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Occurrence and fate of psychiatric pharmaceuticals in the urban water system of Shanghai, China

Minghong Wu [a,b], Jiajia Xiang [a], Chenjing Que [a], Fenfen Chen [a], Gang Xu [a,*]

[a] School of Environmental and Chemical Engineering, Shanghai University, 99 Shangda Road, Shanghai 200444, China
[b] Shanghai Applied Radiation Institute, Shanghai University, 99 Shangda Road, Shanghai 200444, China

HIGHLIGHTS

- We studied 15 psychiatric pharmaceuticals in waste, surface and drinking water.
- WWTPs were low effective in removing most psychiatric pharmaceuticals.
- A significant correlation was observed between waste and surface water.
- Pharmaceuticals may reach drinking water resources via WWTPs and/or surface waters.

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ABSTRACT

Psychiatric pharmaceuticals are the most prescribed active substances throughout the world and their presence in the environment raised concerns. The occurrence and fate of 15 selected psychiatric pharmaceuticals, including eight benzodiazepines, four antidepressants, one antiepileptic and two metabolites of benzodiazepines were investigated in wastewater treatment plant (WWTP) influents and effluents, surface water, and final drinking water in Shanghai. Psychiatric pharmaceuticals were in WWTPs influents ranging from low ng L^{-1} to 68.2 ng L^{-1}, dominated by carbamazepine, doxepin, diazepam and lorazepam. Target analytes were still detected in effluents from low ng L^{-1} range to 47.3 ng L^{-1}, with carbamazepine, diazepam, and oxazepam as most prevalent. WWTPs were low effective (<50%) in removing most of them, excluding amitriptyline (mean 60%), doxepin (mean 70%), temazepam (mean 78%) and lorazepam (mean 93%). In addition, carbamazepine, diazepam, oxazepam and lorazepam were detected in low ng L^{-1} to 75.5 ng L^{-1} in the surface water of Huang Pu Rive. The pattern of contaminants in surface water is similar to the effluent wastewater, which suggested the main source of organic trace pollutants might be WWTPs. Furthermore, carbamazepine (0.8–2.5 ng L^{-1}), diazepam (0.5–3.2 ng L^{-1}) and alprazolam (2.3 ng L^{-1}) were also detected in drinking water and the concentrations were below the health based precautionary value. The investigation was within the range of those results reported in other countries. Our results indicate ubiquity of the investigated compounds in the aquatic system. These pollutants may potentially reach drinking water via WWTP effluents and/or surface waters and require constant attention.

1. Introduction

The occurrence and fate of pharmaceuticals and personal care products (PPCPs) in water bodies have caused increasing environmental concern for their possible threats to aquatic environment and human health (Kolpin et al., 2002; Kummerer, 2003; de Voogt et al., 2009; Lajeunesse et al., 2012; Kostich et al., 2014). One important class of pharmaceuticals which has received recent consideration is psychiatric compounds. Psychiatric drugs are a group of pharmaceuticals commonly prescribed comprising anxiolytics, sedatives, hypnotics, antidepressants-selective serotonin re-uptake inhibitors, tricyclic antidepressants and others (Schultz and Furlong, 2008). These pharmaceuticals have the aptitude to directly affect the central nervous system and disrupt neuro-endocrine signaling (Calisto and Esteves, 2009; Calisto et al., 2011). The alteration of the reproduction patterns in non-target aquatic organisms (Brooks et al., 2003; van der Ven et al., 2006; Sanchez-Arguello et al., 2009) is one good example that

* Corresponding author.
E-mail addresses: mhwu@staff.shu.edu.cn (M. Wu), jiazi831@163.com (J. Xiang), quechenjing@163.com (C. Que), xugang@shu.edu.cn (G. Xu).

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illustrates the possible adverse effects in test organisms, thus reflecting the action mode of this particular group of pharmaceuticals. Benzodiazepines are a large class of commonly prescribed drugs used to treat a variety of clinical disorders including anxiety, insomnia, seizures, and alcohol withdrawal. Diazepam, temazepam, nordiazepam, and oxazepam are the most known drugs among this group. Temazepam, nordiazepam, and oxazepam are human metabolites of diazepam. The main metabolite of diazepam and temazepam is 5-chloro-2-benzophenone under sunlight. Aqueous phototransformation of nordiazepam is 2-amino-5-chorobenzophenone (West and Rowland, 2012).

