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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 concentrations found in this study, and their corresponding risk quotient, indicate a significant threat by PPCPs to the health of the Great Lakes, particularly near shore organisms.

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.