



# Occurrence and risk of neonicotinoid insecticides in surface water in a rapidly developing region: Application of polar organic chemical integrative samplers

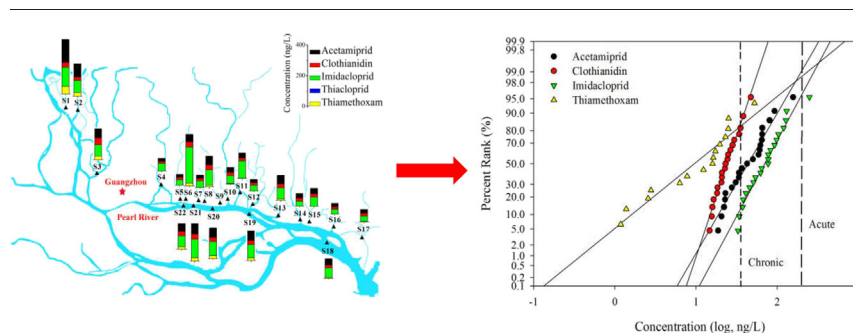
Jingjing Xiong, Zhen Wang, Xue Ma, Huizhen Li, Jing You \*

School of Environment and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou 510632, China

## HIGHLIGHTS

- Modified POCIS has a good performance for sampling neonicotinoids in surface water.
- Environmental exposure distributions of NNIs were generated in Guangzhou, China.
- Chronic thresholds for individual NNIs were exceeded in 16.2–87.8% samples of Guangzhou.
- Acetamiprid and imidacloprid were the dominant NNIs in water of Guangzhou, China.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 30 June 2018

Received in revised form 19 August 2018

Accepted 20 August 2018

Available online 21 August 2018

Editor: Jay Gan

### Keywords:

POCIS

Passive sampling

Urban waterways

Environmental exposure distribution

Predicted environmental concentration

Ecological risk assessment

## ABSTRACT

Extensive use of neonicotinoid insecticides (NNIs) worldwide calls for further knowledge on their environmental occurrence and risk. The present study highlighted the need for more research on long-term exposure of NNIs in aquatic environment, which is important but remains elusive. Time weighted average concentrations of five commonly used NNIs in urban waterways of Guangzhou, China were measured using newly developed polar organic chemical integrative samplers (POCIS). Acetamiprid (from  $18.8 \pm 1.9$  to  $157 \pm 31$  ng/L; mean  $\pm$  standard deviation), clothianidin (from  $14.8 \pm 3.7$  to  $47.6 \pm 10.0$  ng/L) and imidacloprid (from  $32.9 \pm 11.6$  to  $249 \pm 19$  ng/L) were detectable in all samples. Thiamethoxam was found at 71.4% of the 21 sampling sites (from not detected to  $52.4 \pm 9.4$  ng/L), while thiacloprid was not detected at any site. Vegetable planting and sewage effluent were the main sources of NNIs in surface water in Guangzhou. Probabilistic environmental exposure distributions were subsequently constructed using the measured concentrations and the exceedances of predicted environmental concentrations of NNI to ecological thresholds were assessed. In Guangzhou, 63.5%, 16.2%, 87.8% and 17.2% of acetamiprid, clothianidin, imidacloprid and thiamethoxam, respectively, exceeded an interim chronic threshold of 35 ng/L for NNIs. Further risk assessment and control measures for the use of NNIs are advocated for protecting the integrity of aquatic ecosystems.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Neonicotinoid insecticides (NNIs) are highly effective to control crop pests and are among the most extensively used insecticides worldwide (Jeschke et al., 2011). The NNIs have been registered in >120 countries and shared over one-fourth of the total insecticide market in 2014.

\* Corresponding author.

E-mail address: [yujing@jnu.edu.cn](mailto:yujing@jnu.edu.cn) (J. You).

Asia, Latin America and North America are the main users and account for 75% of the total global sales (Bass et al., 2015; Jeschke et al., 2011). As NNIs have high water solubility and long half-lives in soil, they are easily transported to surface water (Anderson et al., 2015; Hladik and Kolpin, 2016; Stamer and Goh, 2012).

Extensive use of NNIs has resulted in their continual release into natural environment. As such, nontarget organisms are continuously exposed to NNIs, possibly jeopardizing aquatic biodiversity (Morrissey et al., 2015; Hladik et al., 2018a). For instance, it has been shown that NNI exposure caused downstream drift and delayed lethality for aquatic macroinvertebrates, which in turn resulted in reduced species abundance (Beketov and Liess, 2008a, 2008b; Berghahn et al., 2012; Tennekes and Sanchez-Bayo, 2011). While ecological risk of NNIs to aquatic non-target species is an emerging concern in many countries (Morrissey et al., 2015; van Dijk et al., 2013), little information is known regarding their occurrence and risk in developing countries or regions where NNIs are also highly used (e.g., Guangzhou, China).

Most of currently available literature regarding reported NNI concentrations in surface water have been obtained using grab sampling (Evelsizer and Skopec, 2016; Hladik et al., 2018b; Hladik and Kolpin, 2016; Yamamoto et al., 2012). However, these results can be biased as water concentrations of pollutants may vary considerably over time and a single grab sampling represents only snapshot in a given moment (Zhang et al., 2008). To reflect fluctuating concentrations within a period of time, high sampling frequency is required, which is labor-intensive and cost-prohibitive. Passive sampling approaches measure time weighted average (TWA) concentrations of pollutants and provide a more sensitive and holistic assessment of long-term exposure at a relatively low cost (Arditsoglou and Voutsas, 2008). A variety of passive samplers have been developed for monitoring waterborne pollutants (Lohmann et al., 2017; Sanchez-Bayo and Hyne, 2014), with polar organic chemical integrative sampler (POCIS) being designed specifically for polar compounds in water, such as pharmaceuticals and herbicides (Alvarez et al., 2004; Harman et al., 2012). Recently, the viability of using POCIS with hydrophilic-lipophilic balance (HLB) sorbents (pha-POCIS) to measure waterborne NNIs was validated in several laboratory-spiked studies (Ahrens et al., 2015; Belles et al., 2014; Poulter et al., 2014), however, the use of this method in the field is still quite limited. van Metre et al. (2017) analyzed imidacloprid in agricultural waterways in the U.S. with pha-POCIS. Recently, we synthesized a new sorbent which has been successfully used to measure multiple classes of insecticides with a broad polarity (including NNIs) in surface water samples. Compared with HLB, this sorbent significantly reduced matrix interference when analyzing insecticides, suggesting that it might be an appropriate POCIS sorbent for NNIs as well (Xiong et al., 2018).

The aims of the present study were to (1) calibrate and validate the use of POCIS with the new sorbent for measuring five NNIs (acetamiprid, clothianidin, imidacloprid, thiamethoxam and thiacloprid) in surface water; (2) analyze occurrence and distribution of NNIs in urban waterways in Guangzhou, China; (3) evaluate aquatic risk of NNIs using probabilistic ecological risk assessment (ERA) by constructing environmental exposure distributions (EEDs). Findings of the present study would help to understand aquatic risk of NNIs after long-term exposure and to advance control measures for NNIs.

