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Pharmaceuticals and organochlorine pesticides in sediments of an urban river in Florida, USA

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Abstract
Purpose Sediments from a rural to urban gradient along the Alafia River in Florida, USA, were collected to determine the risk of environmental contamination with legacy (organochlorine pesticides (OCPs)) and new contaminants (pharmaceuticals).
Materials and methods Bed sediments (0–10 cm) collected from rural and urban sub-basins of the Alafia River were analyzed for OCPs and pharmaceuticals using standard gas chromatography and liquid chromatography-mass spectrometry techniques.
Results and discussion Three most frequently detected pharmaceuticals in sediments were carbamazepine (100 % of samples), trimethoprim (89 % of samples), and pseudoephedrine (63 % of samples). While acetaminophen, diphenhydramine, lidocaine, and nicotine were detected in <30 % of samples. The detection of caffeine in all sediment samples suggests that domestic wastewater from wastewater treatment plants and/or septic systems may be a contributing source at all the sites. Among the OCPs, endosulfan I was most frequently detected (37 % of samples), followed by δ-hexachlorocyclohexane (15 % of samples), γ-chlordane and endosulfan II (both in 11 % of samples), and dichlorodiphenyldichloroethylene and methoxychlor (both in 7 % of samples). The lower concentrations of OCPs (sum 0–16.1 ng g^{-1}) than pharmaceuticals (sum 0.5–61.9 ng g^{-1}) in sediments are probably due to the historic use of OCPs since these were banned for use in the USA in the 1970s, while pharmaceuticals are still used.
Conclusions The variability in detection and concentrations of legacy and new compounds in rural and urban stream sediments is likely due to the different magnitude of input sources, site characteristics, and chemical properties of individual compounds. Significant positive correlations between OCPs and sediment properties (organic matter, silt, and clay) suggest that sediments are a major sink of various contaminants in the Alafia River. We conclude that the concentrations of both pharmaceuticals and OCPs in sediments of this urban river are relatively lower than existing literature; however, these can still be of environmental concern to aquatic organisms.

Keywords Organochlorine pesticides · Pharmaceuticals · River sediments · Urbanizing watershed

1 Introduction

Organic contaminants, including pharmaceuticals and organochlorine pesticides (OCPs), are an environmental concern because of their potential impact on aquatic organisms and capacity to bioaccumulate in the food chain (Nakata et al. 2002; Loganathan et al. 2009; Kummerer 2010; Santos et al. 2010). The effects of pharmaceuticals and OCPs on the environment and aquatic organisms depend on the environmental persistence, dosage frequency, and concentrations of compounds (Heberer 2002; Whalen et al. 2003; Kuranchie-Mensah et al. 2012).

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Pharmaceuticals are used for specific biological functions in animals and humans. The primary source of pharmaceuticals in the aquatic environment is domestic wastewater (Clara et al. 2004), industrial wastewater (Kolpin et al. 2002), wastewater from septic systems (Carrara et al. 2008), landfill leachate (Holm et al. 1995; Barnes et al. 2008), and animal feed lots (Orlando et al. 2004). A number of studies have documented the presence of pharmaceuticals such as analgesics, antibiotics, anticonvulsants, lipid regulators, and even recreational drugs in water bodies that receive domestic wastewater from wastewater treatment plants (Ternes 1998; Clara et al. 2004; Stackelberg et al. 2004; Kummerer 2010). For example, 40 organic wastewater-related contaminants, including antibiotics, prescription and non-prescription drugs, and their metabolites, were detected in one or more stream water or drinking water samples in the USA (Stackelberg et al. 2004). In a reconnaissance survey conducted by the US Geological Survey, pharmaceuticals were detected at various concentrations and frequencies in streams that receive discharge from agricultural, domestic, and industrial sources (Kolpin et al. 2002). Another national-scale study in the USA that sampled areas suspected to be contaminated from either animal or human waste detected multiple pharmaceuticals in groundwater (Barnes et al. 2008). In contrast to the aquatic environment, the occurrence and fate of pharmaceuticals in solid matrices, such as sediments have not yet been thoroughly investigated in most parts of the world.

Several OCPs, including dichlorodiphenyltrichloroethane (DDT), aldrin, chlordane, endosulfan, and lindane have been used worldwide as active insecticides for pest control in agriculture and for vector control in humans. Although most OCPs were banned in the USA and other regions in the 1970s and 1980s, several OCPs are still detected in the environment due to their environmental persistence (Blais 2005; Xue et al. 2006; Daly et al. 2007; Sajwan et al. 2008). Many of the OCPs and their metabolites have been implicated to cause a wide range of health effects on aquatic organisms including changes in reproduction and endocrine disruption (McCain et al. 1996; Fisher et al. 2000). The main sources of OCPs in the aquatic environment included discharge of domestic sewage and industrial wastewater (Doong et al. 2002), agricultural runoff (Kuo et al. 2012), or atmospheric deposition (Daly et al. 2007). Due to the high hydrophobicity and low solubility, OCPs are mainly present in particulate matter such as bed sediment in aquatic ecosystems. Several surveys conducted in different regions of the world have observed OCPs in coastal and river sediments (Carr et al. 1996; Santschi et al. 2001; Doong et al. 2002; Grabe and Barron 2004; Zhang et al. 2004).

Studies have shown that sediment contamination can lead to adverse effects on aquatic organisms (Carr et al. 1996; McCain et al. 1996; Fisher et al. 2000). For example, four species of fish (*Arius felis*, *Fundulus grandis*, *Fundulus majalis*, and *Sciaenops ocellatus*) collected in one segment of Tampa Bay, FL, had elevated tissue concentrations of chlordane, DDT, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) sufficient to cause adverse effects such as higher prevalence of hepatic lesions and DNA adducts (McCain et al. 1996). Further, the concentrations of these contaminants in four fish species generally reflected the concentrations found in sediments, suggesting that sediments were the main contributors of these contaminants in fish tissue. This is not surprising as Tampa Bay is a large, open water subtropical estuary in the Gulf Coast of Florida and parts of the estuary are bordered by highly industrialized and urbanized areas (Carr et al. 1996).

