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Pharmaceuticals and personal care products found in the Great Lakes above concentrations of environmental concern

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HIGHLIGHTS

- Pharmaceuticals and personal care products (PPCPs) were monitored in Lake Michigan.
- Fifty-four PPCPs were assessed in surface water and sediment on six dates.
- Many PPCPs, such as metformin, were detected 3.2 km away from the shore.
- Hydrophobic compounds were detected in sediment at concentrations up to 510 ng g^{-1}.
- Using a risk quotient, the ecosystem risk was found to be high for many PPCPs.

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ABSTRACT

The monitoring of pharmaceuticals and personal care products (PPCPs) has focused on the distribution in rivers and small lakes, but data regarding their occurrence and effects in large lake systems, such as the Great Lakes, are sparse. Wastewater treatment processes have not been optimized to remove influent PPCPs and are a major source of PPCPs in the environment. Furthermore, PPCPs are not currently regulated in wastewater effluent. In this experiment we evaluated the concentration, and corresponding risk, of PPCPs from a wastewater effluent source at varying distances in Lake Michigan. Fifty-four PPCPs and hormones were assessed on six different dates over a two-year period from surface water and sediment samples up to 3.2 km from a wastewater treatment plant and at two sites within a harbor. Thirty-two PPCPs were detected in Lake Michigan and 30 were detected in the sediment, with numerous PPCPs being detected up to 3.2 km away from the shoreline. The most frequently detected PPCPs in Lake Michigan were metformin, caffeine, sulfamethoxazole, and triclosan. To determine the ecological risk, the maximum measured environmental concentrations were compared to the predicted no-effect concentration and 14 PPCPs were found to be of medium or high ecological risk. The environmental risk of PPCPs in large lake systems, such as the Great Lakes, has been questioned due to high dilution; however, the con-

1. Introduction

Pharmaceutical and personal care products (PPCPs) have been found in wastewater worldwide (Ternes, 1998; Gomez et al., 2007; Vieno et al., 2007; Miege et al., 2009; Suarez et al., 2012; Aydin and Talini, 2013; Tewari et al., 2013). The level of removal has been found to vary widely depending on the chemical, the operating conditions, and the treatment technologies (Miege et al., 2009; Oulton et al., 2010; Verlicchi et al., 2012; Blair et al., 2013). Variable removal of PPCPs through WWTPs has led to detection of these compounds in the aquatic environment, albeit mostly in microgram to nanogram per liter concentrations (Halling-Sorensen et al., 1998; Kolpin et al., 2002; Cahill et al., 2004; Glassmeyer et al.,

Abbreviations: BDL, Below Minimum Detection Limit; JIWRF, Jones Island Water Reclamation Facility; MDL, minimum detection limit; MEC, maximum environmental concentration; MGD, million gallons per day; MQL, minimum quantification limit; PNEC, predicted no-effect concentration; PPCPs, pharmaceutical and personal care products; RQ, risk quotient; SSWRF, South Shore Water Reclamation Facility; WWTP, wastewater treatment plant.

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2005; Focazio et al., 2008; Snyder, 2008; Kümmerer, 2009; Scheurer et al., 2009; Yu and Chu, 2009; Li et al., 2010). Higher pharmaceutical concentrations in WWTP effluent have been measured under certain circumstances, such as WWTPs that receive a substantial amount of their flow rate from pharmaceutical manufacturing (Larsson et al., 2007; Phillips et al., 2010). Research has shown that certain PPCPs may have an impact on the environment at the microgram to nanogram per liter concentrations with a range of potential impacts (Brooks et al., 2003; Fent et al., 2006; Han et al., 2006; Hernando et al., 2006; Christensen et al., 2009; Gros et al., 2010; Al Aukidy et al., 2012; Brodin et al., 2013; Tewari et al., 2013).

The emission of PPCPs into the environment from wastewater can depend on the wastewater treatment processes, the flow of the waste stream, and different PPCPs usage patterns that vary by region and season (Dickenson et al., 2011; Yu et al., 2013). In an aquatic environment the fate and concentration of PPCPs can be reliant on the receiving water body flow rate, partitioning to sediments or biological entities, uptake up by biota, volatilization, biological degradation, photodegradation, or transformed through other abiotic mechanisms such as hydrolysis (Yamamoto et al., 2009). In the Great Lakes, which contains 84% of North America's freshwater (USEPA, 2012a), dilution from the source may also be a major factor in the occurrence and detection of PPCPs in surface water and sediments.

