



Sediment–water distribution of contaminants of emerging concern in a mixed use watershed



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HIGHLIGHTS

- Sediment–water distributions of CECs were not governed by hydrophobic partitioning.
- Water concentrations exhibited seasonal variation; sediment concentrations did not.
- Spatial variations correlated with land use for many CECs in water and/or sediment.
- Hydrophobicity and persistence affected predictability of distribution coefficients.

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ABSTRACT

This study evaluated the occurrence and distribution of 15 contaminants of emerging concern (CECs) in stream water and sediments in the Zumbro River watershed in Minnesota and compared these with sub-watershed land uses. Sixty pairs of sediment and water samples were collected across all seasons from four stream sites for over two years and analyzed for selected personal care products, pesticides, human and veterinary medications, and phytoestrogens. Spatial and temporal analyses indicate that pharmaceuticals and personal care products (urban/residential CECs) are significantly elevated in water and/or sediment at sites with greater population density (>100 people/km²) and percentage of developed land use (>8% of subwatershed area) than those with less population density and land area under development. Significant spatial variations of agricultural pesticides in water and sediment were detectable, even though all sites had a high percentage of agricultural land use. Seasonality in CEC concentration was observed in water but not in sediment, although sediment concentrations of three CECs did vary between years. Average measured non-equilibrium distribution coefficients exceeded equilibrium hydrophobic partitioning-based predictions for 5 of the 7 detected CECs by at least an order of magnitude. Agreement of measured and predicted distribution coefficients improved with increasing hydrophobicity and in-stream persistence. The more polar and degradable CECs showed greater variability in measured distributions across different sampling events. Our results confirm that CECs are present in urban and agricultural stream sediments, including those CECs that would typically be thought of as non-sorptive based on their log K_{ow} values. These results and the observed patterns of sediment and water distributions augment existing information to improve prediction of CEC fate and transport, leading to more accurate assessments of exposure and risk to surface water ecosystems.

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1. Introduction

Contaminants of emerging concern (CECs) are widely found in the environment and include natural/synthetic hormones, pharmaceuticals

and personal care products (PPCPs), veterinary medicines, industrial/household products, pesticides, and other chemical and physical agents (Caliman and Gavrilescu, 2009; Kolpin et al., 2002). CECs are not commonly subject to environmental monitoring or regulations, but they have potential adverse effects on human and ecosystem health (USGS, 2011), which include endocrine disruption in aquatic systems (Caliman and Gavrilescu, 2009) and human populations (Damstra, 2002), induction of antibiotic resistance (Pharmaceuticals in the Environment,

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2004), and direct aquatic toxicity (Richardson et al., 2005). Numerous sources of CECs to surface water ecosystems include concentrated animal feeding operations (CAFOs) (Tolls, 2001), row crops (Gilliom et al., 2006), lawns and golf courses (Gilliom et al., 2006), industry (Kolpin et al., 2002), roads (Zhang et al., 2009), landfills (Heberer, 2002), land-applied sludge or biosolids (Kinney et al., 2006), and wastewater treatment system effluent (Heberer, 2002; Drillia et al., 2005). National and international reviews of CEC occurrence in surface waters are available (Caliman and Gavrilescu, 2009; Heberer, 2002) with far fewer reports of CECs in river sediments (Lei et al., 2009; Xue et al., 2005; Lee et al., 2008; Kim and Carlson, 2007).

Sorption is a dynamic process that occurs primarily through hydrophobic interactions or attractive force and is related to the physico-chemical properties of the sediment and the sorbate (Karickhoff, 1984). Observed empirical relationships between the soil organic carbon–water partition coefficient (K_{oc}) and the octanol–water partition coefficient (K_{ow}) for neutral hydrophobic organic contaminants (HOCs) are often able to predict the overall solid–water distribution coefficient (K_d) within an order of magnitude (Doucette, 2000). Although HOC sorption has been studied extensively, relatively little information is available on sorption of hydrophilic and moderately hydrophobic contaminants, including many CECs (Yamamoto et al., 2003). Sorption of polar/ionizable compounds is influenced strongly by non-hydrophobic interactions when relevant mineral or soil organic matter components are present (Tolls, 2001; Yamamoto et al., 2003; Schenzel et al., 2012; Nguyen et al., 2005; MacKay and Vasudevan, 2012; Karickhoff, 1981). For these compounds, K_d is often poorly predicted by K_{ow} and K_{oc} relationships, with non-hydrophobic interactions driving sorption for compounds with relevant functionalities (e.g., amine, carboxylic acid, or hydroxyl groups). Models are being developed for sorption of such compounds (Nguyen et al., 2005; MacKay and Vasudevan, 2012; Smaraweera et al., 2014).

Few studies have analyzed CECs in water and sediment samples collected at the same time and place (Kim and Carlson, 2007; Kim and Carlson, 2006; Yang et al., 2010; Massey et al., 2010; Tomasek et al., 2012). Measured in-stream K_d values for low- K_{ow} antibiotics and natural hormones exceeded K_{ow} -based predictions by at least an order of magnitude (Lei et al., 2009; Kim and Carlson, 2007; Massey et al., 2010). In contrast, hydrophobic synthetic hormones ($\log K_{ow} > 4$) agreed more closely with predictions (Lei et al., 2009). Similarly, the distributions of neutral CECs with $\log K_{ow} > 2$ (e.g., carbamazepine (Scheytt et al., 2005; Yamamoto et al., 2009) and atrazine (Wauchope and Myers, 1985)) have been well-predicted by K_{ow} - K_{oc} relationships. Wide “within-compound” spatial and temporal variations in K_d , often up to three orders of magnitude, have been observed for individual CECs across field sampling events (Kim and Carlson, 2006; Boxall et al., 2003). It has been suggested that this variation is due to non-hydrophobic interactions, hydrologic factors, chemical usage variations, and variable attenuation rates between aqueous and sediment-bound fractions (Tolls, 2001; Kim and Carlson, 2007; Yamamoto et al., 2003; Kim and Carlson, 2006; Massey et al., 2010; Yamamoto et al., 2009). Laboratory studies have corroborated both the within-compound variations and the deviation from K_{ow} -based predictions (up to 4 orders of magnitude) for many low- K_{ow} CECs (Yamamoto et al., 2009; Davis et al., 2006; Yamamoto et al., 2005). Nevertheless, most field studies of sediment–water distribution of CECs have analyzed only a few pairs of samples or sampling periods. Thus, there is little available information on the spatial–temporal variation of sediment concentrations and sediment–water distributions in the environment.