## 2. Materials and methods

### 2.1. Chemicals and materials

The POCIS devices had a surface area of 45.8 cm<sup>2</sup> and 200 mg of sorbents were placed between two pieces of nylon membranes. Two types of POCIS sorbents were used in the present study, including the sorbent synthesized in-house according to our previous study (Xiong et al., 2018) (m-POCIS) and a commercialized HLB sorbent (pha-POCIS). Neat compounds of NNIs, including acetamiprid, clothianidin,

imidacloprid, thiacloprid and thiamethoxam were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), with a purity >98%. Imidacloprid-*d*<sub>4</sub> and acetamiprid-*d*<sub>3</sub> from CDN Isotopes (Quebec, Canada) were used as the internal standard and surrogate, respectively.

Methanol and acetonitrile (HPLC grade) were purchased from Oceanpak (Gothenburg, Sweden) and Merck (Darmstadt, Germany), respectively. Glass fiber filters (0.7 μm) were obtained from Whatman (Dassel, Germany). Nylon membranes (0.45 μm pore size, 100 mm diameter, 100 μm thickness) were bought from Beihua Dawn Membrane Separation Technology (Beijing, China). Empty polypropylene solid phase extraction (SPE) tubes (6 mL) with polyethylene frits and HLB sorbent were purchased from Agela Technologies (Tianjin, China). Ultrapure water was prepared with a milli-Q system (Billerica, MA, USA).

### 2.2. Site description and sampling

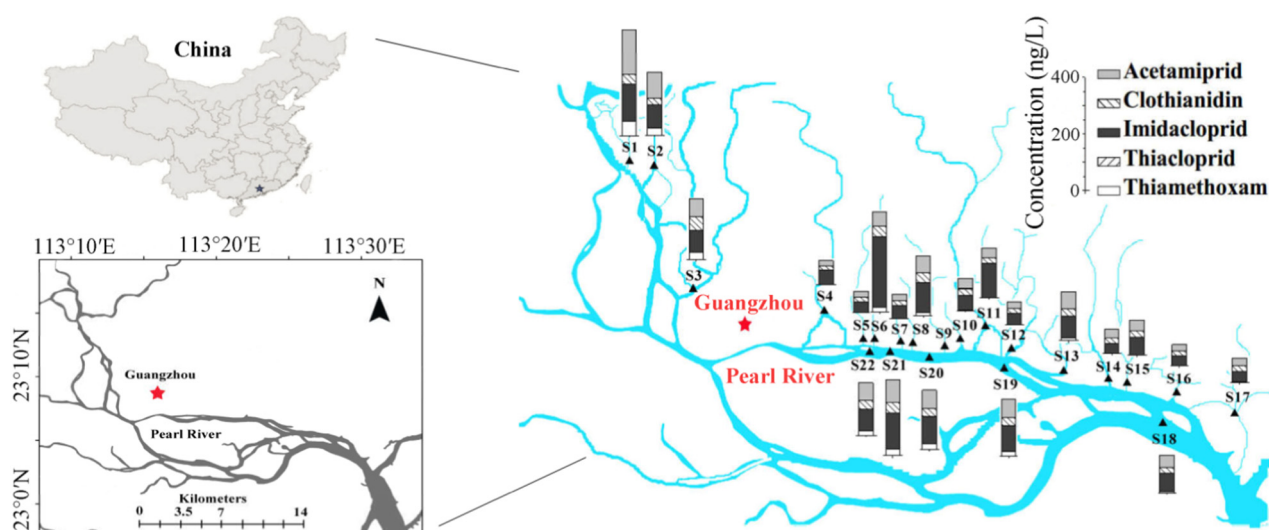
Guangzhou is the largest city in South China and has experienced intense population and economy growth in recent decades, with currently >13.5 million people living in the city (<http://www.gz.gov.cn/gzgov/s2289/sq.shtml>). Warm and humid weather intensified pest control issues and has further promoted the use of insecticides in the region (Li et al., 2014). Current-use pesticides have been frequently detected in Guangzhou urban waterways along with other pollutants, posing significant threats to aquatic organisms (Cheng et al., 2017; Yi et al., 2015). Not surprisingly, NNIs have also been found in Guangzhou surface water during a single-time grab sampling campaign, but their risk was inadequately understood due to the lack of long-term exposure data (Zhang et al., 2017). Thus, Guangzhou was selected as a representative for rapidly developing regions to study the occurrence and risk of NNIs in surface water.

As depicted in Fig. 1, 22 sites were sampled in the Guangzhou reach of the Pearl River and its tributaries. Sites S1–S17 and S18–S22 were in the tributaries and the main stream, respectively (see Table S1 for detailed description of each site, “S” represents figures and tables in the Supplementary Information thereafter). Geographically, sites S1–S3, S11 and S13 were adjacent to vegetable planting areas, sites S4–S10, S12 and S14–S17 were in residential areas and S6 was near a sewage treatment facility. The m-POCIS were placed in steel canisters and deployed at all sites for 14 d (between November and December of 2016). For comparison, pha-POCIS were deployed in half of the sites, with six in the tributaries (three near vegetable planting areas and three in residential areas) and five in the main stream.

Water samples at the 22 sites were also collected twice by grab sampling at the beginning and the end of POCIS exposure (Table S1). Concurrently, water quality parameters including water velocity (inside and outside the canisters), pH, conductivity and temperature were also measured at deployment and retrieval of POCIS using a current meter (Senlod, Nanjing, China), pH (Ohaus, New Jersey, NJ, USA), a conductivity meter (Sanxin, Shanghai, China) and a glass thermometer (Xingming, Hebei, China) (Table S1). All measurements were conducted in triplicate.

### 2.3. POCIS extraction

After 14-d exposure, the POCIS devices were retrieved from the water, transported back to the lab and rinsed with ultrapure water to remove solid debris. Each POCIS was carefully dismantled and the inner membranes were rinsed with ultrapure water to transfer the sorbents into a 6-mL SPE cartridge with polyethylene frits. The sorbents in the cartridges were air-dried for 15 min under vacuum. After loading the surrogate, acetamiprid-*d*<sub>3</sub> (1 μg/mL, 50 μL), the cartridges were eluted with 10 mL of acetonitrile. The effluents were concentrated to 0.5 mL, imidacloprid-*d*<sub>4</sub> (1 μg/mL, 50 μL) was added as the internal standard, and the solution was passed through a 0.22-μm filter. The NNIs were analyzed using high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS).



**Fig. 1.** Concentrations of individual neonicotinoid insecticides at sampling sites in urban waterways in Guangzhou, China. The measurements were conducted using a modified polar organic chemical integrative sampler (m-POCIS).

#### 2.4. POCIS calibration

Before field deployment, kinetic accumulation process of NNIs by POCIS was calibrated in the laboratory. A flow-through system was set up to maintain constant concentrations of NNIs in water throughout a 42-d testing period (25-L tank, completely refreshed every 16.7 h). Water flowed at a rate of 0.03 m/s in the system and temperature was kept at  $22.6 \pm 0.2$  °C throughout. Water concentrations of NNIs in the system were analyzed every 7 d in triplicate and the relative standard deviations (RSD) of the seven measurements over 42 d were 9.9%–16.8% (Table S2). The POCIS were placed in an exposure tank and three devices were randomly removed at 3, 5, 7, 14, 21 and 31 d for analyzing NNIs accumulated in the POCIS. The sampling rates ( $R_s$ , L/d) of NNIs to POCIS were then calculated following Eq. (1) (Alvarez et al., 2004).

$$R_s = C_s \times M_s / (C_w \times t) \quad (1)$$

where  $C_s$  and  $C_w$  are NNI concentrations in the POCIS (ng/g) and TWA concentrations of NNIs in water (ng/L), respectively.  $M_s$  is mass of POCIS sorbent (g) and  $t$  is exposure time (d).