Limited studies are available that assess PPCPs offshore in large water bodies due to the expected low levels of PPCPs from dilution and the complex hydrodynamics in a lake as large as one of the Great Lakes. Site selection for PPCPs research has focused on bodies of water that are potentially contaminated from human, industrial, and agricultural wastewater (Kolpin et al., 2002). Four previous studies have looked at PPCPs levels in the Great Lakes (Metcalfe et al., 2003; Wu et al., 2009; Li et al., 2010; Csiszar et al., 2011) with a wide range of results and they have focused near shore, in harbors, and in rivers that are tributaries to the Great Lakes. No previous studies have assessed PPCPs offshore in Lake Michigan. Lake Michigan is the sixth largest lake in the world by volume and fifth by area (Beeton, 2002) and understanding the concentration of these pollutants in Lake Michigan is critical. Additionally, no previous studies have assessed the extent of the temporal and spatial distribution of PPCPs from a large, urban WWTP into the Great Lakes.

Using a risk quotient (RQ), which is defined as the ratio of the maximum measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC), the ecosystem risk from pollutants can be gauged (Hernando et al., 2006). However, calculating this ratio can be challenging due to a lack of information regarding the effects of PPCPs in the environment and difficulty in establishing the PNEC. Researchers have used the RQ to assess the low levels of PPCPs on ecosystem health with varying results. Recent studies have found limited ecological risk is expected for many PPCPs, which may be due to the risk being partially mitigated by high dilution (Gros et al., 2010; Al Aukidy et al., 2012; Yu et al., 2013). Conversely, other studies have found PPCPs of high or medium risk in secondary effluent, rivers, and small lakes (Christensen et al., 2009; Valcarcel et al., 2011; Verlicchi et al., 2012; Tewari et al., 2013). Additionally, levels of concern have been found in sewage sludge (Yu et al., 2013).

Studies have not been conducted evaluating the occurrence and risk of PPCPs in Lake Michigan and other studies on the Great Lakes have assessed a small number of PPCPs. A better understanding of the occurrence of PPCPs in large water systems, particularly in areas with substantial urban development, needs further investigation. The purpose of our study was to assess the risk of 54 PPCPs in Lake Michigan from varying proximities to a major effluent discharge site and to assess the risk potential to the environment. PPCPs were measured in both surface water and sediment samples over six dates. The sampling pattern was selected due to the prevailing southern current in this portion of the Lake Michigan basin (Rao and Schwab, 2007). When possible, a RQ was estimated to determine which compounds are at a level of concern based on existing effects data or models.

2. Materials and methods

South Shore Water Reclamation Facility (SSWRF) and Jones Island Water Reclamation Facility (JIWRF) service the greater Milwaukee, Wisconsin area. Fifty-four PPCPs were measured in Lake Michigan and compared to the related data on wastewater effluent from Blair et al. (2013). Both SSWRF and JIWRF uses preliminary treatment (bar screens/grit channels), primary clarifiers, activated sludge treatment and chlorine disinfection. SSWRF has a treatment capacity of 1 135 000 $m^3 d^{-1}$ (300 MGD (million gallons per day)) with an average flow of approximately 379 000 $m^3 d^{-1}$ (100 MGD). JIWRF has a treatment capacity of 1 457 000 $m^3 d^{-1}$ (385 MGD) with an average flow of approximately 473 000 $m^3 d^{-1}$ (125 MGD).

Surface water and sediment samples were collected in Lake Michigan the day following the sampling at SSWRF. Sampling was conducted using a Teflon Niskin bottle at a depth of 5 m over sites up to 3.6 km away from the effluent discharge site (Fig. 1). SSWRF discharges directly into Lake Michigan whereas JIWRF discharges into the Milwaukee Harbor. Field blanks were collected on each date using distilled water. Grab sediment samples were collected on 5/15/2009 and 4/9/2010. Water and sediment samples were also collected in the Milwaukee Harbor near JIWRF as a comparison site that has lower dilution and potentially higher PPCPs concentration than the open lake. The final effluent was sampled using a 24-h composite sample as described by Blair et al. (2013).

2.1. PPCPs analysis

PPCPs were extracted and analyzed based upon US EPA Method 1694 (USEPA, 2007a) for pharmaceuticals and US EPA Method 1698 (USEPA, 2007b) for steroids and hormones by using high performance liquid chromatography combined with tandem mass spectrometry (HPLC/MS/MS) with modifications as published by Blair et al. (2013). The PPCPs were selected for this study based on the EPA methods. Forty-one PPCPs were assessed under EPA 1694 and thirteen hormones were assessed under EPA 1698. Sediment samples were collected for a subset of the sampling dates and these data are presented separate from the liquid concentration. The same 54 PPCPs were assessed in both the water and sediment samples.