The objectives of this study were to assess the occurrence, distribution, and spatial–temporal variation of CECs measured in stream water and sediments of a mixed-use watershed and to evaluate the use of equilibrium partition coefficients to predict non-equilibrium sediment–water distribution of CECs in streams. Understanding CEC sediment–water distributions and variation is important because these processes influence the fate and bioavailability of CECs, thus

affecting the sediment's function as a CEC source or sink (Xue et al., 2005). In addition, CEC presence in the sediment will influence benthic organisms' exposures to CECs as well as the development of antimicrobial resistance (Pharmaceuticals in the Environment, 2004). The results of this study will ultimately enhance future CEC research, predictive methods, and effective targeting of monitoring, management, and mitigation solutions.

2. Methods

2.1. Study area and CECs of interest

The South Fork of the Zumbro River (SFZR) watershed (Fig. 1) in southeastern Minnesota contains a gradient of land uses across its subwatersheds. This provides a unique opportunity to study CECs from both agricultural and urban sources. Four sampling sites in four subwatersheds were chosen to reflect different types and extents of land uses, different human and animal populations, and use of septic systems versus a city sanitary sewer system (see Fig. 1 and Table 1).

A detailed land use and hydrologic characterization was conducted by McGhie Betts, Inc. (Rochester, MN) (discussed in Karpuzcu et al. (2014)). Pertinent information is presented in Table 1, and was used to categorize sites as being primarily agricultural or urban/residential for categorical data analysis and interpretation.

Fifteen CECs were selected based on surface water occurrences reported in the literature (Kolpin et al., 2002; Lee et al., 2004), chemical usage patterns (Pharmaceuticals in the Environment, 2004; Lee et al., 2008; Keefe et al., 2009; VanRyswyk and Tollefson, 2008), potential effects (Pharmaceuticals in the Environment, 2004; Combalbert and Hernandez-Raquet, 2010), and land-use associations (Kolpin et al., 2002; Lee et al., 2008). The suite includes three agricultural herbicides, one veterinary antibiotic, five urban/residential PPCPs, and six mixed use compounds (pesticides, phytoestrogens, and antibiotics) (Table 2).

2.2. Sample collection, processing, and analysis

Sampling periods (four in 2011 and five in 2012) were chosen to reflect a variety of seasonal, flow, and land use conditions. In the late summer (August–September), fall (October–November), and winter (January–February) periods, low flows were expected to result in enhanced CEC signals associated with sanitary sewers and with reduced contributions from runoff. During spring melt (March), CECs associated with land-applied manure and other terrestrial components were expected to be transported with snowmelt runoff. During early summer (May–June), runoff of row crop herbicides was expected to be associated with precipitation events.

Two sampling days occurred one week apart for all sites in early summer, late summer, and fall periods. Prior to use, all field, laboratory, and storage equipment was cleaned with CEC-free soap and distilled water, triple rinsed with ultrapure water, methanol-rinsed, and (for glassware and metals) heated to 400 °C for 3 h. Sediment samples were collected from the top 5 cm of multiple areas across the width of the stream using a stainless steel scoop. The samples were deposited into cleaned 1-L glass jars. The jars were sealed with Teflon-lined lids and transported on ice to the storage facility, where they were frozen (−18 °C) until processing. Water samples were collected a few minutes prior to sediment samples by submerging a clean amber glass or stainless steel container into the stream to a depth of 10–20 cm. Water samples were sealed with Teflon-lined or stainless steel lids and transported on ice to the laboratory. Water samples were refrigerated at 4 °C until processing, which was initiated with 72 h of collection. Corollary physical and chemical data were acquired using *in situ* sondes (YSI Inc., Yellow Springs, OH, USA; Hach Hydromet, Loveland, CO, USA), YSI flowmeters, and existing USGS monitoring stations.

Water samples (2 L) were filtered through 0.7 µm glass-fiber filters, spiked with a surrogate standard (metazachlor, which is not approved

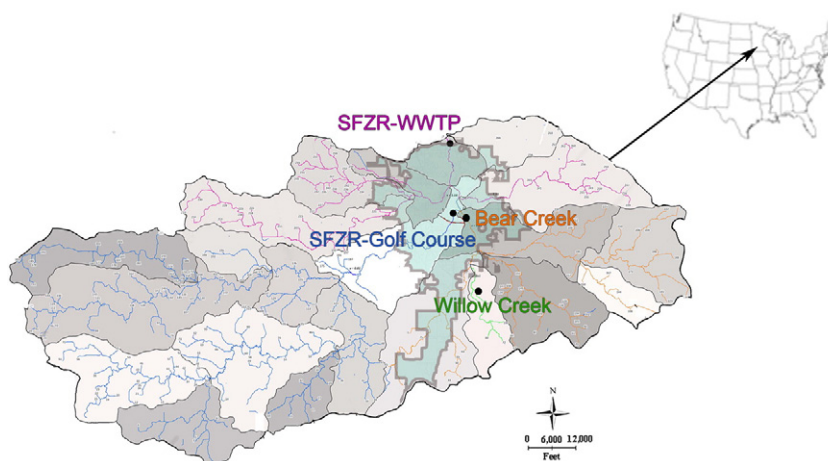


Fig. 1. Map of South Fork of Zumbro River (SFZR) study area. Labels indicate sampling site locations. The City of Rochester is indicated by the outlined area in the middle of the study area. The SFZR flows from the southwest portion of the study area into Rochester; flows past the SFZR-Golf Course site to SFZR-WWTP; and then flows out of the study area. Willow Creek flows into Bear Creek; Bear Creek flows into the SFZR just downstream of SFZR-Golf Course.

for use in the U.S.A.), and processed *via* solid phase extraction (SPE) using an Autotrace 280 (Dionex, Sunnyvale, CA, USA) equipped with Oasis HLB cartridges (6 cm³, with 500 mg HLB sorbent) (Waters, Milford, MA, USA). Extraction solvents were acetonitrile and acetonitrile/0.1% formic acid. Complete SPE parameters are presented in the Supporting Information (SI). The eluate was collected in glass culture tubes and evaporated under nitrogen to near-dryness. Following evaporation, the sample was reconstituted to 1.5 mL with acetonitrile and ultrapure water (1:1), transferred to amber liquid chromatography vials, and stored at -18°C until analysis.