The impacts of chemical concentration and water velocity on  $R_s$  were evaluated. The  $R_s$  of NNIs were measured at three NNI concentrations: low (from  $25.6 \pm 6.4$  to  $74.2 \pm 10.5$  ng/L), middle (from  $61.8 \pm 11.2$  to  $143 \pm 4.7$  ng/L) and high (from  $306 \pm 51.8$  to  $643 \pm 86.9$  ng/L). Constant exposure was confirmed by measuring water concentrations of NNIs in triplicate at 1, 2, 7 and 14 d (Table S2). Three POCIS were randomly removed at each time point for measuring NNI concentrations in POCIS sorbents. Finally,  $R_s$  values were calculated for individual NNIs at various concentrations (Eq. (1)). Additionally,  $R_s$  values were also evaluated at three water velocities (0.03, 0.05 and 0.10 m/s). Similarly, NNI concentrations in water remained constant throughout the 14-d exposure for all tests with RSD for each velocity (0.03, 0.05 and 0.10 m/s) ranging from 3.3%–18.1%, 13.8%–24.0% and 19.0%–26.9%, respectively (Table S2).

#### 2.5. Water sample extraction

Water samples were collected during POCIS calibration tests in the laboratory and at each site in Guangzhou urban waterways. The NNIs in the samples were extracted from water using a previously developed SPE method (Xiong et al., 2018). Briefly, SPE cartridges packed with 200 mg of HLB were preconditioned with methanol and water sequentially, and 1 L of field water samples (filtered through glass fiber filters) were loaded onto the cartridges after adding 40  $\mu$ L of 1  $\mu$ g/mL

acetamiprid- $d_3$  as the surrogate. The cartridges were dried under vacuum for 15 min, and the NNIs were eluted out of the cartridge with 5 mL of acetonitrile. The effluents were concentrated to 0.5 mL, spiked with imidacloprid- $d_4$  (1  $\mu$ g/mL, 50  $\mu$ L) as the internal standard, filtered through 0.22  $\mu$ m filters, and analyzed using HPLC-MS/MS. The water samples dosed in the laboratory were also extracted using the same procedures, except that water volume was 200–500 mL and the water was not filtered through glass fiber filters.

#### 2.6. Instrumental analysis

Analysis of NNIs was performed using a LC-30-AD HPLC (Shimadzu, Japan) coupled with QTRAP 5500 MS/MS (AB SCIEX, USA) following a method described by Zhang et al. (2017) with minor modifications. The instrument was equipped with an electrospray ion source and operated in positive mode and multiple reaction monitoring mode.

The analytes were separated on an Agilent eclipse plus C18 column (100 mm  $\times$  2.1 mm  $\times$  1.8  $\mu$ m) couple with a C18 guard column (12.5 mm  $\times$  2.1 mm  $\times$  5  $\mu$ m), with column temperature of 40 °C. The mobile phase was water containing 0.1% formic acid (A) and acetonitrile (B) and the flow rate was at 0.3 mL/min. The gradient elution programme was as follows: 0–0.5 min, 10% B; 10.0 min, 55% B; 10.1 min, 90% B; 10.1–13.0 min, 90% B; 13.1 min, 10% B; 13.1–15.0 min, 10% B. The injection volume was 2  $\mu$ L. Nitrogen was used as atomizing gas. The pressure of curtain and collision gas was set at 4 and 7 psi, respectively. Ion spray voltage was set at 5500 V. The temperature of drying gas was set at 550 °C. The pressure of ion source gas was 55 psi. Entrance potential and collision cell exit potential were 10.0 and 16.0 V, respectively. More details including the retention time, transition mass and other mass acquisition parameters of the analytes are shown in Table S3.

The NNIs were quantified on the HPLC-MS/MS using internal calibration, with matrix-matched standards and linear ranges of 1 to 500 ng/mL. The instrument limits of detection (LOD) and the limits of quantification (LOQ) were determined as NNI concentrations corresponding to signal-to-noise ratios of 3 and 10, respectively (Table S3). The limits of quantification of POCIS sampling ( $LQ_p$ ) and grab sampling ( $LQ_g$ ) were calculated from LOQ using Eqs. (2) and (3), respectively (Poulier et al., 2014).

$$LQ_p = LOQ \times V_{inj} / (R_s \times t) \quad (2)$$

$$LQ_g = LOQ \times V_{inj} / V_w \quad (3)$$

**Table 1**  
Octanol-water partition coefficients, sampling rates ( $R_s$ , L/d) and limits of quantification ( $LQ_p$ ) of modified polar organic chemical integrative sampler (m-POCIS) and limits of quantification of grab sampling ( $LQ_g$ ) for target neonicotinoid insecticides (NNIs). Recovery and standard deviation (SD) of individual NNIs from m-POCIS and pharmaceutical polar organic chemical integrative sampler (pha-POCIS). The concentrations of NNIs in urban waterways in Guangzhou, China measured by m-POCIS ( $C_w$ ) are also listed. The  $R_s$  is expressed as mean  $\pm$  SD and  $C_w$  is expressed as mean  $\pm$  SD (range among sampling sites) ( $n = 3$ ).

Compound	Log $K_{ow}$ <sup>a</sup>	$R_s$ (L/d)	$LQ_p$ (ng/L)	$LQ_g$ (ng/L)	Recovery (%)		$C_w$ (ng/L)
					m-POCIS	pha-POCIS	
Acetamiprid	0.80	0.081 $\pm$ 0.019	0.09	0.10	96.4 $\pm$ 0.6	90.7 $\pm$ 3.9	51.2 $\pm$ 32.5 (18.8 $\pm$ 1.9–157 $\pm$ 31)
Clothianidin	0.91	0.032 $\pm$ 0.009	1.12	0.50	83.2 $\pm$ 3.8	77.4 $\pm$ 3.5	25.6 $\pm$ 8.90 (14.8 $\pm$ 3.7–47.6 $\pm$ 10.0)
Imidacloprid	0.57	0.052 $\pm$ 0.011	0.34	0.25	86.7 $\pm$ 2.9	89.7 $\pm$ 4.1	81.1 $\pm$ 49.5 (32.9 $\pm$ 11.6–249 $\pm$ 19)
Thiacloprid	1.26	0.053 $\pm$ 0.011	0.13	0.10	96.0 $\pm$ 3.0	85.6 $\pm$ 3.7	ND <sup>b</sup>
Thiamethoxam	−0.13	0.028 $\pm$ 0.007	0.64	0.25	80.1 $\pm$ 4.1	81.1 $\pm$ 3.5	10.9 $\pm$ 13.2 (ND–52.4 $\pm$ 9.4)

<sup>a</sup> <http://sitem.herts.ac.uk/aeru/iupac/index.htm> (Last time accessed: June 12, 2017).

<sup>b</sup> ND: not detected.

where  $V_{inj}$  is the volume of final extract (0.5 mL) and  $V_w$  is the volume of grab water samples used for extraction (1 L).  $R_s$  is the sampling rate of the POCIS and  $t$  is the exposure time (14 d). The  $LQ_p$  and  $LQ_g$  for each analyte are presented in Table 1.