Knowledge of the occurrence and environmental persistence of contaminants is important to improve the management strategies and evaluate the success of contamination control measures. In order to better understand the contamination of organic contaminants in urban streams, we investigated the compounds that represent currently used organic contaminants such as pharmaceuticals and legacy compounds such as OCPs that were once used in agricultural related products but are now banned. Thus, the objectives of this study were to (1) determine the occurrence of select pharmaceuticals and OCPs in stream sediments in sites that represent a rural to urban gradient along the Alafia River, which is a tributary of Tampa Bay, and (2) compare and contrast the concentrations of pharmaceuticals and OCPs found in our study with the existing literature to evaluate the risk of sediment contamination.

2 Materials and methods

2.1 Study area and sampling locations

The Alafia River drains 1093 km^2 of an urban watershed to Tampa Bay estuary in Florida. The locations of sampling sites are shown in Fig. 1 and the characteristics (location, land use, likely contaminant sources) at each of the sites are listed in Table 1. We collected bed sediments from nine sites located in the Alafia River; these sites drain different areas of the watershed representing agricultural, urban, and industrial areas (Table 1). Major land uses in the Alafia River watershed are urban (20 %), agricultural (8 %), pasture (11 %), forest (18 %), and phosphate mining (32 %) (Khare et al. 2012). North Prong and South Prong are two main tributaries of the Alafia River that contributes about 60 % of total discharge. Three streams (Bell Creek, Turkey Creek, and Fishhawk Creek) are the minor tributaries that discharge to the lower reaches of the Alafia River. The area under residential land use in various sub-basins ranged from 3 to 64 %, and built-up area varied from 1 to 14 %. Other major land uses in sub-basins are forest (12–37 %), pasture (2–23 %), and agricultural (1–24 %). In two

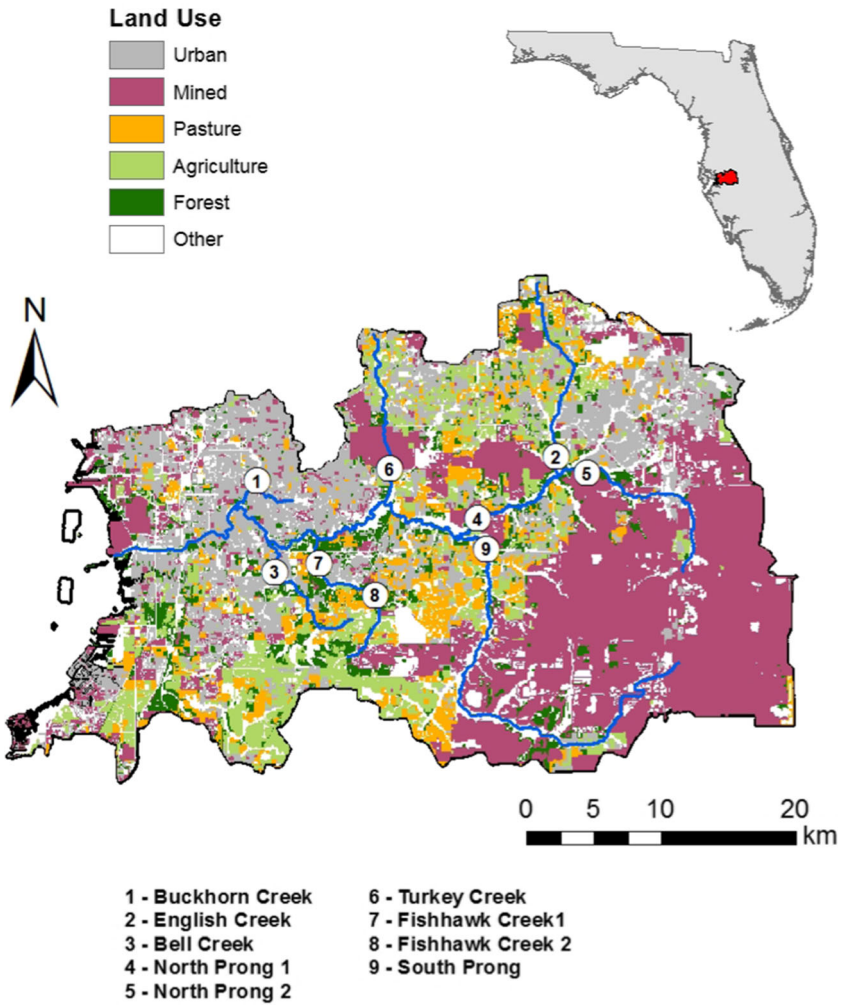

Fig. 1 Location map showing nine sampling sites in the sub-basins of the Alafia River watershed, FL, USA

sub-basins, most of the area is under phosphate mining (both abandoned and active), ranging from 39 % in North Prong to 66 % in South Prong. The Alafia River is tidally influenced for 18 km from its mouth; total length of the river is 80 km (Chen 2004). Lithia Springs, a second magnitude spring, and Buckhorn Spring provide relatively steady freshwater flows to the river (Chen 2004).

At each sampling site, three transects of 1 m×1 m were selected. From each transect, five cores from 0 to 10 cm were collected in April 2009, and then, a composite sample was

Table 1 Location characteristics of the Alafia River watershed, FL, USA

Sub-basin	Sampling location		Drainage area		Land use						Wastewater treatment plant	Number of septic systems per hectare
	Latitude	Longitude	km^2	%	Residential %	Built-up	Agricultural	Pasture	Forest	Mined		
Buckhorn Creek	27.55	−82.03	19	2	64	7	1	2	12	0	No	0.37
Bell Creek	27.51	−82.16	51	5	24	1	12	21	37	1	No	0.12
English Creek	27.93	−82.06	99	9	21	14	19	23	20	3	No	0.10
Turkey Creek	27.91	−82.18	128	13	20	3	24	16	12	0	One	0.11
North Prong	27.86	−82.13	350	32	18	6	4	5	16	39	One	0.57
Fishhawk Creek	27.85	−82.24	71	7	11	3	14	23	32	0	No	0.007
South Prong	27.86	−82.13	277	26	3	1	4	9	15	66	No	0.01

made to represent one replication. This resulted in three replicate samples for each site.

2.2 Sediment analyses: basic properties, pharmaceuticals, and organochlorine pesticides

Sediment samples were analyzed for various physical and chemical properties (Table 2). Sediment pH was measured by equilibrating 10 g of sediment sample with 20 ml of deionized water (1:2) for 1 h with a digital meter (Accumet XL60, Dual channel pH/ion/conductivity/dissolved oxygen meter, Fisher Scientific, Pandan Crescent, Singapore). The electrical conductivity (EC) of was measured using a sediment to deionized water suspension (1:1) with the same digital meter. Sediment samples were analyzed for sand, silt, and clay using the hydrometer method (Day 1965). Sediment organic matter was determined by the oxidation method of Walkley and Black (1934).