2.2. Risk quotient

To determine the risk quotient (RQ) for each compound, the PNECs were found using the review paper from Verlicchi et al. (2012) and ECOSAR v1.11 from the US EPA (USEPA, 2012b). When the values found by Verlicchi et al. (2012) were from an older version of ECOSAR, or if the data were not available, the lowest freshwater toxicity value from ECOSAR v1.11 was used. The PNEC selected from these values also included the chronic values from ECOSAR. An assessment factor (1000) was used to account for sensitivity in other species (Hernando et al., 2006). Using an accepted range for the RQ, where low risk is below 0.1, medium risk is from 0.1 to 1 and high risk is greater than 1 (Hernando et al., 2006, Verlicchi et al., 2012). When a PPCP had a concentration in the blank above the MQL, this value was subtracted from the maximum concentration before the RQ was calculated.

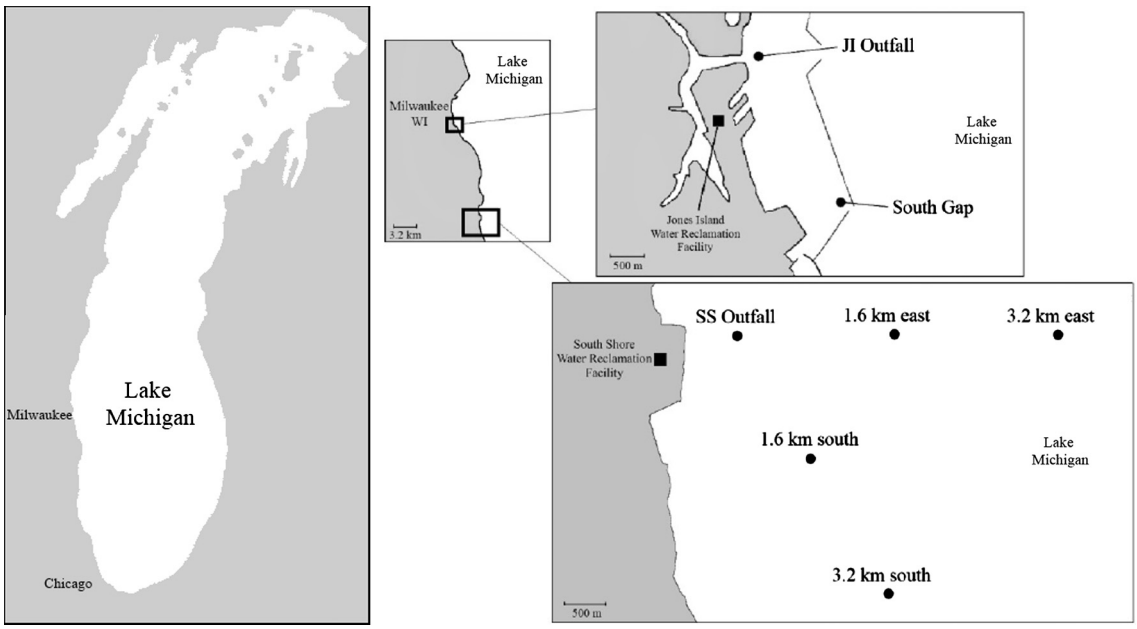

Fig. 1. Lake Michigan and the sampling locations in Lake Michigan near Milwaukee, Wisconsin, USA. Boxes represent the two WWTPs discussed: JIWRF and SSWRF.

3. Results and discussion

3.1. Surface water concentration

Over six sampling dates, 38 of the 54 compounds were detected from effluent or Lake Michigan samples. Four compounds were detected with greater than 50% frequency at all of the sampling sites in Lake Michigan and the Milwaukee Harbor: metformin (100%), caffeine (97.6%), sulfamethoxazole (83.3%), and triclosan (71.4%). Table 1 has the mean and maximum levels from the six samples dates along with the MDL, MQL, and maximum value found in the method blanks. The complete data are available in Supplemental information.

The most widely detected pharmaceutical in our study was the antidiabetic metformin, which was detected above the minimum detection limit with 100% frequency in Lake Michigan (Fig. 2a). Metformin was detected at sites up to 3.2 km away from the shore, which was unanticipated given the volume of such a large lake system and the predominant southern current in this portion of Lake Michigan. Although metformin is less frequently measured than other compounds in PPCP studies, we have found, along with others, that metformin is prevalent in WWTP influent at concentrations as high as 129 000 ng L^{-1} but the removal efficiency ranges from 41% to over 98% (Scheurer et al., 2009, 2012; Trautwein and Kümmerer, 2011; Blair et al., 2013; Oosterhuis et al., 2013). The median value for metformin in Lake Michigan was greater than 100 ng L^{-1}, comparable to stream and small lake studies where metformin has been observed in 4.8% of samples with estimated levels of 110 ng L^{-1} in the U.S. (Kolpin et al., 2002) and was detected at all of the sites assessed at concentration up to 2000 ng L^{-1} in German rivers (Scheurer et al., 2009, 2012). Given the prevailing southern water current, the concentration of metformin was expected to vary at the different sampling sites depending on the direction from source. Yet average metformin concentrations were similar to levels found in smaller water bodies and the prevailing currents did not seem to lead to differences in concentration with location. Other compounds that followed the same general trend as metformin were caffeine, paraxanthine, sulfamethoxazole, and triclosan.