A set of quality control samples were also processed along with the samples. No target NNIs were detected in blank samples. Sorbents (200 mg) were spiked with 0.1  $\mu$ g NNIs and went through the extraction procedure to check the recovery of NNIs from m-POCIS and pha-POCIS materials. The recoveries of NNIs ranged from 80.1%  $\pm$  4.1% (thiamethoxam) to 96.4%  $\pm$  0.6% (acetamiprid) and 77.4%  $\pm$  3.5% (clothianidin) to 90.7%  $\pm$  3.9% (acetamiprid) for m-POCIS and pha-POCIS, respectively (Table 1). Meanwhile, acetamiprid- $d_3$  was added to all samples before extraction to ensure the performance of sample preparation procedures. Recoveries of acetamiprid- $d_3$  were from 51.6%  $\pm$  12.2% to 88.8%  $\pm$  5.1% for all water and POCIS sorbent samples, respectively. Statistical analysis for calculated  $R_s$  of m-POCIS for NNIs at different compound concentrations and water velocity and residues of NNIs among sites were conducted using a one-way analysis of variance (ANOVA; significance level  $\alpha = 0.05$ ) with SPSS (version 16.0, Chicago, IL, USA).

### 2.7. Probabilistic ecological risk assessment

A probabilistic ERA using EEDs were conducted in the present study (Solomon et al., 2000). The EEDs were generated using POCIS measured water NNIs concentrations in Guangzhou. In brief, the concentrations of NNIs were ranked in ascending order and percentiles were assigned using the Weibull formula (Eq. (4)).

$$\text{Percentile} = (i \times 100)/(n + 1) \quad (4)$$

where  $i$  is the numerical rank of the datum in ascending order and  $n$  is the total sample size. The EEDs were constructed using measured concentration (log-transformed) on the  $x$ -axis and percentile (probability) of sites being affected as the  $y$ -axis (SigmaPlot version 10.0, San Jose, CA, USA). Predicted environmental concentrations (PECs) and their 95% confidence intervals corresponding to 5th, 50th and 95th percentiles were determined for each distribution by using the log-normal regression function available in SAS (version 9.4, Cary, NC, USA). The exceedances of NNI concentrations in surface water of Guangzhou were also evaluated with previously developed interim acute (200 ng/L) and chronic (35 ng/L) thresholds for NNIs as suggested by Morrissey et al. (2015).

## 3. Results and discussion

### 3.1. POCIS calibration in laboratory

The sorption of analytes on passive sampling sorbents is proportional to their concentrations in water and the adsorption capacity is dependent on physicochemical properties of each chemical (Sanchez-

Bayo and Hyne, 2014). Thus, different sorbents have been used for hydrophilic or hydrophobic substances (Vermeirssen et al., 2012). The polar sorbent synthesized in-house showed good recovery for NNIs with lower matrix effects compared with HLB sorbent (Xiong et al., 2018), thus it was used as POCIS sorbent (m-POCIS) in the present study. Uptake profiles of the target NNIs by the m-POCIS are shown in Fig. S1. All NNIs exhibited an integrative uptake by m-POCIS within the 21-d exposure period, and gradually reached a plateau afterward. The  $r^2$  of linear regressions ranged from 0.876–0.993 for individual NNIs over the 21-d integrative uptake period. Thus, 14 d was selected for field deployment as it was within the linear uptake regime.

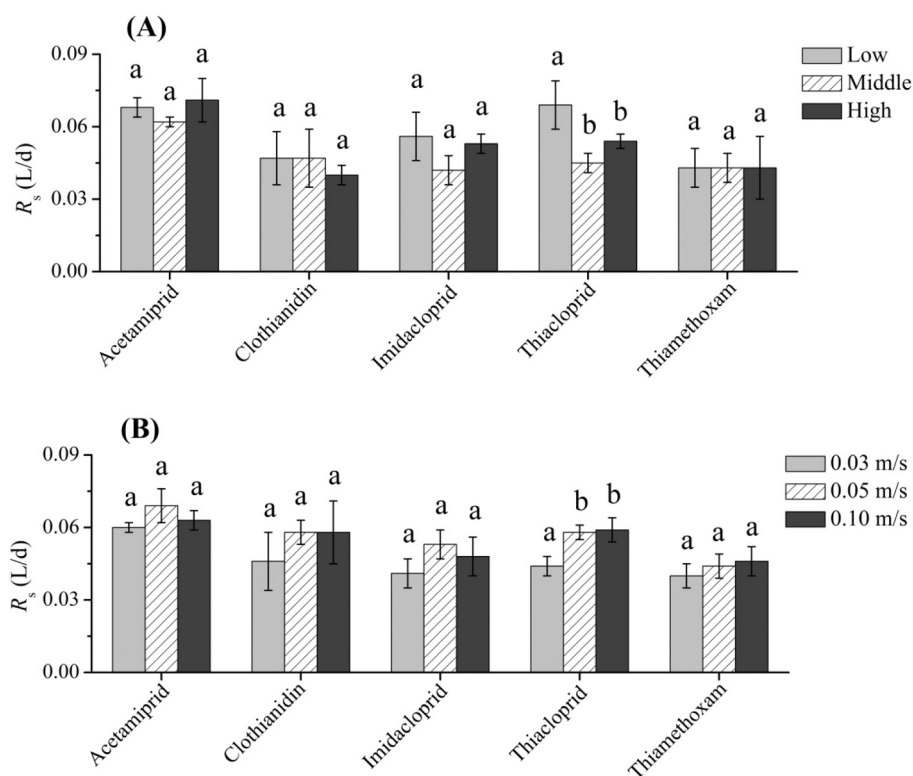
Water concentrations of NNIs have been shown to vary remarkably in the environment (Hladik and Kolpin, 2016), so it was imperative to check the impact of NNI concentrations on  $R_s$ . As shown in Fig. 2A,  $R_s$  values for the same NNI were similar regardless of water concentrations, except thiacloprid which had a higher  $R_s$  at the lowest concentration when compared to the  $R_s$  values at other concentrations. Similar  $R_s$  values guaranteed the applicability of POCIS for NNIs at various concentrations. Other researchers have also reported that  $R_s$  for POCIS was generally independent of the concentrations of target compounds (Alvarez et al., 2004; Arditoglou and Voutsas, 2008; Zhang et al., 2008).

Water velocity was the other important factor that could influence aqueous passive sampling (MacLeod et al., 2007), due to the fact that uptake rates of pollutants to the samplers are controlled by an aqueous boundary layer at the membrane-water interface (Alvarez et al., 2004; Lissalde et al., 2014), but this is not the case in the present experiment. While water velocity increased from 0.03 to 0.10 m/s,  $R_s$  of NNIs were not significantly altered with one exception, which was an increase of  $R_s$  for thiacloprid when water velocity increased from 0.03 to 0.05 m/s (Fig. 2B). Overall, changing water velocity had little effect on  $R_s$ , which has been previously reported as well. Dalton et al. (2014) found that when water velocity increased from 0.006 to 0.59 m/s,  $R_s$  of atrazine was not changed under field conditions. Di Carlo et al. (2014) reported that  $R_s$  of eight pollutants (atrazine, propazine, terbutylazine, diclofenac, ibuprofen, ketoprofen, perfluorooctanoic acid and perfluorooctane sulfonate) kept constant when water velocity increased from 0.02 to 0.153 m/s. After reviewing numerous studies, Harman et al. (2012) concluded that the change of  $R_s$  was generally small (<2-fold) and that when water velocity increased from static to 0.37 m/s, there was no need to adjust  $R_s$ , which is in agreement with our present results.