Sediment samples (10 g dry weight) were processed by the following methods: (a) sieving the wet sediment through a 2 mm sieve, (b) homogenizing, (c) freeze-drying, (d) adding the surrogate standard, (e) allowing overnight equilibration, (f) extracting using a Dionex ASE 350 (Dionex, Sunnyvale, CA, USA) with 33-mL ASE cells (details in the SI), and (g) evaporation, cleanup, and subsequent processing as described in the SI.

Concentrations of the CECs were quantified on a Shimadzu (Kyoto, Japan) high performance liquid chromatograph coupled to an Applied Biosystems (Carlsbad, CA, USA) API 3200 triple quadrupole mass spectrometer using electrospray ionization in scheduled multiple reaction monitoring mode in either positive or negative mode. Tuning parameters were optimized for each analyte by direct infusion and are detailed along with other parameters in the SI.

Two sediment samples from each site were analyzed for total organic carbon (TOC), composition, and major elements and ions at the University of Minnesota Soil Testing Research Analytical Laboratory (St. Paul, MN, USA).

2.3. Modeling and statistical analysis

The KocWIN application in EPI Suite (EPA, U.S., 2013) was used to generate predicted log K_{oc} values (using the K_{ow} and Molecular

Connectivity Index approaches). Sediment–water distributions from previous field studies and laboratory partitioning data for the CECs were collected from available publications (citations listed in Section E of the SI). Statistical analysis was conducted using Stata (StataCorp LP, College Station, TX, USA), and SPSS (IBM, Armonk, NY, USA). Box–Cox assessments and transformations were used to satisfy assumptions of normality and constant variance. Categorical analysis was the primary focus of statistical analysis due to the small number of sites ($n = 4$). Two-way analysis of variance (ANOVA) and the protected least significant difference multiple comparison procedure were used to determine the significance and magnitude of between-group variation for the investigated factors using both censored/ranked and uncensored/transformed datasets (with $\alpha = 0.05$). Spearman's rank correlation analysis was used to assess the influence of numerical independent variables and corroborate the categorical analysis and interpretation.

2.4. Data quality assurance/quality control and presentation

Method reporting limits (MRLs) were established using published U.S. EPA methods (EPA, U.S., 2012). These were compared with a USGS method (Sandstrom, 2001) and the minimum CEC mass that consistently produced a signal-to-noise ratio of at least nine in order to ensure consistency across numerous analytical runs. Calibration curves were generated using six standard levels across three orders of magnitude of analyte concentration. R-squared values were greater than 0.98 for all detected analyte calibration curves.

Each analytical run included laboratory spikes to assess analytical accuracy and precision and laboratory blanks to assess contamination and instrument carryover. Laboratory spikes were ultrapure water/HPLC-grade acetonitrile (1:1) samples that were spiked with compounds of interest directly into the liquid chromatography vials before injection into the liquid chromatograph. Laboratory blanks were identical to laboratory spikes except that they were not spiked with compounds

Table 1
Characteristics of subwatersheds in the South Fork of the Zumbro River (SFZR) watershed that were sampled in this study. Average flows are for 2011–2012. Percent sewer or septic indicates the portion of the given population using municipal sewer or private onsite sanitary (septic) systems, respectively.

| Sampling sites | Subwatershed characteristics | | | | | |
|--|-------------------------------|-------------------------|----------------------|-------------------------|------------------------------------|---|
| | Ave. flow (m ³ /s) | Area (km ²) | Extent developed (%) | Agricultural extent (%) | Est. human pop. (% sewer/% septic) | Livestock types (pop.) |
| Willow Creek | 0.08 | 18.7 | 2.6% | 53.2 | 432 (15/85) | Poultry (35k) |
| Bear Creek | 1.5 | 212 | 12.0% | 52.3 | 28,173 (75/25) | Poultry (50k)/swine (20k)/cattle (7k) |
| SFZR at Golf Course (SFZR-Golf Course) | 3.7 | 404 | 3.0% | 73.3 | 13,187 (70/30) | Poultry (8k)/swine (47k)/cattle (12k) |
| SFZR downstream of WWTP (SFZR-WWTP) | 5.7 | 786 | 8.1% | 64.9 | 97,173 (85/15) | Poultry (101k)/swine (68k)/cattle (22k) |
| Total SFZR area | | 809 | 10.5% | 61.8 | 98,655 (85/15) | Poultry (101k)/swine (73k)/cattle (23k) |

Table 2
Description of use and selected physical-chemical characteristics of CECs in this study.

| Compound | Primary use/class | CAS# | K_{ow} | Solubility (mg/L) | pK _a |
|-----------------------------------|---|------------|---------------------------------------|-------------------------------------|---|
| Acetaminophen | Urban/residential – PPCP analgesic | 103-90-2 | 0.46 ^a | 14,000 ^a | 9.4 ^d |
| Acetochlor | Agriculture – herbicide | 34256-82-1 | 3.03 ^a , 3 ^b | 233 ^a | N/A |
| Atrazine | Agriculture – herbicide | 1912-24-9 | 2.61 ^a , 2.75 ^b | 35 ^a | 1.68 ^d |
| Caffeine | Urban/residential – PPCP stimulant | 58-08-2 | –0.07 ^a | 21,600 ^a | 0.6 ^d , 14 ^d |
| Carbamazepine | Urban/residential – PPCP prescription | 298-46-4 | 2.45 ^a | 112 ^a | 13.94 ^d |
| Carbaryl | Mixed – pesticide | 63-25-2 | 2.36 ^a | 110 ^a | 10.4 ^d |
| Cotinine | Urban/residential – PPCP metabolite | 486-56-6 | 0.07 ^a | 55,000 ^f | <5.0 ^d |
| Daidzein | Mixed – phytoestrogen | 486-66-8 | 2.55 ^c | 570 ^e , 620 ^f | 7.4 ^g , 9.9 ^g |
| N,N-Diethyl-meta-toluamide (DEET) | Urban/residential – PPCP insect repellent | 134-62-3 | 2.18 ^a | 174 ^e , 666 ^f | N/A |
| Erythromycin | Mixed – PPCP prescription antibiotic | 114-07-8 | 3.06 ^a | 2 ^d , 0.51 ^e | 8.8 ^d |
| Genistein | Mixed – phytoestrogen | 446-72-0 | 2.84 ^c | 258 ^e , 412 ^f | 6.7 ^g , 9.6 ^g , 13.0 ^g |
| Iprodione | Mixed – fungicide | 36734-19-7 | 3.00 ^a | 13.9 ^a | N/A |
| Metolachlor | Agriculture – herbicide | 51218-45-2 | 3.13 ^b | 530 ^a | N/A |
| Monensin | Veterinary – antibiotic | 17090-79-8 | 5.43 ^c | 0.003 ^e | 4.3 ^d |
| Sulfamethoxazole | Mixed – PPCP prescription antibiotic | 723-46-6 | 0.89 ^a , 0.48 ^c | 610 ^a | 1.8 ^d , 5.6 ^d |

PPCP = pharmaceuticals and personal care products. N/A = not available.