As a contrast to metformin, the anticonvulsant compound carbamazepine, shown in Fig. 2b, was detected on all of the sampling dates in the final effluent at SSWRF but rarely in Lake Michigan water or sediment. Carbamazepine has been found to be highly persistent in wastewater since it is expected to resist biological degradation (Gomez et al., 2007; Santos et al., 2007; Radjenovic et al., 2009; Rosal et al., 2010; Blair et al., 2013). However, carbamazepine was not detected in the water or sediment samples surrounding SSWRF. Dilution of the wastewater effluent may have been adequate to reduce the concentration to below the MDL. However, carbamazepine was detected with 66.7% frequency at both locations in the Milwaukee harbor at levels above the MDL. Given the lack of detection of carbamazepine around SSWRF, the fate of carbamazepine in Lake Michigan is unknown.

Twenty-seven PPCPs were detected at notable levels at the JI outfall and South gap in the Milwaukee harbor. JI Water Reclamation Facility discharges into the Milwaukee harbor and this is a potential source of these PPCPs, although effluent levels were not assessed at this WWTP. Additionally, the Milwaukee River also flows into the harbor and is an additional potential source of the PPCPs that were detected. As shown in Table 1, the PPCPs concentrations in the Milwaukee Harbor were higher overall than the area surrounding SSWRF. This was used as a reference site as previous research has shown chronic fecal pollution in the harbor (Newton et al., 2011). These results agree with other studies assessing harbors on the Great Lakes (Metcalfe et al., 2003; Csiszar et al., 2011). Hormones were not consistently detected above the minimum detection limit in Lake Michigan. The concentrations of hormones were low and inconsistent in the final effluent at SWWRF which may be due to the high expected removal from a WWTP through adsorption, biodegradation, and exposure to chlorine (Joss et al., 2006; Esperanza et al., 2007; Benotti et al., 2009; Huerta-Fontela et al., 2011). Given the inconsistent and low levels detected in the effluent and the high dilution from entering Lake Michigan, the levels of hormones in the lake from the WWTP would be expected to be below the detection limit.

3.2. Sediment levels

Thirty compounds were detected in the sediment at levels above the MDL in Lake Michigan and these compounds are listed in Table 2. The most commonly detected compounds were: azithromycin, clarithromycin, diphenhydramine, metformin, triclosan

Table 1
Concentration of PPCPs at the final effluent and at seven locations in Lake Michigan (Below Detection Limit (BDL)).