Seventeen pharmaceuticals, as listed in Table 3, were extracted from the sediments using a methodology similar to Williams and McLain (2012). In brief, freeze-dried sediments were extracted for pharmaceutical analysis by accelerated solvent extraction (ASE-300, Dionex, Sunnyvale, CA, USA). Sediments were mixed with Hydromatrix® (15 g sediment/2 g Hydromatrix; Agilent Technologies, Santa Clara, CA, USA) and poured into 34-ml stainless steel extraction cell already containing a glass fiber filter and 1 cm of sand. The remainder of the extraction cell was filled with sand followed by another glass fiber filter. Cells were extracted using three static cycles with 75:25 (*v*/*v*) water/methanol at 100 °C and 10,340 kPa. Each cycle was 5 min long, and the final flush was 60 % of the pore volume. Extract solutions (60–70 ml) were then diluted with nano-pure water (~400 ml) so that the final solution had an organic solvent content of less than 5 %. Pharmaceuticals were extracted from solution using a conditioned Strata-X (Phenomenex, Torrance, CA, USA) solid-phase extraction cartridge, followed by three 20-ml rinses of nano-pure water. The cartridge was then dried for 2 min and eluted with 3 ml of 1:1 methanol/water. Solvent was then evaporated to dryness under nitrogen gas at 35 °C. Samples were reconstituted with 1:9 methanol and nano-pure water to match the aqueous content of the mobile phase. Samples were then transferred to high-performance liquid chromatography (HPLC) vials for liquid chromatography (LC) mass spectrometry (MS) analysis. Table 4 lists the compound ionization mode along with parent and daughter compounds and limits of detection of selected pharmaceuticals.

Pharmaceutical separation was performed using a 2.1 × 30 mm XTerra MS C18 column with a 2.5-μm stationary phase (Waters Co., Milford, MA, USA). Operating conditions of the LC included a mobile phase flow rate of 0.25 ml min^{-1} with a binary mobile phase of acetonitrile and water. Ion production was enhanced by the addition of 0.1 % formic acid (positive ion mode) or 0.1 % NH_4OH (negative ion mode) to the mobile phase. Initial conditions were 10:90 acetonitrile/water, followed by isocratic flow for 1.5 min. At 1.5 min, a linear gradient from 10:90 acetonitrile/water to 90:10 acetonitrile/water was applied over 5 min, followed by 1.5-min isocratic flow at 90:10 acetonitrile/water.

Twenty OCPs, as listed in Table 5, were extracted from sediments to investigate the environmental persistence of legacy compounds using modified EPA method 1699 for extraction (USEPA 2007a) and EPA method 8081 for analysis (USEPA 2007b). In brief, 10 g of sediment was suspended in 25 ml of petroleum ether-acetone mixture (1:1 *v*/*v*) and sonicated for 20 min in an ultrasonic bath (35 kHz, 320 W, Super RK 510, Sonorex, Bandelin, Berlin, Germany). The extraction procedure was repeated four times, and the extract from the same sample was combined and filtered using Whatman filter paper. The extract was concentrated to 2 ml using rotary evaporator at 40 °C under a gentle nitrogen stream (Turbo Vap II, Zymark Inc.) and then transferred onto a Resprep Florisil cartridge (3 ml, 250 mg). Prior to sample loading, the cartridge was conditioned with 4 ml hexane. The sample was eluted with 100 ml of hexane/ethyl acetate (7:3 *v*/*v*) and concentrated to 1 ml prior to gas chromatography with an electron capture

Table 2 Physical and chemical properties of sediments in the 0- to 10-cm layer

	Buckhorn Creek	English Creek	Bell Creek	North Prong 1	North Prong 2	Turkey Creek	Fishhawk Creek 1	Fishhawk Creek 2	South Prong
pH	7.5	6.7	6.3	7.3	7.4	6.7	7.1	6.7	6.8
EC (μS cm^{-1})	151.6	159.2	89.4	93.6	115.3	342.5	139.0	56.2	102.1
Sand (%)	95.0	85.3	93.3	94.7	93.7	75.0	95.0	95.3	94.3
Clay (%)	4.0	8.3	4.3	3.7	5.0	18.3	4.3	3.7	3.0
Silt (%)	1.0	6.3	2.3	1.7	1.3	6.7	0.7	1.0	2.7
OM (%)	0.3	1.6	0.7	0.2	0.2	2.1	0.2	0.4	0.2

EC electrical conductivity, *OM* organic matter

Table 3 Target pharmaceutical classes and use, detection frequency, and concentration range

Compound	Class	Use	DF (%)	Range (ng g^{-1})
Carbamazepine	Antiepileptic	Seizure disorders, neuropathic pain	100	0.1–32.89
Caffeine	Stimulant	Coffee, tea, soft drinks	100	0.2–24.38
Trimethoprim	Antibiotic	Urinary tract infection, pneumocystis pneumonia	89	0.01–0.83
Pseudoephedrine	Ephedrine	Common cold, nasal congestion, sinus inflection	63	ND–0.22
Acetaminophen	Antiphlogistic	Pain, fever, sinus infection	26	ND–5.23
Diphenhydramine	Antiphlogistic	Common cold, hives, nausea	4	ND–0.32
Lidocaine	Anesthetic	Ventricular tachycardia, heart attack, burn	4	ND–0.03
Nicotine	Stimulant	Ulcerative colitis, tobacco abuse	4	ND–0.02
Atenolol	Beta-blocker	High blood pressure, heart attack	ND	NA
Chloramphenicol	Antibiotic	Salmonella infections, otitis externa, rickettsiosis	ND	NA
Ciprofloxacin	Antibiotic	Urinary tract infection, gonorrhea, gladder inflammation	ND	NA
Cimetidine	Antacid	Gastroesophageal reflux disease, heartburn	ND	NA
Diclofenac	Antiphlogistic	Inflammation, osteoarthritis, ankylosing spondylitis	ND	NA
Gemfibrozil	Lipid regulating	High blood cholesterol level, high triglyceride	ND	NA
Lincomycin	Antibiotic	Staphylococcus bacterial infection, streptococcus bacteria inflection	ND	NA
Oxytetracycline	Antibiotic	Chest inflection psittacosis, eye inflection trachoma	ND	NA
Ofloxacin	Antibiotic	Urinary tract infection, gonorrhea	ND	NA

DF detection frequency, *ND* not detected, *NA* not applicable

detector (GC-ECD; Perkin Elmer Clarus 500, Waltham, MA, USA). During the analysis, verification of method performance was conducted by using matrix spike recovery, blank, and duplicate samples in a set of each ten samples.