^a EpiSuite Experimental Database.

^b Gilliom et al. (2006).

^c EpiSuite KOWWIN Est.

^d TOXNET Hazardous Substances Data Bank.

^e EpiSuite WSKOW Est.

^f EpiSuite WATERNT Est.

^g Kelly et al. (2012).

of interest. Procedural spikes and blanks were created and subjected to the various extraction steps in order to assess contamination or loss of recovery resulting from sample processing. Field blanks were included to assess a potential contamination resulting from sample collection, handling, and storage. Spiked environmental samples were used to assess matrix interference. If a laboratory blank response was more than 20% of that in an associated environmental sample, data were flagged and reviewed. If a laboratory blank response was above 50% of that in an associated environmental sample, the data were reported as “non-detect”. This occurred once for caffeine in a single sediment sample. No other blank responses were above 20% of the MRLs of any detected CECs.

Analytical recoveries for all detected CECs were between 64 and 170% in laboratory spikes, 48–150% in matrix water samples spiked before injection, 60–110% in sediment samples spiked prior to SPE cleanup, and 21–103% in sediment samples spiked prior to ASE. For individual detected CECs, relative standard deviations (RSDs) ranged from 4.5 to 17% for repeated analyses of environmental sediment samples ($n = 3$) and from 5.2 to 9.8% for replicate spiked sediment samples ($n = 3$). Quality assurance/quality control results are presented in Table SI 2.

2.5. Analytical method considerations

The samples were quantified using the external calibration approach (quantification of unknown CEC concentrations in environmental samples by comparison with calibration curves that are generated from analysis of laboratory standards of known concentration). It was not possible to use the internal standard calibration approach due to the diversity of compounds included in this study. It was not feasible to include the number of standards that would be required to confidently represent each of these CECs for internal standard calibration and correction against surrogate standard recoveries.

Comparison of recoveries from ultrapure water, matrix water, and matrix sediment samples that were spiked with CECs of interest indicated that recoveries of most CECs were acceptable and within a range that might be expected for a multi-residue method for diverse CECs (data are presented in Table SI 2). Measurement precision as indicated by relative standard deviations (RSDs) of replicate analyses of the same unspiked environmental samples and spiked environmental samples was also

considered acceptable (RSDs < 20% in most instances). Coefficients of determination (r^2) of linear regressions of external calibration curves were consistently greater than 0.992 for all CECs.

We did not correct data for matrix effects or surrogate recovery. Some losses of recovery are expected to occur due to matrix effects and sample processing, and will vary for different CECs. Correction for these losses would tend to increase the reported concentrations of CECs in environmental samples. Thus, not correcting for matrix effects is a conservative approach. In reality, the actual environmental concentrations may be greater than those reported herein. Also, correction for matrix effects will not affect the spatiotemporal comparison of water or sediment samples when comparing the same CECs; each CEC would receive the same correction in a given matrix such that different samples would maintain approximately the same proportionality. In developing the K_{d-obs} , reduced recovery due to matrix effects would be likely to affect sediment values more than water values, which would result in actual K_{d-obs} values that may be greater than those reported herein.

Correction for surrogate recoveries can account for sample-specific issues that may arise during sample processing and analysis. While it is preferable to correct for surrogate losses in most instances, the number of surrogate samples that would be required in this study in order to properly conduct this procedure precluded the use of surrogate corrections. However, any anomalous surrogate and internal standard responses were examined for possible sampling or measurement error.

3. Results and discussion

3.1. Detection and concentrations of CECs in sediment and water

In total, 60 paired sets of water and sediment samples were analyzed for CECs (15 pairs from each of 4 sites). Eight of the fifteen investigated CECs were detected in at least one sediment sample (Table 3), and thirteen CECs were detected in at least one water sample (Table SI 3). All of the CECs found in sediment were also found in water, but not necessarily in the same sample pair. Individual sediment samples are contained between two and six CECs, with an average of four CECs per sample (Table SI 3). Metolachlor was only detected in one sediment sample and is not discussed further. All sample data are presented in the SI (Table SI 3), including basic sediment and water characteristics (Table SI 4).

Table 3^aSediment (n=60) and water (n=60) occurrence data for the 7 CECs detected in more than one sediment sample.

| CEC | MRLs in sediment (ng/g)/water (ng/L) | Detection frequency sediment/water, % | Concentration range (mean) in sediment (ng/g) | Concentration range (mean) in water (ng/L) | Avg. log K_{d-obs} | Difference between average measured log K_{d-obs} and predicted log K_d |
|---------------|--------------------------------------|---------------------------------------|---|--|----------------------|---|
| Caffeine | 0.12/0.58 | 100/98.3 | 0.16–1.3 (0.44) | 0.84–250 (44) | 1.3 | 4.1 |
| Acetaminophen | 0.11/0.56 | 90.0/88.3 | 0.16–21 (2.8) | 0.99–7.0 (3.5) | 2.5 | 4.8 |
| DEET | 1.3/6.4 | 30.0/88.3 | 1.3–3.5 (2.2) | 7.2–110 (27) | 2.0 | 2.6 |
| Carbamazepine | 0.02/0.11 | 13.3/45.0 | 0.03–0.11 (0.06) | 0.27–150 (49) | –0.2 | 0.1 |
| Daidzein | 0.10/0.51 | 21.7/31.7 | 0.17–1.1 (0.50) | 0.54–3.1 (1.1) | 2.3 | 2.5 |
| Atrazine | 0.06/0.30 | 21.7/100 | 0.06–0.28 (0.13) | 1.8–390 (40) | 0.6 | 0.7 |
| Acetochlor | 0.18/0.89 | 56.7/43.3 | 0.21–49 (5.2) | 1.2–180 (28) | 2.2 | 1.9 |

^a All sediment concentrations are in units of ng/g dry weight. Method reporting limits (MRLs), detection frequencies, summary concentration data, and mean K_{d-obs} (over all sampling events in which the CEC was detected in both water and sediment) for the CECs in sediment and water are included. For each CEC, the difference between its mean log K_{d-obs} and a K_{ow} -based prediction (Karickhoff, 1981) is given. Rows are arranged in order of increasing K_{ow} .