The average values of  $R_s$  for individual NNIs to m-POCIS at different time intervals in the integrative uptake phase (3, 5, 7, 14 and 21 d) are provided in Table 1, ranging from 0.028  $\pm$  0.007 (thiamethoxam) to 0.081  $\pm$  0.019 L/d (acetamiprid). The  $R_s$  values were used in field sampling and no adjustments were made for varying chemical concentration or water velocity.

### 3.2. POCIS validation in field

Although seldom studied, HLB-based pha-POCIS has been validated for estimating NNIs in laboratory-spiked water (Ahrens et al., 2015;



**Fig. 2.** Calculated sampling rates ( $R_s$ ) of modified polar organic chemical integrative sampler (m-POCIS) for neonicotinoid insecticides at different compound concentrations (A) and water velocity (B). Different letters indicate significant differences of  $R_s$  for each neonicotinoid.

Belles et al., 2014) and used for quantifying imidacloprid in agricultural waterways in France and the U.S. (Poulier et al., 2014; van Metre et al., 2017). These studies revealed the applicability of pha-POCIS for NNI measurements. In these previous versions of pha-POCIS, polyethersulfone membranes (PES) were used to enclose HLB sorbents, yet PES tended to release polyethylene glycol (PEG) compounds which would result in increased matrix effects for analyzing pesticides with mass spectrometry (Guibal et al., 2015). To validate the use of m-POCIS in the field, pha-POCIS containing HLB resins were co-deployed in half of the sampling sites in Guangzhou. Instead of PES, nylon membranes were used for both POCIS devices in the present study, improving analytical accuracy by reducing PEG-related matrix effects. The NNI concentrations in Guangzhou waterways measured by passive sampling (m-POCIS and pha-POCIS) are presented in Table S4. As shown in Fig. S2, the measurements between m- and pha-POCIS for individual NNIs were quite similar. The consistent results between m- and pha-POCIS validated the performance of m-POCIS in evaluating NNI concentrations in surface water.

Grab samples at all sites were collected when deploying and retrieving the POCIS in the field as well (Table S5). The individual NNI concentrations quantified by m-POCIS were compared with their counterparts by grab sampling (Fig. S3). The POCIS measured TWA concentrations of NNIs over the 14-d exposure, while NNI concentrations obtained by grab sampling were the average values of two instantaneous concentrations at the time of deployment and retrieval of m-POCIS. As such, NNI concentrations measured by m-POCIS were several times different from those in concurrent grab water samples, with concentration ratios ranging from 0.26 to 2.15 (acetamiprid), 1.35 to 2.94 (clothianidin), 0.65 to 4.16 (imidacloprid) and 0.16 to 4.21 (thiamethoxam). The deviation between passive and grab sampling would likely be reduced if the frequency of grab sampling increased, although this would also mean increased sampling labor and cost (Ahrens et al., 2015).

In the field, contaminant concentrations in water fluctuated due to changing flow and episodic input (Ahrens et al., 2015) and grab sampling just measured the instantaneous concentration at the sampling

moment, which was reflected by the larger standard deviations of NNI concentrations measured by grab sampling when compared with m-POCIS for most samples (Fig. S3). Comparatively, TWA from POCIS better represented long-term exposure and had less uncertainty than concentrations obtained through the use of grab sampling. In summary, the calibration and validation data showed that the modified version of POCIS with the new sorbent (m-POCIS) was viable to monitor TWA concentrations of NNIs in field water with laboratory-calibrated  $R_s$  values.

### 3.3. Occurrence and distribution of NNIs in Guangzhou

The TWA concentrations of NNIs in Guangzhou urban waterways were assessed using m-POCIS. The samplers at site S9 went missing, so this site is excluded from the discussion. As shown in Table S4, the mean concentration of all NNIs across the 21 sites was  $169 \pm 89$  ng/L, with the minimum and maximum values being  $73.1 \pm 6.9$  and  $375 \pm 78$  ng/L, respectively. Acetamiprid, clothianidin, imidacloprid and thiamethoxam were detected at frequencies of 100%, 100%, 100% and 71.4%, respectively, yet thiacloprid was not found at any site. In all sites, acetamiprid (from  $18.8 \pm 1.9$  to  $157 \pm 31$  ng/L) and imidacloprid (from  $32.9 \pm 11.6$  to  $249 \pm 19$  ng/L) were the dominant NNIs with a mean concentration of  $51.2 \pm 32.5$  and  $81.1 \pm 49.5$  ng/L, respectively. The concentrations of clothianidin ranged from  $14.8 \pm 3.7$  to  $47.6 \pm 10.0$  ng/L, with a mean value of  $25.6 \pm 8.9$  ng/L. The highest detected concentration of thiamethoxam was  $52.4 \pm 9.4$  ng/L (site S1) with a mean value of  $10.9 \pm 13.2$  ng/L. It was not surprising to detect NNIs in Guangzhou urban waterways with high frequencies. Guangzhou is located in a subtropical zone with mild temperature and heavy rainfall. Intensive anthropogenic activity and warm and humid weather have encouraged the use of insecticides in this region to combat pest issues (Li et al., 2014). Various current-use pesticides have been detected and identified as one of the main sources of risk to aquatic organisms in Guangzhou urban waterways (Li et al., 2011; Qi et al., 2017; Yi et al., 2015).

As shown in Fig. 1, NNI concentrations varied among the sampling sites. The highest concentration of total NNIs ( $375 \pm 78$  ng/L) was detected at site S1, which is a tributary site near a vegetable field. Due to an unbalanced urbanization process in Guangzhou, patches of urban villages are interspersed in the modernized areas of the city. Heavy pesticide usage for vegetable planting is a common practice in these villages and has become an important source of pesticide residues in aquatic environment (Li et al., 2013). The average value of total NNI concentrations at the sites near vegetable fields (S1–S3, S11 and S13) was  $232 \pm 86$  ng/L, which was significantly higher than the average concentration of  $102 \pm 43$  ng/L at sites adjacent to residential areas (S4, S5, S7, S9, S10, S12 and S14–S17) ( $p < 0.05$ ).

In addition to vegetable planting, sewage effluent was also found to be a significant source of NNIs in Guangzhou waterways. The total NNI concentration detected at site 6 was  $354 \pm 30$  ng/L. This tributary site is adjacent to a sewage treatment plant, suggesting that sewage effluent could also likely be a source of NNIs in surface water. Similar finding has also been reported in previous studies investigating NNIs in water (Klarich et al., 2017; Münze et al., 2017; Sadaria et al., 2016). Münze et al. (2017) concluded that treated wastewater was possibly the exclusive source of acetamiprid and imidacloprid in the streams in central Germany.