Target OCP analysis was performed using a GC-ECD coupled with a MultiPurpose sampler (MPS 2, GERSTEL, Mülheim, Germany). An Rtx®-CLPesticides2 column (30 m× 0.1 mm id×0.25 μm, Restek Corp, USA) was used for separation of OCPs. An aliquot of 1 μl sample was injected at 250 °C in splitless mode. Hydrogen was used as the carrier gas at a constant flow rate of 1 ml min^{-1}. The oven temperature was programmed at 110 °C (hold 0.5 min), increased to 230 °C at 25 °C min^{-1}, and further to 330 °C (hold 1 min) at 15 °C min^{-1}.

Table 4 Ionization mode and limit of detection of selected pharmaceuticals

Compound	ES ionization mode	Parent (*m*/*z*)	Daughter (*m*/*z*)	LOD (ng g^{-1})
Carbamazepine	Positive	237.21	194.11	0.0014
Caffeine	Positive	194.92	137.94	0.0013
Trimethoprim	Positive	291.17	230.21	0.0019
Pseudoephedrine	Positive	166.21	148.09	0.0017
Acetaminophen	Positive	152.12	109.91	0.0038
Diphenhydramine	Positive	256.26	167.13	0.0099
Lidocaine	Positive	235.16	85.94	0.0075
Nicotine	Positive	163.17	129.94	0.0018

LOD limit of detection

3 Results and discussion

3.1 Physicochemical characteristics of sediments

Sediment pH in all samples was 6.3–7.5, and electrical conductivity (EC) was 56.2–342.5 μS cm^{-1} (Table 2). Of the nine sampling sites, seven sites had 93.3–95.3 % sand, 3–5 % clay, and 0.7–2.7 % silt. The remaining two sites had less sand and more clay and silt: Turkey Creek (75 % sand, 18.3 % clay, 6.7 % silt) and English Creek (85.3 % sand, 8.3 % clay, 6.3 % silt). The organic matter in all sediment samples ranged from 0.2 to 2.1 % (Table 2).

3.2 Detection frequency and concentrations of pharmaceuticals in sediments

At all sites, eight pharmaceuticals, including one antiepileptic (carbamazepine), two antiphlogistics (acetaminophen and diphenhydramine), one antibiotic (trimethoprim), two stimulants (caffeine and nicotine), one anesthetic (lidocaine) and one ephedrine (pseudoephedrine), were measured in at least one sediment sample, with concentrations ranging from 0 to 32.9 ng g^{-1} (Table 3 and Fig. 2). Among the 17 analyzed pharmaceuticals, caffeine (100 % detected; 0.2 to 24.4 ng g^{-1}), carbamazepine (100 % detected; 0.1 to 32.9 ng g^{-1}), trimethoprim (89 % detected; 0.01 to 0.83 ng g^{-1}), and pseudoephedrine (63 % detected; not detected (ND) to 0.22 ng g^{-1}) were frequently detected compounds in sediments. Other pharmaceuticals were detected fewer times, such as 26 % detection for acetaminophen (ND to

Table 5 Target OCP use, detected frequency, and concentration range

Compound	Use	This study		Grabe and Barron (2004); n=165–769	
		DF (%)	Range (ng g^{-1})	DF (%)	Maximum (ng g^{-1})
Endosulfan I	Insecticide	37	ND–4.67	1	4.9
δ-HCH	Insecticide, ingredient in ointment	15	ND–1.27	NA	NA
γ-Chlordane	Insecticide, control termites in homes	11	ND–1.54	17	166
Endosulfan II	Insecticide	11	ND–6.31	7	2.88
DDE	Degradation product of DDT	7	ND–3.14	19	34.9
Methoxychlor	Insecticide	7	ND–3.94	4	2.5
Endosulfan sulfate	Degradation product of endosulfan	4	ND–0.64	4	2.64
Heptachlor	Insecticide, termite control	4	ND–1.18	4	1.9
β-HCH	Insecticide, ingredient in ointment	4	ND–0.64	NA	NA
γ-HCH	Insecticide, ingredient in ointment	4	ND–3.61	NA	NA
Aldrin	Insecticide, wood preserve, termite control	ND	NA	1	0.8
α-Chlordane	Insecticide, control termites in homes	ND	NA	NA	NA
DDD	Degradation product of DDT	ND	NA	19	56.3
DDT	Insecticide	ND	NA	6	12.03
Dieldrin	Insecticide, wood preserve, termite control	ND	NA	3	9.5
Endrin	Insecticide, rodenticide	ND	NA	9	2.64
Endrin aldehyde	Insecticide, rodenticide, avicide	ND	NA	5	3
Endrin ketone	Degradation product of endrin	ND	NA	2	5.1
α-HCH	Insecticide, ingredient in ointment	ND	NA	NA	NA
Heptachlor epoxide	Insecticide, termite control	ND	NA	5	0.94

DF detection frequency, *ND* not detected, *NA* not applicable

5.23 ng g^{-1}) and only 4 % detection for diphenhydramine (ND to 0.32 ng g^{-1}), lidocaine (ND to 0.03 ng g^{-1}), and nicotine (ND to 0.02 ng g^{-1}). Antiphlogistics (diclofenac), beta-blocker (atenolol), lipid-regulating agent (gemfibrozil), antibiotics (chloramphenicol, ciprofloxacin, lincomycin, oxytetracycline, and ofloxacin), and antacid (cimetidine) were not detected in any of the samples (Table 3).