3.2. Seasonal and spatial differences in CECs present in sediment versus water

Figs. 2A, B and 3A, B express mean CEC concentrations by season and site, respectively, in sediment and water. The ANOVA and pairwise comparison results are provided in Table 4.

No CECs exhibited seasonality in sediment (Fig. 2A), but several CECs exhibited seasonality in water (denoted with an asterisk (*) in Fig. 2B). Elevated water concentrations occurred in summer periods for four CECs ($p < 0.05$), including caffeine, acetaminophen, and the agricultural herbicides acetochlor and atrazine. Daidzein exhibited its highest water concentrations in spring. The seasonality in water as compared to sediment is likely explained by water concentrations responding more rapidly to changes in aqueous inputs and in-stream flows, as well as to seasonal fate-related parameters such as sunlight and temperature variation, than do sediment concentrations (Antonic and Heath, 2007). In fact, dissolved and sorbed CEC fractions are affected differently by common transformation/transport processes including photodegradation (Caliman and Gavrilescu, 2009), biodegradation (Combalbert and Hernandez-Raquet, 2010), concentration/dilution, and temporal input variations. Concentrations of some CECs in sediment did occasionally exhibit variations of an order of magnitude or more in between weekly sampling events. These tended to follow precipitation events in early and late summer when in-stream flows exhibited large variations. This correlation of sediment concentrations with hydrologic flow may be due to deposition of fresh sediments having differing concentrations of CECs than existing sediments, or due to resuspension and mixing of sediments with different concentrations.

None of the CECs exhibited significant annual variation in water concentrations. Sediment CEC concentrations did exhibit changes on this

longer, annual time scale (Table 4), as has been previously observed (Antonic and Heath, 2007). Acetaminophen, caffeine, and acetochlor varied annually in sediment, and all exhibited higher concentrations in 2012 than 2011. These yearly trends and high detection frequencies may be reflective of increasing inputs, ongoing accumulation of these CECs in sediment, or other factors. For instance, total flow at the study sites was smaller in 2012 than 2011. This would increase the effective exposure time of sediments to aqueous CEC concentrations, resulting in higher sediment concentrations. Additionally, annual sales of acetochlor in Minnesota increased from 2009 to 2011, and were as follows (in millions of pounds): 2.63 (2009), 3.35 (2010), and 3.98 (2011); 2012 sales data were not available at the time of writing (MDA, 2009). Increased pesticide application may therefore also explain the increased concentrations of acetochlor and other CECs in sediments between years. Longer-term studies would be required to confirm annual patterns.

Location (site) affected similar numbers of CECs in water and sediment, but with divergent patterns between phases. Sites with elevated CEC concentrations in sediment generally did not exhibit elevated concentrations in water, and vice versa; nevertheless, patterns of CEC detection with respect to location could be discerned. Land use associations of PPCPs were stronger compared to agricultural pesticides (Table 4). For example, the site downstream from the WWTP (SFZR-WWTP) exhibited significantly elevated concentrations of all PPCPs (acetaminophen, caffeine, carbamazepine, DEET) in water (Fig. 3A), and of carbamazepine in sediment (Fig. 3B). Bear Creek was associated with the highest human population density among sites, and exhibited elevated sediment concentrations of acetaminophen and caffeine. Indeed, even with only four sites for analysis, sediment concentrations of caffeine were positively correlated with population density (Spearman's rank correlation coefficient (ρ) = 0.297, p = 0.021) and percentage of

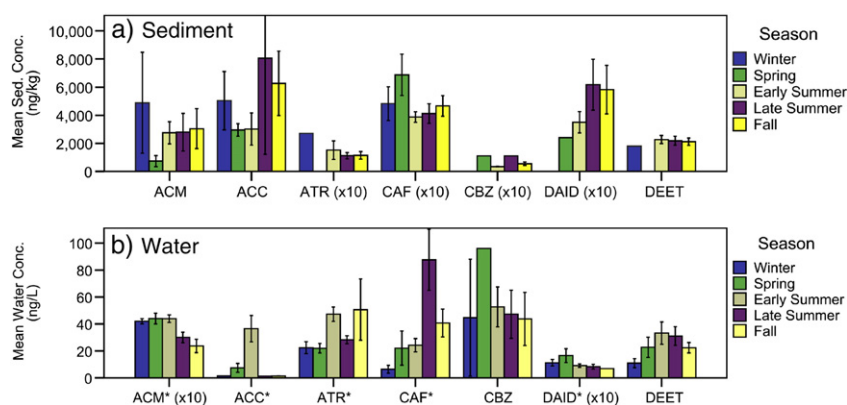


Fig. 2. Seasonal mean CEC concentrations in (a) sediment (ng/kg dry weight) and (b) water (ng/L). A (x10) notation indicates that the displayed concentration is ten times greater than actual concentration. Asterisks (*) indicate significant seasonality for that CEC. Error bars represent standard error of the mean. If no error bar is present, this is due to lack of sufficient number of detections during that season to calculate standard error. Seasonal detection frequencies are presented in Table S1. Acetaminophen (ACM), acetochlor (ACC), atrazine (ATR), caffeine (CAF), carbamazepine (CBZ), daidzein (DAID).