Collectively, the average water concentration of NNIs in the tributaries ( $164 \pm 99$  ng/L) was comparable to that in the main stream of the Pearl River ( $201 \pm 56$  ng/L) ( $p = 0.164$ ). This is in stark contrast to the distribution of sediment-bound pyrethroid insecticides, whose concentrations in the main stream of the Pearl River were much lower than those in the tributaries (Cheng et al., 2017). Compared with pyrethroids, NNIs are more polar and water soluble, thus it is likely that they are transported more easily from the small tributaries and into the large river, resulting in a more homogenous distribution in surface water. Among the five main river sites (S18–S22), the highest concentration of NNIs was detected at S21 ( $271 \pm 64$  ng/L) (Fig. 1 and Table S4). Site S21 is just located downstream of site S6 which is the tributary site near the sewage treatment plant. The NNI concentration was much lower at site S22 (upstream of the tributary outlet) when compared to S21, and then again after S21 the concentrations gradually decreased along the river, suggesting the strong influence of NNI input from the tributaries on their distribution in the main stream.

The concentrations of NNIs in Guangzhou were compared with those in other regions, although most of these previous reports were obtained using grab sampling (Table S6). The TWA concentrations of NNIs by m-POCIS in Guangzhou were slightly higher than the concentrations previously measured by grab sampling in Guangzhou (Xiong et al., 2018; Zhang et al., 2017). This may be partially explained by the different sample size (more samples were collected in the present study) and sampling techniques (TWA by POCIS vs. instantaneous concentrations by grab sampling). Geographically, NNI concentrations in Guangzhou were in the moderate range when compared to other sites in the world. For instance, the concentrations were greater than those in agricultural catchments in Queensland, Australia (Smith et al., 2012) and streams in the U.S. (Hladik and Kolpin, 2016), but lower than those in rivers around Sydney, Australia (Sanchez-Bayo and Hyne, 2014), wetlands in Canada (Main et al., 2014) and other U.S. sites (Evelsizer and Skopec, 2016) (Table S6).

The NNIs were ubiquitous in surface water with high detection frequency. In the present study, detection frequencies were 100% for acetamiprid, clothianidin and imidacloprid, and 71.4% for thiamethoxam, with the maximum concentrations of individual NNIs across sites being 157 (acetamiprid), 47.6 (clothianidin), 249 (imidacloprid) and 52.4 ng/L (thiamethoxam). Among the samples collected from Sacramento and Orange County in the U.S., clothianidin and imidacloprid were detected in approximately 50% of samples (Ensminger et al., 2013). Hladik et al. (2014) analyzed NNI residues in streams on a nationwide scale in the U.S. and found that 53% of the samples contained at least one NNI. In wetlands of prairie pothole region in

Canada, NNIs were detected in 91% of the samples, with the maximum concentration of clothianidin, imidacloprid and thiamethoxam reaching 3110, 260 and 1490 ng/L, respectively (Main et al., 2014). In agricultural regions of California, the detection frequency of imidacloprid was 89.3% with a maximum concentration up to 3290 ng/L (Starnes and Goh, 2012). The high detection frequency and high concentrations of NNIs in surface water showed the need for further research on the risk of NNIs to aquatic organisms.

#### 3.4. Probabilistic ecological risk assessment

To assess the potential risk of NNI exposure to aquatic organisms, EEDs were constructed for individual NNIs detected in Guangzhou urban waterways (Fig. 3). As shown in Table 2, imidacloprid had the highest 5<sup>th</sup> PECs (26.2 ng/L), followed by acetamiprid (15.0 ng/L) and clothianidin (13.1 ng/L), while thiamethoxam was detected at relatively low concentrations with a PEC5 of 0.98 ng/L. Interestingly, although their PEC5 values were similar, the high end of PECs (e.g., PEC95) for acetamiprid (127 ng/L) and clothianidin (44.9 ng/L) varied considerably, implying distinct distribution patterns for individual NNIs.

Several water quality reference values have been proposed for determining acceptable levels of NNIs in surface water, most of which are limited to imidacloprid; toxicity thresholds for other NNIs are not well established due to a lack of data availability (Morrissey et al., 2015; Smit et al., 2015). This would be especially concerning considering the known variation in toxicity of individual NNIs to aquatic organisms. However, as imidacloprid is more potent than the other NNIs, toxicity thresholds established mainly based on imidacloprid data are generally considered to be conservative and sufficiently protective for aquatic species (Guy et al., 2011; Morrissey et al., 2015). Recently, Morrissey et al. (2015) used probabilistic approaches, on the basis of available NNI studies which used similar study designs (using LC<sub>50</sub> and EC<sub>50</sub> endpoints), to recommend 200 and 35 ng/L as acute and chronic thresholds, respectively, for protecting aquatic invertebrate community. As evaluating the quality of thresholds of NNIs for aquatic risk assessment was beyond the scope of the present study, these acute and chronic values proposed by Morrissey et al. (2015) were directly used to compute the percent probabilities of NNI concentrations in Guangzhou surface water that exceeded these thresholds (Table 2).

Aquatic risk of acute exposure to NNIs in the study area was low, and the probability for any NNI concentrations over the acute threshold was <4.2%. However, as TWA concentrations are the average concentrations over a period of time, they may fail to monitor acute risk at peak concentrations. Overall, this may result in a source of uncertainty in evaluating acute risk using POCIS. On the contrary, TWA concentrations do provide

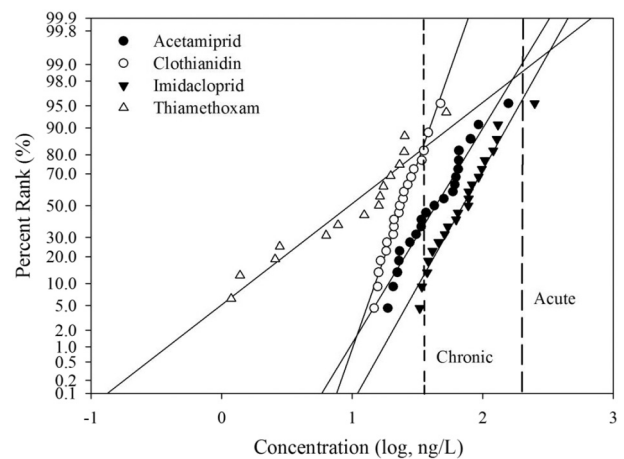


Fig. 3. Environmental exposure distributions of water concentrations of neonicotinoid insecticides in Guangzhou, China. Vertical lines represent chronic and acute ecological thresholds for NNIs water concentrations proposed by Morrissey et al. (2015).

**Table 2**

Slope and intercept for regression lines and values corresponding to 5<sup>th</sup>, 50<sup>th</sup> and 95<sup>th</sup> centiles of predicted environmental concentrations (PECs) for individual and total neonicotinoid insecticides (NNIs) in Guangzhou, China. Percent probabilities of environmental concentrations higher than the proposed ecological thresholds of NNIs (acute and chronic thresholds of 200 and 35 ng/L, respectively) are also included.