The lack of detection of several pharmaceuticals in sediment samples could be attributed to natural attenuation processes such as degradation or transformation to other compounds and existence of minimal sources of these compounds in the Alafia River watershed, as indicated in Table 3. In general, our findings are in line with previous research that investigated distribution and fate of 17 pharmaceuticals in water, sediment, and soil samples in the Pego-Oliva marsh, Spain (Vazquez-Roig et al. 2012). They found that carbamazepine (in 100 % samples), acetaminophen (87 %), and trimethoprim (20 %) were more frequently detected in sites impacted by discharge from wastewater treatment plants (WWTPs), while diclofenac and oxytetracycline were not detected in sediments.

Variability in the concentrations of pharmaceutical in sediments across rural to urban stream sediments may reflect the variable loading from different sources. For example, among all the sampling sites, Buckhorn Creek is the most urbanized (71% of residential and built up area, septic systems density of 0.37 ha^{-1}; Table 1) where caffeine, which is a marker of human excretory input, was observed at a high concentration of 16.7 ng g^{-1} (Fig. 2). The highest concentrations of carbamazepine (32.9 and 12.8 ng g^{-1}) and acetaminophen (4.18 and 5.23 ng g^{-1}) were observed in the South Prong and North Prong 1 sites along with caffeine (24.4 and 22.3 ng g^{-1}); these sites are likely influenced by wastewater from septic systems and WWTP, respectively.

Total concentrations of pharmaceuticals varied from 0.5 ng g^{-1} (Fishhawk Creek) to 61.9 ng g^{-1} (South Prong), with the highest levels found at South Prong and North Prong 1 (Fig. 2), suggesting that wastewater discharges from septic systems and the WWTP (Table 1) are important sources of pharmaceuticals in this part of the watershed. As the detection and concentrations of different compounds are dependent on the source strength (concentration), sediment characteristics, time of sampling (seasonality), and other factors (e.g., degradation), interpretation of this data is limited. However, the detection frequencies of pharmaceuticals are often consistent with their persistence in WWTPs or septic systems and associated with differences in partitioning behavior and (bio)transformation of the individual compounds (Conn et al. 2006; Caliman and Gavrilescu 2009).

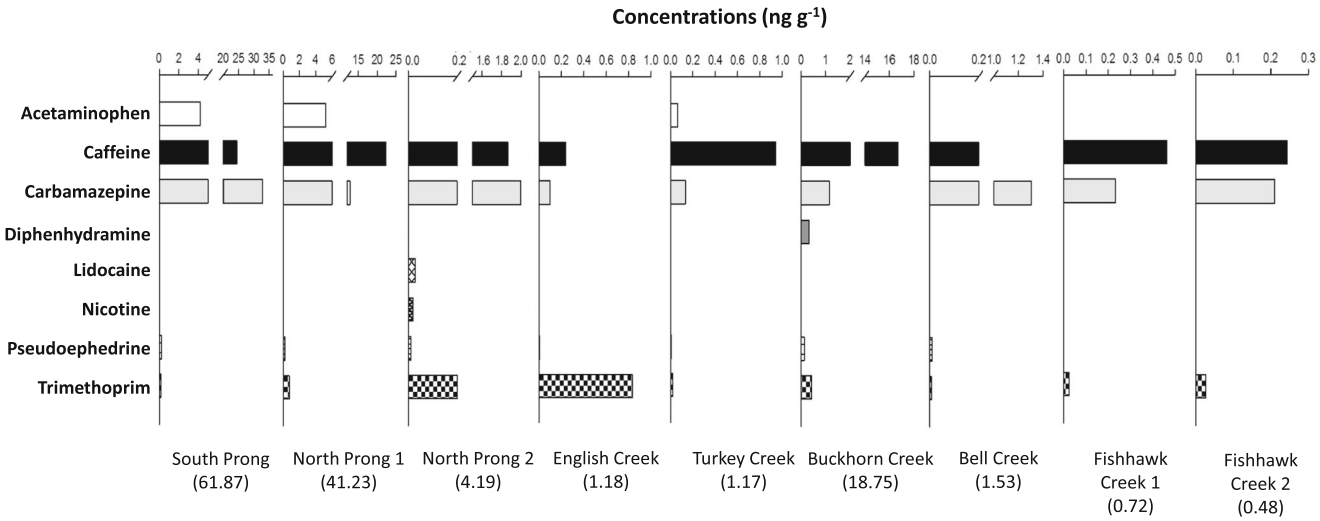

Fig. 2 Concentrations of pharmaceuticals in the Alafia River sediments. *Values in parentheses* (next to the sub-basin names) are total concentrations (ng g^{-1}) of eight detected pharmaceuticals at each site

3.3 Persistence of pharmaceuticals in sediments

The two most persistent compounds in our study were carbamazepine (100 % detection) and trimethoprim (89 % detection). There are two transport pathways that may be responsible for their occurrence in sediments as the main source of these compounds in the environment is wastewater. These pathways include surface transport with wastewater from WWTPs and leaching of wastewater from septic system drainfield to shallow groundwater. It is worth noting that there are more than 120,000 septic systems, groundwater is less than 3 m deep below the surface, and there is high connectivity of groundwater with surface waters in Hillsborough County where the Alafia River watershed is located.

Studies have shown that carbamazepine (Ternes 1998; Miao et al. 2005; Gómez et al. 2007) and trimethoprim (Göbel et al. 2004; Pérez et al. 2005) are relatively resistant to removal in WWTPs operated with biological treatment. For example, low elimination rate (20 %) of carbamazepine was found in a WWTP located in the south of Spain (Gómez et al. 2007). It was estimated that only 37 % of carbamazepine and 60 % of trimethoprim were removed from a WWTP that discharged into Jamaica Bay in New York City (Benotti and Brownawell 2007). The elimination efficiency of pharmaceuticals in WWTPs is further complicated by (bio/photo)transformation of compounds (Buser et al. 1998; Poiger et al. 2001; Quintana et al. 2005). Benotti and Brownawell (2009) measured microbial degradation rates of 19 pharmaceuticals in estuarine and coastal surface water samples and observed that the most persistent pharmaceuticals, including carbamazepine and trimethoprim, were found to be least labile with half-life ($t_{1/2}$) always greater than 40 days. Löffler et al. (2005) also found that 83 % of the carbamazepine was unchanged in an artificial water/sediment system during more than 100 days. Based on field measurements, Tixier et al. (2003) calculated an overall elimination rate for carbamazepine with a $t_{1/2}$ of 63 days.