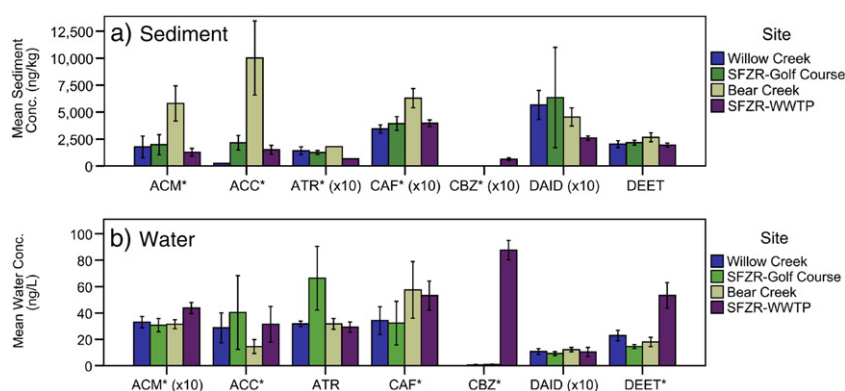


Fig. 3. Mean concentrations of CECs by site in (a) sediment (ng/kg dry weight) and (b) water (ng/L). A (x10) notation indicates that the displayed concentration is ten times greater than actual concentration. Asterisks (*) indicate significant variation across sites for that CEC. Error bars represent standard error of the mean. If no error bar is present, this is due to lack of sufficient number of detections at that site to calculate standard error. Detection frequencies by site are presented in Table SI 5. Acetaminophen (ACM), acetochlor (ACC), atrazine (ATR), caffeine (CAF), carbamazepine (CBZ), Daidzein (DAID), South Fork of the Zumbro River (SFZR).

residential land use ($\rho = 0.319$, $p = 0.013$). Other location-based influences on CEC detection appeared to be hydrological or morphological in nature. For example, Bear Creek exhibited a uniquely shallow (~30 cm) and wide (~15 m) morphology, with a primarily bedrock streambed and frequent low-level turbulence. These characteristics affect sediment deposition and CEC concentrations. Sediment deposition appeared to occur only along the stream bank and in isolated ridges and clefts of the streambed. Complete light penetration of the water column at Bear Creek, particularly in the summer, helps explain the lack of correspondingly elevated water concentrations of caffeine and acetaminophen, both of which are photodegradable (Calza et al., 2012; Lam et al., 2004).

Although less clear and consistent, spatial variations of agricultural CECs were evident in this study. These more ambiguous occurrence patterns of agricultural *versus* urban/residential CECs reflect a more consistent allocation of agricultural land use among sites, in contrast to the greater spread in urban/residential land use allocation among sites (Table 1). Acetochlor concentrations were elevated in water and sediments at Bear Creek, a site with 52.3% agricultural land use (along with its aforementioned high human population density). Atrazine concentrations were elevated in sediments at Willow Creek (a site with 53.2% agricultural land use and the lowest human population density among study sites). Atrazine showed marginally significant spatial variation in water concentrations ($p = 0.083$), which speaks to diffuse sources such as atmospheric deposition in addition to agricultural runoff. Acetochlor and atrazine are used on the same crops, with acetochlor use increasing and atrazine use decreasing in Minnesota. The lack of covariance of these CECs across sites could be due to varying usage among farmers in the subwatersheds or to differences in their relative persistence and transport. The elevation of atrazine concentrations in Willow

Creek sediments but not in water compared to other sites may reflect a historical input and record in sediment in this subwatershed that is less evident in water concentrations with atrazine's recent sales decline. Karpuzcu et al. (2014) used a multivariate technique (principal component analysis (PCA)) with an expanded set of water samples collected from this study area to discern patterns among groups of CECs that are not as apparent when investigating individual CECs. Atrazine, acetochlor, and metolachlor were strongly associated with a principal component that was attributed to agricultural land uses. The results of Karpuzcu et al. (2014) thus reinforce our observation that occurrence patterns of agricultural CECs in this mixed use area are evidence of a gradient of seasonal agricultural land use influences, and associated inputs to streams. This also highlights the importance of robust statistical and sampling methodologies to discern such patterns, especially in watersheds such as the SFZR where all studied sites are associated with more than 50% agricultural land use.

3.3. Sediment–water distributions (K_{d-obs})

An observed sediment–water distribution coefficient, K_{d-obs} , was calculated each time that a CEC was detected in sediment and water samples from the same sampling event (Table 3, Fig. 4, and Table SI 3). In Fig. 4, two trends are apparent as follows: (1) most of the CEC K_{d-obs} values are above the K_{ow} -based line, and (2) K_{d-obs} values generally span orders of magnitude for a given CEC.

The K_{d-obs} values are not assumed to be true equilibrium partitioning coefficients, for flowing systems cannot be assumed to be at equilibrium. However, understanding sediment–water distribution behavior is desirable for chemical fate, ecotoxicological, and risk assessment considerations. Models relating K_{ow} to K_{oc} are well-established, use readily

Table 4

^aP-values of ANOVA results and pairwise comparisons for the significance of site, year, and seasonal factors on CEC variability.

| Factor | Parameter | Acetaminophen | Acetochlor | Atrazine | Caffeine | Carbamazepine | Daidzein | DEET |
|--------|----------------------|-----------------|----------------|----------|------------------|----------------|----------|---------|
| Season | [C] _{sed} | 0.072 | 0.192 | 0.829 | 0.125 | 0.577 | 0.334 | 0.342 |
| | [C] _{water} | 0.004* | 0.001* | 0.001* | 0.005* | 0.170 | 0.010* | 0.208 |
| | K_{d-obs} | 0.013* (LS/F/W) | 0.0001* (LS/F) | 0.109 | <0.0001* (W/SPR) | 0.084 | NC | 0.443 |
| Site | [C] _{sed} | 0.0003* | <.0001* | 0.021* | 0.001* | 0.031* | 0.449 | 0.462 |
| | [C] _{water} | <0.0001* | 0.017* | 0.083 | 0.003* | <0.0001* | 0.641 | 0.0004* |
| | K_{d-obs} | 0.015* (BC) | 0.023* (BC) | 0.071 | 0.082 | 0.0084* (WWTP) | NC | 0.765 |
| Year | [C] _{sed} | 0.003* (2012) | 0.016* (2012) | 0.292 | 0.032* (2012) | 0.939 | 0.404 | 0.656 |
| | [C] _{water} | 0.236 | 0.133 | 0.063 | 0.094 | 0.169 | 0.956 | 0.134 |
| | K_{d-obs} | 0.317 | 0.854 | 0.227 | 0.347 | 0.024* (2011) | NC | 0.153 |

^a Significant p-values are indicated with an asterisk (*). For significant effects on K_{d-obs} , the factor level listed in parenthesis indicates the group(s) that was significantly higher than other groups. For significant effects of site or season on water or sediment concentrations, see Figs. 2 and 3 for point estimates of the mean; for effect of year on water or sediment concentrations, the higher of the two years is listed in parentheses. NC = not calculated due to lack of sufficient number of data points; winter (W), spring (SPR), late summer (LS), fall (F), Bear Creek (BC), SFZR-WWTP (WWTP).

