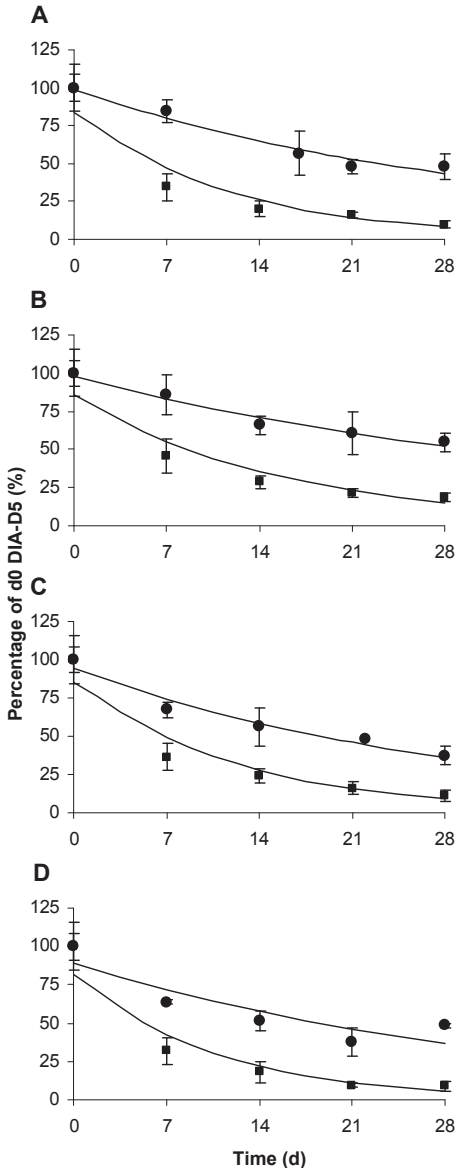

Fig. 6. Desorption of deuterated desisopropyl atrazine (DIA-D5) from polar organic chemical integrative samplers (POCIS) deployed in A) Little Castor R, B) Middle Castor R, C) North Branch South Nation R, D) South Castor R during ● 16 Sep–14 Oct 2010 and ■ 12 Jul–9 Aug 2011. Averages ± standard deviation and modeled response (solid lines) are shown.

Table 1
Deuterated desisopropyl atrazine (DIA-D5) *in situ* elimination rate constants ($k_{ePRCinsitu}$) and corrected atrazine (ATR) sampling rates (R_{scorr}) (±standard error (SE)) determined during fall 2010 and summer 2011 calibration studies in four tributaries of the South Nation River watershed, Canada.

Site[a]	Deployment period	$k_{ePRCinsitu}$ ± SE (d^{-1})	Regression statistics	R_{scorr} ± SE (L/d)[b]
Little Castor (8 ●)	16 Sep–14 Oct 2010	0.030 ± 0.004	$F = 69$; df = 1,17; $p < 0.001$; $R^2 = 0.812$	0.124 ± 0.015
Middle Castor (6 ■)	16 Sep–14 Oct 2010	0.023 ± 0.003	$F = 47$; df = 1,17; $p < 0.001$; $R^2 = 0.746$	0.094 ± 0.014
North Branch (5 ■)	16 Sep–14 Oct 2010	0.034 ± 0.004	$F = 94$; df = 1,16; $p < 0.001$; $R^2 = 0.862$	0.143 ± 0.015
South Castor (7 ■)	16 Sep–14 Oct 2010	0.031 ± 0.005	$F = 39$; df = 1,17; $p < 0.001$; $R^2 = 0.708$	0.131 ± 0.021
Little Castor (8 ●)	12 Jul–9 Aug 2011	0.083 ± 0.007	$F = 164$; df = 1,17;$p < 0.001$; $R^2 = 0.911$	0.349 ± 0.027
Middle Castor (6 ■)	12 Jul–9 Aug 2011	0.063 ± 0.005	$F = 137$; df = 1,17; $p < 0.001$; $R^2 = 0.895$	0.264 ± 0.023
North Branch (5 ■)	12 Jul–9 Aug 2011	0.080 ± 0.006	$F = 169$; df = 1,17; $p < 0.001$; $R^2 = 0.914$	0.334 ± 0.026
South Castor (7 ■)	12 Jul–9 Aug 2011	0.093 ± 0.008	$F = 125$; df = 1,17; $p < 0.001$; $R^2 = 0.886$	0.391 ± 0.035

[a] Numbers and symbols following site names correspond to Fig. 1.
[b] R_{scorr} values were calculated using published $k_{ePRCcal}$ (0.057 d^{-1}) and R_{scal} (0.239 L/d) values (Mazzella et al., 2010).