These studies indicated that carbamazepine and trimethoprim have great environmental significance due to their partial elimination during the wastewater treatment process and their high stability in the environment. Likewise, there is paucity of literature on the fate and transport of pharmaceuticals from septic system drainfields to ground and surface waters. Four hormones and six pharmaceuticals were detected in Cape Cod kettle ponds, which are primarily fed by groundwater, with greater detection frequencies and concentrations in ponds located in higher residential density areas (Standley et al. 2008). Recently, three antibiotics and six prescription medications were detected in 20 public drinking water supply wells on Cape Cod, suggesting that septic systems are the primary source of pharmaceuticals in groundwater (Schaider et al. 2014). It is possible that many of these compounds are not effectively eliminated in the septic system drainfields; otherwise, they would not be present in stream sediments in the sites where there are no WWTPs.

Another compound identified as a major constituent in the sediments was caffeine. Caffeine has been used as a chemical marker for human excretory products discharged from WWTPs (Buerge et al. 2003; Thomas and Foster 2005). It has been shown to have variable removal efficiencies in WWTPs due to different treatment processes and conditions. For example, caffeine was largely eliminated (>99 %) in Swiss WWTPs (Buerge et al. 2006), 85 % removed in a Spanish sewage treatment plant (Gómez et al. 2007), and 64 % removed in the WWTP discharging into Jamaica Bay (Benotti and Brownawell 2007). The high detection frequency (100 %) of caffeine in our sediments may be due to the excretion of caffeine (from coffee, beverages) in wastewater, which

accumulated in stream sediments over a period of time. Overall, pharmaceuticals (i.e., carbamazepine, caffeine, and trimethoprim) that were frequently detected in sediments of the Alafia River were also frequently detected in other river and surface waters impacted by WWTPs in the world (Kolpin et al. 2002; Tixier et al. 2003; Stackelberg et al. 2004), suggesting that these compounds resist removal during wastewater treatment processes.

Unlike carbamazepine and trimethoprim, acetaminophen and nicotine had much higher removal efficiencies of 87 to 99 % in WWTPs (Benotti and Brownawell 2007; Gómez et al. 2007). This is attributed to the short biodegradation rate of nicotine ($t_{1/2}$=0.68 to 9.7 days) and acetaminophen ($t_{1/2}$=1.2 to 11 days) (Benotti and Brownawell 2009), which may explain why acetaminophen and nicotine were only detected in 26 and 4 % of the sediment samples, respectively.

In our sediments, pseudoephedrine was detected in 63% of samples. To date, there is a little information about the occurrence of pseudoephedrine in the environment. Pseudoephedrine can be present in both raw and treated wastewater as this is a common cold, nasal congestion, and sinus infection pharmaceutical that frequently escapes treatment in WWTPs (Kasprzyk-Hordern et al. 2010).

Many pharmaceuticals not detected in this study are hydrophilic compounds (e.g., atenolol, ciprofloxacin, ofloxacin, and oxytetracycline), which means that they are more likely to be found in water than solid matrix. A recent study investigated the sorption of 75 common pharmaceuticals and found that only 14 have strong affinity with sludge (solid phase), whereas 37 pharmaceuticals were present in the liquid phase (Hörsing et al. 2011). Other compounds that are more hydrophobic (e.g., diclofenac and gemfibrozil) might be eliminated via different mechanisms during the transport. For example, photodegradation is important in the attenuation of some pharmaceuticals such as diclofenac (Poiger et al. 2001; Andreozzi et al. 2003). Diclofenac was not very persistent in tributaries of a lake in Switzerland, which received wastewater discharge (Buser et al. 1998). It was estimated that more than 90 % of the diclofenac entering the lake is eliminated, most likely by photodegradation with $t_{1/2}$<1 h. Buser et al. (1998) did not detect diclofenac in the lake sediments, and diclofenac showed negligible sorption onto sediment particles in a laboratory experiment.

The ability of pharmaceuticals to sorb to sediment is affected by their octanol-water partitioning coefficient (K_{ow}), pK_a, and pH of the water (Lorphensri et al. 2007). The greater log K_{ow} values for a given compound, the greater is the tendency to partition to solid phase, such as sediments. The frequently detected compounds in sediments ranked in the following order: carbamazepine=caffeine (100 %)>trimethoprim (89 %)>pseudoephedrine (63 %)>acetaminophen (26 %). In general, the log K_{ow} of the frequently detected compounds in sediments was consistent with the capability for sediment sorption: carbamazepine (log K_{ow}=2.25)>trimethoprim (0.73)>pseudoephedrine (0.68)>acetaminophen (0.46)>caffeine (0.16). However, log K_{ow} values were not well correlated with concentrations in sediments for all compounds. Due to the polar and often ionic nature of pharmaceuticals, sorption in sediments can be affected by ionic interactions. For example, acidic pharmaceuticals (e.g., nicotine, pK_a=3.1; diclofenac, pK_a=4.2; gemfibrozil, pK_a=4.7) are present as anions, while basic pharmaceuticals (e.g., carbamazepine, pK_a=13.9, and caffeine, pK_a=10.4) are present as cations at pH 6–8. Thus, sorption onto the sediments is expected to be (1) strong for cationic pharmaceuticals due to the electrostatic attraction between negatively charged sediment particles and positively charged (cationic) pharmaceutical and (2) weak for the anionic pharmaceuticals due to the electrostatic repulsion between negatively charged sediment particles and negatively charged (anionic) pharmaceutical. This may explain why carbamazepine and caffeine were detected in all of the samples, while others were not detected in any of the samples.

3.4 Concentrations of organochlorine pesticides in sediments

Of 20, only 10 legacy OCPs, including β-, δ-, and γ-hexachlorocyclohexane (HCH), γ-chlordane, dichlorodiphenyldichloroethylene (DDE), endosulfan I, endosulfan II, endosulfan sulfate, heptachlor, and methoxychlor, were detected at eight sites (Fig. 3, Table 5). Total concentrations of ten OCPs (∑OPCs) ranged from not detected (North Prong 2) to 16.1 ng g^{-1} (Turkey Creek). The concentration of the sum of endosulfan I, endosulfan II, and endosulfan sulfate (∑END) was greater (ND–6.31 ng g^{-1}) than other pesticides. The concentrations of ∑HCH (sum of α-, β-, δ-, and γ-HCH), ∑DDT (DDT, DDE, and dichlorodiphenyldichloroethane (DDD)), and ∑CHL (α- and γ-chlordane) ranged from ND to 4.78 ng g^{-1}, ND to 3.14 ng g^{-1}, and ND to 1.51 ng g^{-1}, respectively (Fig. 3). The concentrations of heptachlor and methoxychlor were ND to 1.18 ng g^{-1} and ND to 3.94 ng g^{-1}, respectively. The higher concentrations of ∑DDT, ∑END, ∑CHL, heptachlor, and methoxychlor were observed at Turkey Creek (agricultural dominant sub-basin); this site also had greater clay, silt, and organic matter (see Table 2).