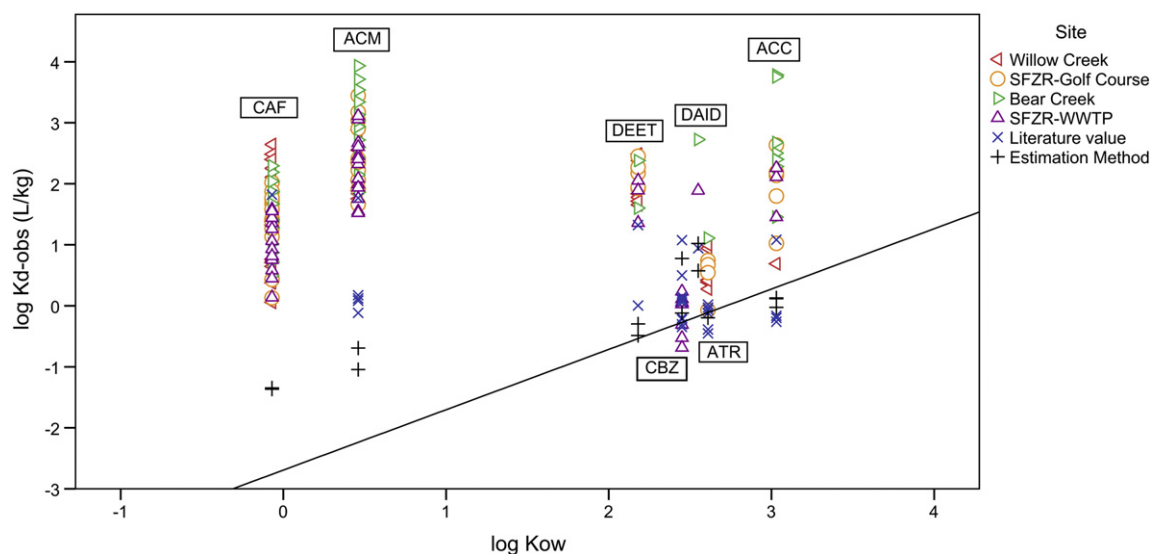


Fig. 4. Plot of calculated log K_{d-obs} vs. literature log K_{ow} for CECs detected in water and sediment across the study sites. Results from the current study are provided, along with batch equilibrium and field studies results reported in the literature, predicted values (based on EpiSuite's MCI and Kow methods), and a Kow-Koc relationship observed by Karickhoff (1981) (converted to Kd, and represented by the black line) for comparison. All numerical data and associated citations are presented in Tables SI 3 and SI 6 and Section SI E. ACM = acetaminophen, CAF = caffeine, CBZ = carbamazepine, ACC = acetochlor, ATR = atrazine, DAID = Daidzein. Kow was used rather than Koc because the range of sediment TOC was low and similar across sites.

available information, and perform reasonably well for HOCs (Doucette, 2000). This approach has been attempted with a wide variety of chemical and soil types due to convenience and a lack of common, feasible alternatives (Doucette, 2000). Other than temporal and spatial influences, as discussed above, several factors related to sediment chemistry or to the chemistry of the sorbing compounds themselves affect the accuracy of these predictions (Karickhoff, 1984). Indeed, numerous field and laboratory CEC studies have reported K_{d-obs} values that deviate widely from equilibrium predictions and each other, often by an order of magnitude or more (Lei et al., 2009; Kim and Carlson, 2007; Yamamoto et al., 2003; Schenzel et al., 2012; Yang et al., 2010; Massey et al., 2010; Scheytt et al., 2005; Yamamoto et al., 2009; Davis et al., 2006; Yamamoto et al., 2005). Therefore, it is useful to assess for which compounds sorption is governed primarily by hydrophobic partitioning, by polar-ionic interactions with mineral components, or by a mix of influences, and under what conditions (MacKay and Vasudevan, 2012).

Fig. 4 and Table 3 indicate that K_{d-obs} approaches K_{ow} -based predictions with increasing K_{ow} . The observed deviations of K_{d-obs} may be due to seasonally and/or spatially influenced variations as discussed above, the fact that the system is not truly at equilibrium, or non-hydrophobic interactions between CECs and sediment. In this research, in all instances when the K_{d-obs} values of a given CEC exhibited significant seasonal or spatial variation, so too did its water concentration (Table 4). Moreover, in only two cases did water concentration exhibit significant variation without corresponding K_{d-obs} variation. Sediment concentration variations did not exhibit similar association with K_{d-obs} variation. Thus, variation of K_{d-obs} is partially driven by variations in in-stream water concentration for these CECs, which supports the assumption that the system is not at equilibrium. This could explain some of the discrepancies between laboratory and field results for these and other organic compounds.

Non-hydrophobic interactions between CECs and sediment exert significant effects on sorption behavior. It is known that sorbate polarity, ionizability, and pK_a strongly influence sorption. Potential interactions include cation exchange, cation bridging, hydrogen-bonding, and mineral complexation (Drillia et al., 2005; Karnjanapiboonwong et al., 2010). Amines have been noted to consistently exceed estimated K_d 's by an order of magnitude due to cation exchange (Karickhoff, 1984). Hydroxyl, carboxylic acid, and other N- and O-containing functionalities exert similar effects through cation bridging, anion exchange, and

mineral complexation. Most CECs in the current study exhibit at least one such functionality and the majority of PPCPs are polar and hydrophilic, with low K_{ow} (Caliman and Gavrilescu, 2009). Thus, predictions based solely on K_{ow} are unlikely to accurately predict CEC sorption due to unaccounted non-hydrophobic interactions (Tolls, 2001; Kinney et al., 2006; Nguyen et al., 2005; Scheytt et al., 2005; Yamamoto et al., 2005). In addition, a high clay content (e.g., clay to organic carbon ratio of >30) indicates that significant mineral contributions to sorption are likely, especially for molecules with polar functional groups (Sheng et al., 2001). For pesticides, a clay to organic matter ratio as low as 15 was found to result in significant mineral contributions to sorption (Harris and Sheets, 1965), an order of magnitude above organic carbon-based predictions (Brown and Flagg, 1981). The average clay to organic carbon ratio in the current study was 39, again suggesting the importance of non-hydrophobic interactions.