	Field blank Max ng L^{-1}	MDL ng L^{-1}	MQL ng L^{-1}	Outfall Mean, max ng L^{-1}	1.6 km East (1 mi. east) Mean, max ng L^{-1}	1.6 km South (1 mi. south) Mean, max ng L^{-1}	3.2 km East (2 mi. east) Mean, max ng L^{-1}	3.2 km South (2 mi. south) Mean, max ng L^{-1}	JI outfall Mean, max ng L^{-1}	South gap Mean, max ng L^{-1}
17,20-Dihydroxyprogesterone	BDL	1.4	4.2	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
17-Alpha-estradiol	BDL	1.2	3.5	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
17-Beta-estradiol	BDL	1.3	3.8	BDL, 1.7*	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, 1.3*
4-Androstene-3,17-dione	4.5	0.5	1.4	97, 580	BDL, 2.0	0.9*, 5.3	3.1, 17	0.8*, 3.5	0.3*, 1.4	BDL, 0.9*
5-Alpha-androstane-3,17-dione	BDL	2.3	6.9	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Acetaminophen	BDL	2.5	7.5	4.2*, 21	BDL, BDL	BDL, BDL	BDL, BDL	BDL, 2.5*	17, 73	13, 45
Albuterol	BDL	1.4	4.2	BDL, BDL	BDL, BDL	BDL, 5.9	BDL, BDL	BDL, BDL	BDL 4.3	BDL, BDL
Azithromycin	15.9	3.7	11	BDL, BDL	BDL, 12	BDL, 12	BDL, 7.5*	BDL, 11	BDL, 22	BDL, 12
Boldenone	BDL	1.3	4.0	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Caffeine	62.1	3.1	9.3	44, 110	18, 42	37, 86	21, 35	24, 39	67, 230	71, 190
Carbadox	44.9	3.4	10	7.2*, 20	BDL, 17	12, 49	BDL, 6	6.7*, 33	6.1*, 22	4.2*, 19
Carbamazepine	BDL	2.7	8.2	BDL, 6.2*	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	15, 38	6.4*, 17
Cimetidine	BDL	1.3	3.8	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Ciprofloxacin	BDL	3.3	9.9	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Clarithromycin	BDL	3.2	9.6	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Codeine	BDL	3.6	11	BDL, 11	BDL, 8.7*	BDL, 9.2*	BDL, 5.4*	BDL, 7.2*	4.4*, 11	5.3*, 15
Cotinine	BDL	3.5	11	BDL, 7.4*	BDL, 6.5*	BDL, 5*	BDL, 6.1*	BDL, 11	BDL, 20	3.5*, 21
Digoxigenin	BDL	4.4	13.2	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Diltiazem	5.4	3.5	10	BDL, 7.9*	BDL, 5.5*	BDL, 7.8*	BDL, BDL	BDL, BDL	6.3, 21	BDL, 10
Diphenhydramine	4.2	3.6	11	4.1*, 14	BDL, 6.6*	BDL, 9.2*	BDL, 4.9*	BDL, 6.7*	10*, 43	3.6*, 12
Estriol	BDL	2	6.1	BDL, BDL	BDL, 3.9*	BDL, BDL	BDL, 5.0*	BDL, BDL	BDL, BDL	BDL, 4.9*
Estrone	BDL	2.2	6.7	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, 3.4*	BDL, BDL	BDL, BDL
Fluoxetine	BDL	3.5	11	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	8.2*, 49	10*, 62
Gemfibrozil	BDL	1.6	4.8	9.1, 42	BDL, BDL	1.6*, 4.5*	BDL, BDL	3.1*, 19	14, 36	13, 43
Ibuprofen	BDL	4.7	14	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Lincomycin	BDL	3.1	9.3	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Lomefloxacin	BDL	4.7	14.2	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Melengestrol	BDL	1.3	4	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Melengestrol Acetate	BDL	0.6	1.7	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Metformin	35.5	0.5	1.5	1200, 3800	240, 820	270, 840	120, 160	110, 160	4100, 9200	1200, 2400
Miconazole	BDL	2.7	8.1	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Naproxen	BDL	1	2.9	4.9, 19	BDL, BDL	2.5*, 15	BDL, BDL	BDL, BDL	8.4, 31	4.8, 18
Norfloxacin	BDL	5.1	15.3	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Ofloxacin	BDL	3.9	12	10*, 61	BDL, 21	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Oxacillin	BDL	2.5	7.4	BDL, BDL	BDL, BDL	BDL, BDL	2.9*, 17	BDL, BDL	BDL, BDL	BDL, BDL
Paraxanthine	11.6	6.1	18	6.3*, 23	BDL, 9.7*	11*, 39	BDL, BDL	BDL, 8.7*	15*, 57	15*, 45
Progesterone	17.8	0.7	2	2.0, 11	1.0*, 4.9	1.5*, 8.7	15, 88	2.6, 13	BDL, BDL	BDL, BDL
Ranitidine	BDL	0.9	2.6	BDL, BDL	BDL, 3.7	BDL, BDL	BDL, BDL	BDL, BDL	5.4, 27	BDL, BDL
Roxithromycin	5.5	4.3	13	BDL, 8.7*	BDL, BDL	BDL, 7.5*	4.5*, 15	6.5*, 39	BDL, 9.2*	BDL, BDL
Sarafloxacin	BDL	5.4	16	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Sulfachloropyridazine	BDL	4.1	12	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Sulfadiazine	BDL	2.8	8.5	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, 3.8*	BDL, BDL
Sulfadimethoxine	BDL	2.4	7.1	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Sulfamerazine	BDL	2.1	6.2	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, 3.6*
Sulfamethazine	BDL	4.0	12	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Sulfamethizole	BDL	4.2	13	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Sulfamethoxazole	BDL	4.1	12	6.9*, 14	BDL, 6.2*	5.1,* 7.0*	BDL, 7.3*	4.5*, 10*	29, 77	16, 30
Sulfanilamide	BDL	2.9	8.6	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	6.3*, 20	BDL, BDL
Sulfathiazole	BDL	2.6	8	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Testosterone	12.4	1.1	3.2	2.2*, 13	BDL, 4.5	1.5*, 9.1	6.4, 38	1.4*, 7.0	BDL, BDL	BDL, BDL
Thiabendazole	BDL	1.8	5.3	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL
Triclocarban	BDL	0.5	1.4	2.6, 16	BDL, BDL	BDL, BDL	BDL, BDL	BDL, BDL	3.9, 9.9	BDL, BDL
Triclosan	5.4	0.5	1.6	9.9, 41	0.8*, 2.1	3.0, 16	2.7, 7.4	1.4*, 6.5	7.7, 24	5.0, 11
Trimethoprim	BDL	3.4	10	BDL, 3.4*	BDL, BDL	BDL, 6.0*	BDL, BDL	BDL, BDL	17, 52	6.9*, 13