Numerical sediment quality guidelines have been developed using a variety of approaches to assist regulators in dealing with contaminated sediments. In general, toxic effects occur at concentrations greater than the probable effects level (PEL). In all of our sediment samples, concentrations of OCPs were below PEL values except for γ-HCH. For example, published PEL values for chlordane, DDE, and γ-HCH are 8.9, 6.75, and 1.38 ng g^{-1}, respectively (MacDonald et al. 2000). In our samples, concentrations of chlordane, DDE, and γ-HCH were ND to 1.54, ND to 3.14, and ND to 3.61 ng g^{-1}, respectively. Among these three compounds, concentrations

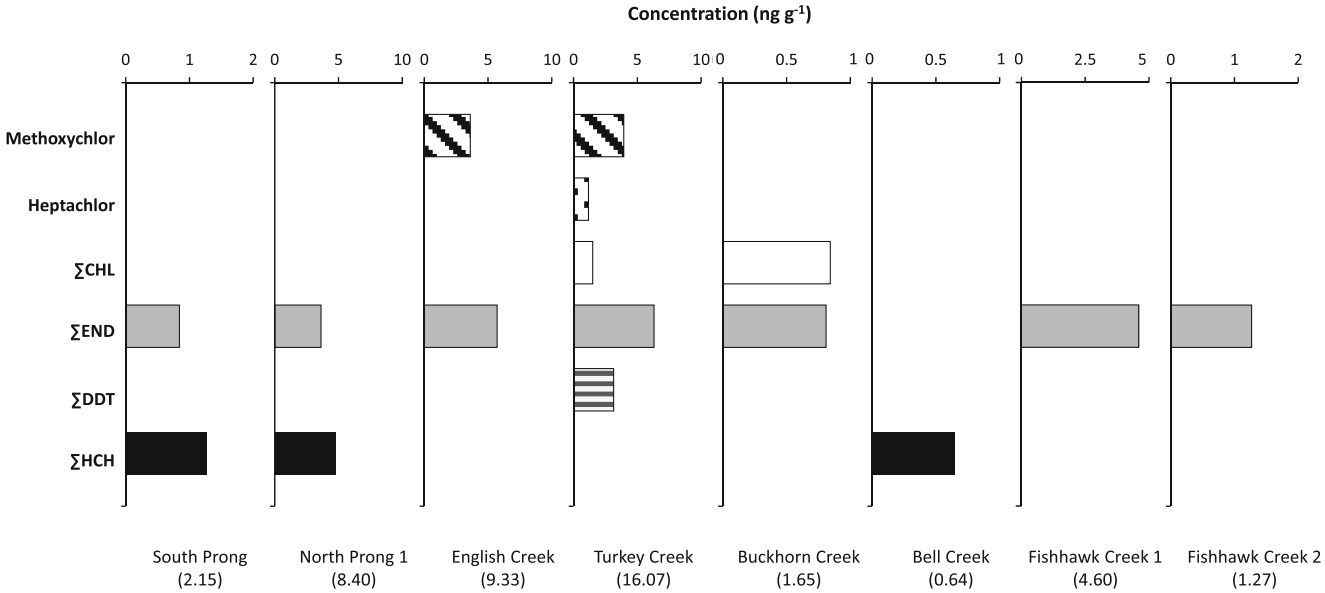

Fig. 3 Total concentrations of organocchlorine pesticides (OCPs) in the Alafia River sediments. No OCPs were detected at North Prong 2. *Values in parentheses* (next to the sub-basin names) are total concentrations (ng g^{-1}) of ten detected OCPs at each site

of only γ-HCH were greater than the PEL value. This suggests that sediments in Alafia River streams are slightly contaminated, but well below the levels that can cause toxic effects.

3.5 Persistence of organochlorine pesticides in sediments

The most frequently detected OCP in this study was endosulfan I (detected in 37% of samples), with concentrations ranging from ND to 4.67 ng g^{-1} (Table 5). Endosulfan, which consists of two isomers (endosulfan I and endosulfan II), is a chlorinated cyclodiene insecticide typically applied as 7:3 mixture of endosulfan I to II. Endosulfan was detected in seven sites, and concentrations of endosulfan I (ND to 4.67 ng g^{-1}) were generally higher than endosulfan II (ND to 1.04 ng g^{-1}). Endosulfan II (6.31 ng g^{-1}) was only found at higher concentration than endosulfan I at Turkey Creek. Greater concentrations and detection frequency of endosulfan I may reflect the composition of the technical mixture used in agricultural areas. Isomer conversion from endosulfan II to I can also occur (Schmidt et al. 2001). Endosulfan sulfate (ND to 0.64 ng g^{-1}), which is a degradation product of endosulfan I and II, was only detected at North Prong 1. Endosulfan I and II concentrations in the analyzed sediments were more predominant than the metabolite endosulfan sulfate, which indicates a slow rate of degradation of endosulfan I and II.

The detection frequencies of other OCPs were 15 % for δ-HCH, 11 % for γ-chlordane and endosulfan II, and 7 % for DDE and methoxychlor (Table 5). An earlier (1993–1997) study conducted in Tampa Bay (Grabe and Barron 2004) detected DDD, DDE, and total chlordane in 17–19 % of sediment samples, while endosulfan I was detected in only 1 % of the sediment samples (Table 5). This is not surprising as most OCPs including DDT have been banned in the USA since the 1970s. Previous studies demonstrated that the relative concentrations of the parent DDT compound and its metabolites (i.e., DDD and DDE) can be used to indicate the age of DDT residues (Doong et al. 2002; Sun et al. 2010). A small value of DDD+DDE/DDT suggests relatively new DDT inputs, while a high value (>0.5) indicates the age of DDT residues (Doong et al. 2002). Non-detected DDT and detected DDE (ND to 3.28 ng g^{-1}) in this study suggest that current levels in our sediments primarily originated from the historical use.