Considering a few specific compounds in light of their physicochemical properties and spatiotemporal variability provides further insight into when the use of equilibrium partition coefficients might be useful to estimate non-equilibrium sediment-water distribution in streams, as well as potential sources of K_{d-obs} variability. For example, acetaminophen and caffeine log K_{d-obs} values deviated farthest from equilibrium-based log K_d predictions (by 3–6 orders of magnitude). This parallels previous literature reports that suggested the deviation is explained by non-hydrophobic mechanisms (Yamamoto et al., 2009; Yamamoto et al., 2005; Karnjanapiboonwong et al., 2010). These CECs are polar and hydrophilic as demonstrated by their high solubilities, log K_{ow} less than one, and amine/amide functional groups. Photolytic and overall in-stream half-lives for these hydrophilic CECs are on the order of a few days (Yamamoto et al., 2009; Lam et al., 2004; Buerge et al., 2003; Jacobs et al., 2012). These CECs may not desorb or degrade as quickly in sediment compared to water (due to reduced exposure to sunlight or bioavailability for microbial degradation, for example), resulting in increased K_{d-obs} . Additionally, fluctuations in CEC inputs would result in water concentrations that change more rapidly than sorption-desorption processes. This is seen in the seasonality in water concentration for several CECs, whereas no such seasonality was evident in sediment concentrations.

For daidzein, DEET, and acetochlor (log $K_{ow} > 2$), K_{d-obs} values diverge from predictions by 1–3 orders of magnitude, in agreement with some previous literature reports (Fig. 4). These CECs are

moderately hydrophobic and weakly polar as exhibited by log K_{ow} range of 2–3 and solubilities of 200–600 mg/L. The in-stream half-lives of these moderately hydrophobic CECs, including photolytic half-lives, are reported to be on the order of hours-to-weeks (Calza et al., 2012; Kelly and Arnold, 2012; Hoerger et al., 2009; Benitez et al., 2013; Brezonik and Fulkerson-Brekken, 1998). Thus, in comparison with acetaminophen and caffeine, the more moderate aqueous attenuation rates and increased hydrophobicity of these CECs may explain the somewhat better agreement of their K_{d-obs} with equilibrium predictions.

For the more hydrophobic CECs atrazine and carbamazepine, sediment–water distributions were generally well-predicted by K_{ow} and had the lowest magnitude and variability of K_{d-obs} among the CECs in this study. These results agree with previous literature reports (Fig. 4). These CECs, which are neutral at the pHs of this study (Schaffer et al., 2012; Laird et al., 1994), are the least soluble among detected CECs (Table 2) (EPA, U.S., 2013) and have log $K_{ow} > 2$. Carbamazepine's sorption is dominated by organic carbon-partitioning (Schaffer et al., 2012) and well-predicted by K_{ow} (Scheytt et al., 2005). Although atrazine sorbs to both organic carbon and clay fractions (Laird et al., 1994), organic carbon partitioning dominates total sorption at the clay to organic carbon ratios observed in this study (Grundl and Small, 1993). Photolytic and overall aqueous environmental half-lives are on the order of months or greater for these hydrophobic CECs (Yamamoto et al., 2009; Lam et al., 2004; Rice et al., 2004). The increased hydrophobicity and much greater aqueous persistence of atrazine and carbamazepine likely explains why their K_{d-obs} values exhibited reduced variability and better agreement with equilibrium predictions than did the other CECs in this study.

Based on these observations, it is suggested that polarity and degradability in the water column influence the consistency of K_{d-obs} and its predictability by K_{ow} . Atrazine and carbamazepine had the best-predicted and least variable K_{d-obs} values. Compared to the other CECs, they are also more persistent and less soluble, with sorption dominated by hydrophobic mechanisms. The CECs that have been observed to participate in non-hydrophobic interactions and generally have higher rates of degradation (acetaminophen, acetochlor, caffeine, daidzein and DEET) are those that exhibited greater deviations of log K_{d-obs} from K_{ow} -based predictions, often by orders of magnitude. Indeed, as the degradability and spatial–temporal variability in both phases increased, a greater spread in the K_{d-obs} values was observed. Likewise, when the polarity or hydrophilicity of a compound increased, a lower correlation of K_{d-obs} to K_{ow} was observed.

4. Implications for CEC monitoring

This study addresses the importance of the sediment phase for the reported CECs. These results provide information that aids in the consideration and development of sediment monitoring activities. This study indicates that CECs are present in sediments, even those traditionally thought of as non-sorptive. Generally, K_{ow} underestimated sorption of these CECs to sediments. The absence of seasonality in CEC sediment concentrations indicates that selection of sampling time may not be crucial when planning sediment monitoring, although increases of CEC concentration in the sediment from 2011 to 2012 for several CECs suggests that external source functions must also be considered. It also suggests that sediment might provide a more stable marker of CEC sources and land use influences with fewer samples than would be required to ascertain similar differences with water samples. However, it may be desirable to consider finer-scale runoff events when planning monitoring activities, as these may affect sediment CEC concentrations by temporarily affecting sediment deposition and resuspension. Sediment CEC concentrations were linked with land use, with PPCPs showing strong associations with more urban/residential sites. Occurrence profiles of agricultural CECs are consistent with the prevalence of upstream

agricultural land use at the study sites and exhibited temporal increases in water concentrations during seasons of increased usage and runoff.

Traditional predictive parameters like K_{ow} often fail to accurately estimate CEC distributions in sediment in the field or laboratory. Non-hydrophobic interactions are commonly identified as factors contributing to underestimation of sediment distributions. Our results indicate that spatial and temporal variability in the water column are significant drivers of variability in K_{d-obs} . A “one-size-fits-all” approach to CEC monitoring may be unlikely to adequately capture the variability of different classes of CECs, especially if only a few grab samples are collected, which may lead to incorrect interpretations. Aqueous persistence and other temporal factors of individual CECs should be considered when designing field studies to properly characterize CEC sources, fate, transport, and risk.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.10.046>.

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