Under turbulent conditions, the aqueous boundary layer may thin to the point that the rate-limiting barrier to solute transport becomes the PES membrane rather than the boundary layer and further increases in turbulence do not increase R_s (Alvarez et al., 2004). In-stream turbidity, planktonic chlorophyll *a* and conductivity were measured as proxies of concentrations of suspended particles, biofouling potential and dissolved inorganic ions respectively. While no direct effect of these environmental factors was observed (Table 2), they may have been present in sufficient concentrations at the four sites to impede solute transport across the PES membrane and result in membrane control at stream velocities lower than would be predicted by laboratory studies.

Stepwise linear regression confirmed that of the environmental variables measured, only temperature had a significant effect on k_e values ($F = 79$; df = 2,37; $p < 0.001$). Both temperature and velocity are expected to have positive effects on k_e values and in this study a weak negative correlation between temperature and velocity may have confounded detection of subtle effects of velocity on k_e (Pearson's correlation coefficient (PCC) = −0.712; $p = 0.047$), with temperature overriding effects of velocity.

3.5. Field calibration and the performance reference compound approach for POCIS

Harman et al. (2011) state that one of the biggest challenges in quantitative use of POCIS is the lack of a method to correct for factors known to affect R_s. There is currently no consensus on whether the PRC approach is suitable for POCIS (Harman et al., 2012), given that POCIS tends to act as an infinite sink during the integrative uptake phase (Alvarez et al., 2004) but may also exhibit two-way isotropic exchange for some compounds (Mazzella et al., 2007). For a PRC to be effective, it must follow first order kinetics with equal uptake, release and resistance to mass transfer across boundaries in both directions (Alvarez et al., 2007). Data shown in the present study demonstrated that similarly to Mazzella et al. (2010), loss of DIA-D5 followed pseudo first order kinetics (Fig. 6). One further challenge with the PRC approach for POCIS is that PRCs must be poorly sorbed to be useful and are therefore likely to elute early along with interfering compounds that complicate LC-MS/MS analysis. Signal suppressing matrix effects were observed in this study, whereas Mazzella et al. (2010) observed enhancing matrix effects.

Further work is needed to better understand the displacement of PRCs by compounds with a greater affinity for POCIS sorbent (Harman et al., 2011), the effects of interactions between PRCs, target analytes and PES membranes (Vermeirssen et al., 2012) and whether factors controlling the release of DIA-D5 and those controlling uptake of target analytes are equivalent (Harman et al., 2012). Despite these challenges, the use of PRCs such as DIA-D5 has potential for improving quantitative use of POCIS that warrants further investigation. Desorption of DIA-D5 demonstrated that R_s between four field sites appeared to differ temporally but not spatially (Fig. 6; Table 1) and was useful in identifying potential factors affecting field R_s (Table 2). However, further understanding of the mechanisms governing PRC desorption and target analyte uptake is necessary before the PRC approach can accurately correct R_s for a broad suite of target analytes.

4. Conclusions

A gradient of atrazine (ATR) contamination across the South Nation River watershed in Eastern Ontario was observed. While time-weighted-average concentrations did not exceed Canadian water quality guidelines, the detection of elevated concentrations at a number of sites is cause for concern. POCIS was an effective tool to assess ATR contamination at the watershed level and ATR concentrations were positively correlated with measures of agricultural intensity. Field calibration studies using a performance reference compound (PRC) demonstrated that sampling rates (R_s) were similar between four field sites but differed seasonally. Temperature appeared to be the only significant environmental factor affecting R_s and future work could be directed to develop temperature corrected R_s. While further work is needed to validate a PRC approach for POCIS, the inclusion of a PRC can provide

Table 2
Environmental variables measured weekly at four field sites during fall 2010 ($n = 40$) and summer 2011 ($n = 40$) deployment of polar organic chemical integrative samplers (POCIS) and their correlation with *in situ* elimination rate constants ($k_{ePRCinsitu}$) ($n = 8$). Averages are shown with minimum and maximum values in brackets. Significant correlations ($p < 0.001$) are indicated in bold.

Variable	Fall 2010 (16 Sep–14 Oct)	Summer 2011 (12 Jul–9 Aug)	Pearson correlation coefficient (p)
Temperature (°C)	12.73 (9.37–14.97)	23.73 (21.30–26.44)	**0.952 (<0.001)**
Velocity (cm/s)	21.0 (3.8–59.0)	4.5 (0.6–18.2)	−0.582 (0.130)
Turbidity (NTU)	13.7 (2.7–47.0)	8.5 (3.1–23.8)	−0.486 (0.222)
pH	8.08 (7.70–8.66)	8.12 (7.78–8.45)	0.283 (0.498)
Planktonic chlorophyll *a* (μg/L)	3.6 (1.2–11.9)	4.5 (1.7–16.4)	0.245 (0.558)
Conductivity (μS/cm)	634.5 (391.9–825.4)	632.8 (465.1–894.2)	−0.214 (0.612)

valuable information on environmental factors with potential to affect R_s and function as an alternative and complement to *in situ* uptake calibration studies.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.02.028.

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