Compound	n	r <sup>2</sup>	Slope	Intercept	PECs (ng/L)			Percent probability	
					5%	50%	95%	Acute	Chronic
Acetamiprid	21	0.95	3.54	−5.81	15.0 (13.3–16.7)	43.6 (41.5–46.0)	127 (115–145)	1.0%	63.5%
Clothianidin	21	0.98	6.13	−8.48	13.1 (12.5–13.7)	24.2 (23.8–24.8)	44.9 (43.2–47.4)	0%	16.2%
Imidacloprid	21	0.95	3.83	−7.08	26.2 (23.6–29.2)	70.4 (67.6–74.2)	189 (174–215)	4.2%	87.8%
Thiamethoxam	15	0.91	1.67	−1.63	0.98 (0.60–1.37)	9.53 (7.93–11.3)	92.5 (64.3–145)	1.4%	17.2%
Total NNIs	21	0.96	3.86	−8.38	55.6 (48.6–62.1)	148 (141–157)	396 (356–453)	NA <sup>a</sup>	NA

<sup>a</sup> ND: not applicable.

a strong estimation of chronic risk. A high probability of chronic risk existed in the Guangzhou surface water evaluated for acetamiprid (63.5%), clothianidin (16.2%), imidacloprid (87.8%) and to a lesser degree thiamethoxam (17.2%), suggesting that NNIs would pose long-term impacts on aquatic organisms (Table 2 and Fig. 3). Acetamiprid and imidacloprid contributed the greatest degree of risk of those studied (Table 2). Future studies, should not only study imidacloprid, which is a common focal point, but also acetamiprid. As not only did acetamiprid show high frequency and high concentrations in these water, but it also is still being intensively used in this areas, as acetamiprid was regarded as one of three most widely used insecticides in China (Jin et al., 2015). It is highly likely that other streams and rivers in China would be exhibit potential chronic risk from NNIs contamination, thus it is imperative to conduct long-term monitoring for their occurrence in surface water, and the development of POCIS method provided herein helps in providing accurate results that can be achieved in a labor efficient and cost savings manner.

#### 4. Conclusions

A newly validated m-POCIS method was used to assess the occurrence and distribution of NNI residues in surface water in a rapidly developing city (Guangzhou, China). At all the sampling sites, at least three NNIs were detected, with acetamiprid and imidacloprid being the dominant contaminants. The total concentrations of NNIs for a given site ranged from 73.1 ± 6.9 to 375 ± 78 ng/L with a mean value of 169 ± 89 ng/L. Vegetable planting fields and sewage treatment plants were the main sources of NNIs in Guangzhou urban waterways. Constructed EEDs indicated that PEC<sub>5</sub> varied for individual NNIs, with 15.0 ng/L for acetamiprid, 13.1 ng/L for clothianidin, 26.2 ng/L for imidacloprid and 0.98 ng/L for thiamethoxam. The probability of individual NNIs, particularly acetamiprid and imidacloprid exceeding chronic thresholds was high. The results present here show the need for more measures to assess and control risk of NNIs in surface water, especially in developing areas, to provide appropriate protections for functions and biodiversity of aquatic ecosystem.

#### Acknowledgements

This research was supported by the National Science Foundation of China (41473106 and 41773101), the Ministry of Science and Technology of the People's Republic of China (2017ZX07301005-002) and Guangdong Provincial Department of Science and Technology (2017A020216002, 2015A030310219 and 2015TX01Z168).

#### Conflict of interest

The authors declare no conflict of interest.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.08.256>.

#### References

- Ahrens, L., Daneshvar, A., Lau, A.E., Kreuger, J., 2015. Characterization of five passive sampling devices for monitoring of pesticides in water. *J. Chromatogr. A* 1405, 1–11.
- 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.
- Anderson, J.C., Dubez, C., Palace, V.P., 2015. Neonicotinoids in the Canadian aquatic environment: a literature review on current use products with a focus on fate, exposure, and biological effects. *Sci. Total Environ.* 505, 409–422.
- Arditsoglou, A., Voutsas, D., 2008. Passive sampling of selected endocrine disrupting compounds using polar organic chemical integrative samplers. *Environ. Pollut.* 156, 316–324.
- Bass, C., Denholm, I., Williamson, M.S., Nauen, R., 2015. The global status of insect resistance to neonicotinoid insecticides. *Pestic. Biochem. Physiol.* 121, 78–87.
- Beketov, M.A., Liess, M., 2008a. Acute and delayed effects of the neonicotinoid insecticide thiacloprid on seven freshwater arthropods. *Environ. Toxicol. Chem.* 27, 461–470.
- Beketov, M.A., Liess, M., 2008b. Potential of 11 pesticides to initiate downstream drift of stream macroinvertebrates. *Arch. Environ. Contam. Toxicol.* 55, 247–253.
- Belles, A., Pardon, P., Budzinski, H., 2014. Development of an adapted version of polar organic chemical integrative samplers (POCIS-nylon). *Anal. Bioanal. Chem.* 406, 1099–1110.
- Berghahn, R., Mohr, S., Hubner, V., Schmiediche, R., Schmiedling, I., Svetich-Will, E., Schmidt, R., 2012. Effects of repeated insecticide pulses on macroinvertebrate drift in indoor stream mesocosms. *Aquat. Toxicol.* 122–123, 56–66.
- Cheng, F., Li, H., Qi, H., Han, Q., You, J., 2017. Contribution of pyrethroids in large urban rivers to sediment toxicity assessed with benthic invertebrates *Chironomus dilutus*: a case study in South China. *Environ. Toxicol. Chem.* 36, 3367–3375.
- Dalton, R.L., Pick, F.R., Boutin, C., Saleem, A., 2014. Atrazine contamination at the watershed scale and environmental factors affecting sampling rates of the polar organic chemical integrative sampler (POCIS). *Environ. Pollut.* 189, 134–142.
- Di Carro, M., Bono, L., Magi, E., 2014. A simple recirculating flow system for the calibration of polar organic chemical integrative samplers (POCIS): effect of flow rate on different water pollutants. *Talanta* 120, 30–33.
- Ensminger, M.P., Budd, R., Kelley, K.C., Goh, K.S., 2013. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008–2011. *Environ. Monit. Assess.* 185, 3697–3710.
- Evelsizer, V., Skopec, M., 2016. Pesticides, including neonicotinoids, in drained wetlands of Iowa's prairie pothole region. *Wetlands* 36, 1–12.
- Guibal, R., Lissalde, S., Charriau, A., Guibaud, G., 2015. Improvement of POCIS ability to quantify pesticides in natural water by reducing polyethylene glycol matrix effects from polyethersulfone membranes. *Talanta* 144, 1316–1323.
- Guy, M., Singh, L., Mineau, P., 2011. Using field data to assess the effects of pesticides on Crustacea in freshwater aquatic ecosystems and verifying the level of protection provided by water quality guidelines. *Integr. Environ. Assess. Manag.* 7, 426–436.
- Harman, C., Allan, I.J., Vermeirssen, E.L., 2012. Calibration and use of the polar organic chemical integrative sampler—a critical review. *Environ. Toxicol. Chem.* 31, 2724–2738.
- Hladik, M.L., Kolpin, D.W., 2016. First national-scale reconnaissance of neonicotinoid insecticides in streams across the USA. *Environ. Chem.* 13, 12–20.
- Hladik, M.L., Kolpin, D.W., Kuivila, K.M., 2014. Widespread occurrence of neonicotinoid insecticides in streams in a high corn and soybean producing region, USA. *Environ. Pollut.* 193, 189–196.
- Hladik, M.L., Main, A.R., Goulson, D., 2018a. Environmental risks and challenges associated with neonicotinoid insecticides. *Environ. Sci. Technol.* 52, 3329–3335.
- Hladik, M.L., Corsi, S.R., Kolpin, D.W., Baldwin, A.K., Blackwell, B.R., Cavallin, J.E., 2018b. Year-round presence of neonicotinoid insecticides in tributaries to the Great Lakes, USA. *Environ. Pollut.* 235, 1022–1029.
- Jeschke, P., Nauen, R., Schindler, M., Elbert, A., 2011. Overview of the status and global strategy for neonicotinoids. *J. Agric. Food Chem.* 59, 2897–2908.
- Jin, S., Bluemling, B., Mol, A.P., 2015. Information, trust and pesticide overuse: interactions between retailers and cotton farmers in China. *NJAS-Wagen. J. Life Sci.* 72, 23–32.
- Klarich, K.L., Pflug, N.C., DeWald, E.M., Hladik, M.L., Kolpin, D.W., Cwiertyny, D.M., LeFevre, G.H., 2017. Occurrence of neonicotinoid insecticides in finished drinking water and fate during drinking water treatment. *Environ. Sci. Technol. Lett.* 4, 168–173.
- Li, H., Mehler, W.T., Lydy, M.J., You, J., 2011. Occurrence and distribution of sediment-associated insecticides in urban waterways in the Pearl River Delta, China. *Chemosphere* 82, 1373–1379.