Among the sampling sites, ∑OCP concentrations were greater at Turkey Creek than other sites (Fig. 3). A possible explanation for this observation could be that it is located in a sub-basin that primarily drains agricultural land uses (Table 1). Secondly, this site also had the highest clay, silt, and organic matter, which may have resulted in sorption of these OCPs in sediments. The relationship between hydrophobic organic compounds and organic matter has been well documented in the literature (Gong et al. 2004) as sediments with high organic matter are most likely to sorb hydrophobic pesticides than those with lower organic matter. In the sediments, a significant positive correlation was observed between ∑OCPs and organic matter (r=0.85, p=0.0079) and between ∑OCPs and sum of clay and silt (r=0.96, p=0.0002), suggesting that organic matter and fine sediments accumulated OCPs. This relationship agrees well with previous studies showing that the fate and distribution of organic pollutants in the environment is influenced by the organic matter content (Gong

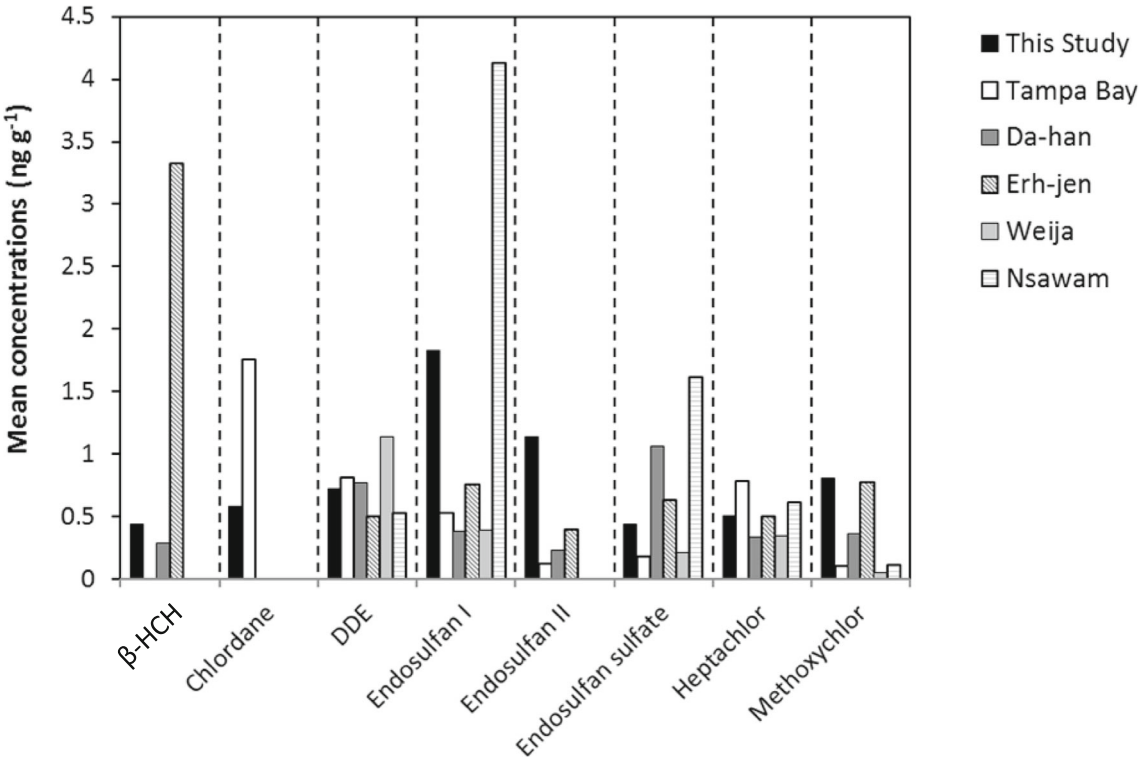

Fig. 4 Comparison of concentrations of OCPs in our sediment samples with selected previous studies. Reported data from previous studies were as follows: Tampa Bay in USA from Grabe and Barron (2004), Da-han and Erh-jen rivers in Taiwan from Doong et al (2002), and Weija and Nsawam reservoirs of Densu river in Ghana from Kuranchie-Mensah et al. (2012)

et al. 2004; Daly et al. 2007; Hung et al. 2007; Wang et al. 2012).

The concentrations of OCPs in our sediments were similar to previous studies (Fig. 4). For example, the mean concentrations of DDE and heptachlor in the Alafia River sediments are similar to those detected in a previous sediment study in Tampa Bay that included Alafia River (Grabe and Barron 2004) and other studies such as Da-han and Erh-jen River in Taiwan (Doong et al. 2002), and Densu River (Weija and Nsawam reservoirs) in Ghana (Kuranchie-Mensah et al. 2012). The mean concentration of endosulfan I in our sediments was higher than Tampa Bay, Da-han River, Erh-jen River, and Weija reservoir, but lower than Nsawam reservoir. The mean concentration of endosulfan II in the Alafia River sediments is two to nine times greater than other regions. These results reflect the importance of historical use of OCPs in different regions.

4 Conclusions

Eight pharmaceuticals and 10 OCPs were detected in nine sediment sampling sites that drain various land uses ranging from rural to urban gradient in the Alafia River watershed. Total concentrations of pharmaceuticals and OCPs in sediments were 0.48–61.87 and 0–16.07 ng g^{-1}, respectively. Carbamazepine, trimethoprim, and pseudoephedrine were the main pharmaceuticals detected along with caffeine and endosulfan I in the Alafia River sediments. Domestic wastewater from WWTP and septic systems are two sources of pharmaceuticals in the environment since they are used daily in the households, and only a small percentage of pharmaceuticals is absorbed in the body; the rest are excreted in urine and feces. Concentrations of OCPs were significantly related to organic matter and the sum of clay and silt, suggesting that these are major sinks of OCPs in the sediments. Low concentrations of pharmaceuticals and OCPs in sediments may imply that these are unlikely to cause significant risk; however, little is known about the risk of low level of pharmaceuticals in river sediments to aquatic biota. Further, many pharmaceuticals are more recalcitrant than pesticides to degradation and their degradation products are still of potential concern due to endocrine disruption potential. Research is needed to evaluate the environmental impacts of low concentration dosage of pharmaceuticals to aquatic organisms from urban river sediments.

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