* Value above MDL, but below MQL.

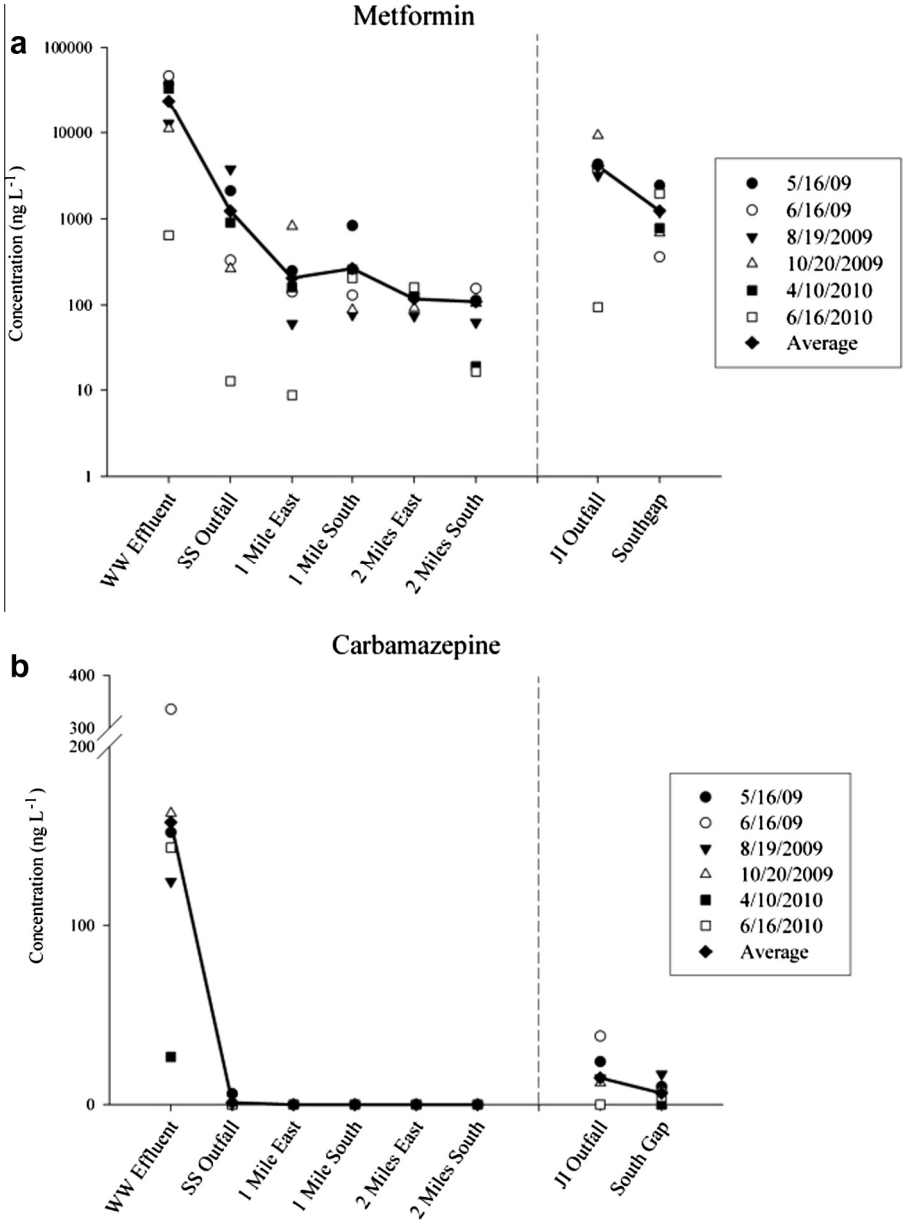

Fig. 2. Concentration of metformin (a) and carbamazepine (b) in wastewater effluent and in Lake Michigan on six dates.

and triclocarban. Of these compounds, all of them were regularly detected in the final effluent, with the exception of the macrolide antibiotic clarithromycin, which was detected only once. Given the low occurrence in the final effluent and across the stages of SSWRF (Blair et al., 2013), the regular and widespread occurrence of clarithromycin in sediment is of interest. Azithromycin and clarithromycin were found to have limited sorption to sludge in WWTPs (Verlicchi et al., 2012) therefore their detection in sediment needs further investigation. Triclosan and triclocarban were detected in Lake Michigan sediment due to their regular occurrence in effluent and their known hydrophobic characteristics (Loranzo et al., 2013). Additionally, the detection of metformin and diphenhydramine in Lake Michigan sediment is notable.