- Li, H., Sun, B., Lydy, M.J., You, J., 2013. Sediment-associated pesticides in an urban stream in Guangzhou, China: implication of a shift in pesticide use patterns. *Environ. Toxicol. Chem.* 32, 1040–1047.
- Li, H., Zeng, E.Y., You, J., 2014. Mitigating pesticide pollution in China requires law enforcement, farmer training, and technological innovation. *Environ. Toxicol. Chem.* 33, 963–971.
- Lissalde, S., Mazzella, N., Mazellier, P., 2014. Polar organic chemical integrative samplers for pesticides monitoring: impacts of field exposure conditions. *Sci. Total Environ.* 488–489, 188–196.
- Lohmann, R., Muir, D., Zeng, E.Y., Bao, L.-J., Allan, I.J., Arinaitwe, K., Booi, K., Helm, P., Kaserzon, S., Mueller, J.F., Shibata, Y., Smedes, F., Tsapakis, M., Wong, C.S., You, J., 2017. Aquatic global passive sampling (AQUA-GAPS) revisited: first steps toward a network of networks for monitoring organic contaminants in the aquatic environment. *Environ. Sci. Technol.* 51, 1060–1067.
- 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.
- Main, A.R., Headley, J.V., Peru, K.M., Michel, N.L., Cessna, A.J., Morrissey, C.A., 2014. Widespread use and frequent detection of neonicotinoid insecticides in wetlands of Canada's prairie pothole region. *PLoS One* 9, e92821.
- Morrissey, C.A., Mineau, P., Devries, J.H., Sanchez-Bayo, F., Liess, M., Cavallaro, M.C., Liber, K., 2015. Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: a review. *Environ. Int.* 74, 291–303.
- Münze, R., Hannemann, C., Orlinskiy, P., Gunold, R., Paschke, A., Foit, K., Becker, J., Kaske, O., Paulsson, E., Peterson, M., Jernstedt, H., Kreuger, J., Schuurmann, G., Liess, M., 2017. Pesticides from wastewater treatment plant effluents affect invertebrate communities. *Sci. Total Environ.* 599–600, 387–399.
- Poulier, G., Lissalde, S., Charriau, A., Buzier, R., Delmas, F., Gery, K., Moreira, A., Guibaud, G., Mazzella, N., 2014. Can POCIS be used in Water Framework Directive (2000/60/EC) monitoring networks? A study focusing on pesticides in a French agricultural watershed. *Sci. Total Environ.* 497–498, 282–292.
- Qi, H., Li, H., Wei, Y., Mehler, W.T., Zeng, E.Y., You, J., 2017. Effect-directed analysis of toxicants in sediment with combined passive dosing and in vivo toxicity testing. *Environ. Sci. Technol.* 51, 6414–6421.
- Sadaria, A.M., Supowit, S.D., Halden, R.U., 2016. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: nationwide reconnaissance in United States wastewater. *Environ. Sci. Technol.* 50, 6199–6206.
- Sanchez-Bayo, F., Hyne, R.V., 2014. Detection and analysis of neonicotinoids in river waters-development of a passive sampler for three commonly used insecticides. *Chemosphere* 99, 143–151.
- Smit, C., Posthuma-Doodeman, C., Van Vlaardingen, P.d., De Jong, F., 2015. Ecotoxicity of imidacloprid to aquatic organisms: derivation of water quality standards for peak and long-term exposure. *Hum. Ecol. Risk Assess.* 21, 1608–1630.
- Smith, R., Middlebrook, R., Turner, R., Huggins, R., Vardy, S., Warne, M., 2012. Large-scale pesticide monitoring across Great Barrier Reef catchments-paddock to reef integrated monitoring, modelling and reporting program. *Mar. Pollut. Bull.* 65, 117–127.
- Solomon, K., Giesy, J., Jones, P., 2000. Probabilistic risk assessment of agrochemicals in the environment. *Crop Prot.* 19, 649–655.
- Starner, K., Goh, K.S., 2012. Detections of the neonicotinoid insecticide imidacloprid in surface waters of three agricultural regions of California, USA, 2010–2011. *Bull. Environ. Contam. Toxicol.* 88, 316–321.
- Tennekes, H.A., Sanchez-Bayo, F., 2011. Time-dependent toxicity of neonicotinoids and other toxicants: implications for a new approach to risk assessment. *J. Environ. Anal. Toxicol.* 4, 1–8.
- van Dijk, T.C., Van Staalduinen, M.A., Van der Sluijs, J.P., 2013. Macro-invertebrate decline in surface water polluted with imidacloprid. *PLoS One* 8, e62374.
- van Metre, P.C., Alvarez, D.A., Mahler, B.J., Nowell, L., Sandstrom, M., Moran, P., 2017. Complex mixtures of pesticides in Midwest U.S. streams indicated by POCIS time-integrating samplers. *Environ. Pollut.* 220, 431–440.
- Vermeirssen, E.L.M., Dietschweiler, C., Escher, B.I., van der Voet, J., Hollender, J., 2012. Transfer kinetics of polar organic compounds over polyethersulfone membranes in the passive samplers POCIS and Chemcatcher. *Environ. Sci. Technol.* 46, 6759–6766.
- Xiong, J., Li, H., Ma, X., You, J., 2018. Synthesis and application of a novel solid-phase extraction adsorbent for multiresidue analysis of insecticides in water. *J. Sep. Sci.* 41, 525–533.
- Yamamoto, A., Terao, T., Hisatomi, H., Kawasaki, H., Arakawa, R., 2012. Evaluation of river pollution of neonicotinoids in Osaka City (Japan) by LC/MS with dopant-assisted photoionisation. *J. Environ. Monit.* 14, 2189–2194.
- Yi, X., Li, H., Ma, P., You, J., 2015. Identifying the causes of sediment-associated toxicity in urban waterways in South China: incorporating bioavailability-based measurements into whole-sediment toxicity identification evaluation. *Environ. Toxicol. Chem.* 34, 1744–1750.
- Zhang, Z., 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.
- Zhang, J., Wei, Y., Li, H., Zeng, E.Y., You, J., 2017. Application of Box-Behnken design to optimize multi-sorbent solid phase extraction for trace neonicotinoids in water containing high level of matrix substances. *Talanta* 170, 392–398.