Other PPCPs detected in the sediment cannot be clearly contributed to the effluent from SSWRF. For example, thiabendazole, a fungicide, was detected at low levels in the final effluent, but was only located in the sediment at the 1.6 km east and 3.2 km east sampling locations and was not detected in the surface water. The detection at these locations implies the potential source is from land runoff, not discharged from SSWRF. With detection only at the eastern locations, not the southern locations, the source may be from area north of the WWTP. Significant agricultural developments are not present in the area north of SSWRF, but a residential area that includes many parks and golf courses are a possible source of this fungicide.

3.3. Ecological risk quotient

Overall, a total of twenty-four compounds were detected in the final effluent or Lake Michigan at a level of medium or high risk. As shown in Fig. 3, fourteen compounds were detected in Lake Michigan itself with high or medium risk. Metformin, the most widespread compound, did not correspond with high or medium risk at the concentrations detected; however, this may be due to the lack of predictive toxicity data on the chronic effects of this compound. When comparing the final effluent RQs to the values in Lake Michigan, many compounds drop below the threshold to medium or low risk after the compound is discharged from the WWTP, such

Table 2
PPCPs levels in sediment from Lake Michigan (compounds listed in Table 1 that were not detected above the MDL in the sediment samples are omitted from this table).

	MDL ng g^{-1}	MQL ng g^{-1}	SS outfall Mean ng g^{-1}	1.6 km East (1 mi. east) Mean ng g^{-1}	1.6 km South (1 mi. south) Mean ng g^{-1}	3.2 km East (2 mi. east) Mean ng g^{-1}	3.2 km South (2 mi. south) Mean ng g^{-1}	JI outfall Mean ng g^{-1}	South gap Mean ng g^{-1}
Acetaminophen	2.5	7.5	BDL	18	29	BDL	BDL	BDL	29
Azithromycin	3.7	11	490	16	72	19	25	59	350
Caffeine	3.1	9.3	25	BDL	24	30	14	4.2*	BDL
Carbadox	3.4	10	BDL	BDL	BDL	BDL	BDL	BDL	14
Ciprofloxacin	3.3	9.9	42	7.7*	9.0*	46	52	43	BDL
Clarithromycin	3.2	9.6	33	28	130	5*	120	90	BDL
Codeine	3.6	11	BDL	BDL	BDL	BDL	BDL	4*	BDL
Cotinine	3.5	11	8.0*	BDL	BDL	BDL	BDL	39	BDL
Digoxigenin	4.4	13	BDL	BDL	BDL	BDL	BDL	4.9*	9.2*
Diltiazem	3.5	10	4.0*	BDL	BDL	BDL	BDL	5.2*	3.9*
Diphenhydramine	3.6	11	81	13	43	7.3*	82	150	160
Enrofloxacin	1.4	4.1	BDL	BDL	BDL	6.6	BDL	BDL	BDL
Erythromycin	9.9	30	BDL	BDL	BDL	BDL	BDL	25*	BDL
Flumequine	5.2	16	BDL	BDL	BDL	6.9*	BDL	BDL	6.0*
Fluoxetine	3.5	11	7.6*	BDL	BDL	BDL	BDL	20	12
Ibrupoven	4.7	14	BDL	BDL	8.8*	BDL	BDL	BDL	No Data
Lincomycin	3.1	9.3	BDL	BDL	BDL	BDL	BDL	BDL	5*
Metformin	0.51	1.5	50	43	3.8	16	2.3	59	140
Miconazole	2.7	8.1	7.6	BDL	BDL	BDL	BDL	3.7*	8.4
Naproxen	0.97	2.9	4.8	1.0*	BDL	BDL	BDL	2.6*	No Data
Norfloxacin	5.1	15	BDL	BDL	BDL	12*	36	BDL	BDL
Ofloxacin	3.9	12	4.3*	BDL	BDL	7.7*	BDL	BDL	7.3*
Oxacillin	2.5	7.4	BDL	BDL	BDL	BDL	2.8*	BDL	9.1
Paraxanthine	6.1	18	BDL	BDL	BDL	BDL	BDL	BDL	15*
Roxithromycin	4.3	13	28	BDL	31	BDL	44	71	BDL
Sarafloxacin	5.4	16	BDL	BDL	BDL	9.9*	BDL	BDL	BDL
Thiabendazole	1.8	5.3	BDL	230	BDL	68	BDL	BDL	BDL
Triclocarban	0.48	1.4	170	4.5	33	BDL	11	510	No Data
Triclosan	0.53	1.6	37	18	22	26	12	150	No Data
Tylosin	3.5	11	9.4*	12	3.9*	BDL	14	20	BDL

* Value above MDL, but below MQL.

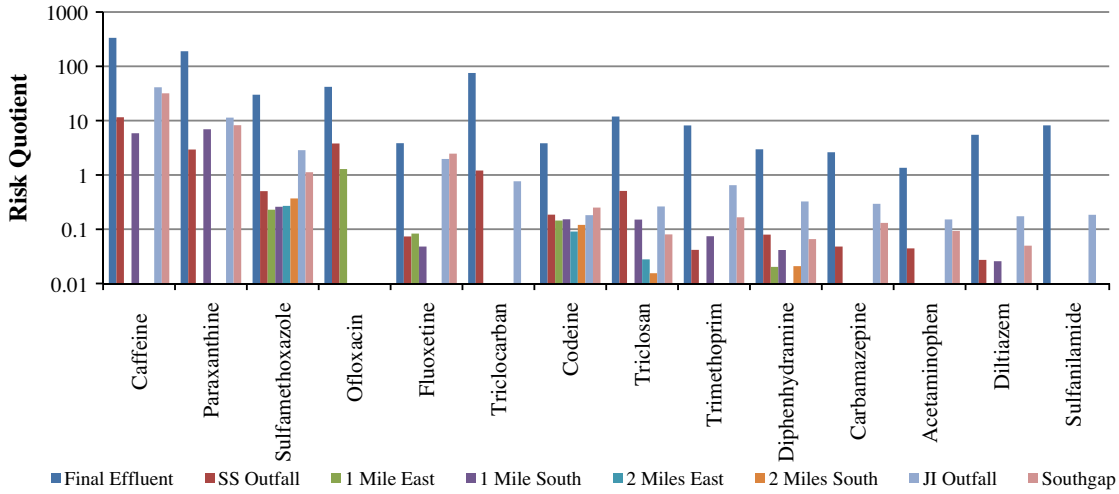

Fig. 3. Risk quotient for 14 PPCPs in wastewater effluent and in Lake Michigan (RQ > 1 is high risk, RQ from 0.1 to 1 is medium risk, and RQ < 0.1 is low risk).

as gemfibrozil and diltiazem. However, dilution is not sufficient to reduce the risk of all compounds to below the high and medium threshold, even at a distance of 3.2 km from shore, such as for sulfamethoxazole and codeine.

4. Conclusion

The detection of such a large number of PPCPs with high or medium risk in the Great Lakes is novel and of concern. The area surrounding the SS outfall and the sites within the Milwaukee Harbor are important as they are near locations for fish spawning and aquatic organisms, such as perch, can be found congregating around the effluent pipes of SSWRF and are exposed to effluent concentration with little dilution. Knowing that PPCPs can impact the behavior of aquatic organisms (Brodin et al., 2013; Brooks et al., 2003) leads to the conclusion that the endpoints used to assess the PNEC values for PPCPs may not properly address the ecological impacts and further testing is needed to identify the PPCPs of greatest concern. Additionally, the RQ may also underestimate risk due to potential mixture effects of PPCPs with similar mechanisms of action that may be additive in their impact. Reliance on a model such as ECOSAR is useful for identification of

PPCPs that warrant further research, but these models are not a replacement for experimental tests to determine the full ecological impacts from PPCPs.

PPCPs were frequently detected in the water and sediments at the ng L^{-1} level, including sites 3.2 km from shore in Lake Michigan at concentrations that are estimated to cause environmental concern. At the concentrations detected, medium or high risk was associated with twenty-four compounds in the final effluent, and fourteen were found to be of medium or high risk in Lake Michigan. The most frequently detected PPCPs were metformin, caffeine, sulfamethoxazole, and triclosan. Given the widespread detection of PPCPs, these pollutants are not ephemeral and pose an environmental risk to the sixth largest lake in the world. Therefore, high dilution is not adequate to mitigate the risk from this cocktail of PPCPs and the potential ecological risk for large lake systems is much higher than previously understood.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.07.057.

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