Psychiatric pharmaceuticals have been detected in wastewater originating from hospitals as well as in effluents from municipal wastewater treatment plants (Ternes et al., 2001; Castiglioni et al., 2006; Baker and Kasprzyk-Hordern, 2011a; Yuan et al., 2013; Dai et al., 2014; Carmona et al., 2014a). Pharmaceutical residues may not be fully eliminated during sewage treatment and are thus discharged into receiving waters, so the main source of organic trace pollutants in aquatic systems may be wastewater treatment plant. Further, psychiatric pharmaceuticals were also found in surface water (33 ng L^{-1} in German rivers (Ternes et al., 2001), 21 ng L^{-1} in rivers in the region of Madrid (Matilainen and Sillanpaa, 2010), 2.4 ng L^{-1} in France surface water (Togola and Budzinski, 2008)). Psychiatric pharmaceuticals were further found up to 23.5 ng L^{-1} in drinking water (Zuccato et al., 2000a). Table 1 shows occurrence of psychiatric pharmaceuticals in the environment. It is suggested that psychiatric drugs may occurrence in the whole urban water system.

Shanghai (China), a fast-paced city, has a population of 25 million. The dosage of the psychiatric drugs is huge (http://www.imshealth.com). Pharmaceutical residues may not be fully eliminated during sewage treatment and are thus discharged into receiving waters. The city, where drinking water production mainly relies on surface water recharge, may face a lot of threat of contaminants.

Until recently, research and monitoring data on the environmental occurrence of psychiatric drugs in water environment of Shanghai have been limited to studies focused on a small number of targeted compounds (carbamazepine, 17 ng L^{-1}) in wastewater treatment plants (Wang et al., 2014), with no considerations on the whole urban water cycle. Very little data are currently available in Shanghai on the occurrence and fate of psychoactive compounds in urban water cycle system. It is necessary to research psychiatric pharmaceuticals in Shanghai water environment.

The objectives of this investigation were to: (i) determine and monitor the occurrence of the described psychoactive compounds in environmental water sample from Shanghai, including WWTP influents and effluents, surface water and final drinking water; (ii) study the elimination of these substances during WWTP and investigate the link between WWTP discharges and concentrations of psychoactive compounds in Shanghai's surface water, and (iii) evaluate the risk of contamination of drinking water. This work provides important information on the distribution and the fate of these contaminants in the aquatic environment.

Table 1
Occurrence of psychiatric pharmaceuticals in the environment.

Pharmaceutical	Concentration (maximum)	Sample	Reference
Diazepam	33 ng/L	Influent of STP; Germany	Ternes et al. (2001)
Lorazepam	334 ng/L	influent of STP; China	Yuan et al. (2013)
Fluoxetine	20 ng/L	Influent of STP; China	Yuan et al. (2013)
Diazepam	1180 ng/L	Influent of STP; Belgium	van der Ven et al. (2006)
Oxazepam	250 ng/L	Effluent of STP; Germany	Heberer (2002)
Nordiazepam	8.3 ng/L	Effluent of STP; France	Togola and Budzinski (2008)
Fluoxetine	12 ng/L	Effluent of STP; USA	Schultzt and Furlong (2008)
Diazepam	53 ng/L	Surface waters; Germany	Ternes et al. (2001)
Nordiazepam	2.4 ng/L	Surface waters; France	Togola and Budzinski (2008)
Fluoxetine	12 ng/L	Surface waters; USA	Kolpin et al. (2002)
Oxazepam	40 ng/L	Surface waters; Germany	Hass et al. (2012)
Fluoxetine	<5 ng/L	Drinking water; USA	Snyder (2008)
Amitriptyline	1.4 ng/L	Drinking water; France	Togola and Budzinski (2008)
Diazepam	23.5 ng/L	Drinking water; Italy	Zuccato et al. (2000a)

2. Materials and methods

2.1. Chemicals

Standards of diazepam, oxazepam, lorazepam, alprazolam, estazolam, bromazepam, nordiazepam, amitriptyline, doxepin, fluoxetine and mianserin were purchased from Cerilliant (Round Rock, TX, USA). 2-Amino-5-chorobenzophenone and 5-chloro-2-benzophenone standards were purchased from Toronto Research Chemicals (North York, Canada). Temazepam was provided by o2si smart solutions (Charleston, South Carolina, USA). Carbamazepine was obtained from Sigma–Aldrich (The Woodlands, Texas, USA). Diazepam-d_5, oxazepam-d_5 and lorazepam-d_4 from Cerilliant were used as internal standards. Physicochemical properties and molecular structures of the 15 targeted psychiatric pharmaceuticals are shown in the Supplementary content Table S1. Approximately 1 mg of individual standard (2-amino-5-chorobenzophenone, 5-chloro-2-benzophenone, carbamazepine) was accurately weighed and placed in a 10 mL brown flask and then diluted to 10 mL with methanol. HPLC grade methanol and acetonitrile were purchased from Merk (Darmstadt, Germany). Other chemicals and solvents were of analytical grade provided by Shanghai Anpel scientific instrument corporation. Ultrapure water was produced by a Milli-Q water purification system (Millipore, Bedford, MA, USA) with resistance >18.2 MΩ.

2.2. Site description and sampling

Surface water samples were collected in different locations (sampling points are georeferenced in Table S4) along the Huangpu River (Fig. 1). This river originates in the Dianshan Lake and flows into the Yangtze River. Huangpu is a 113 km river with an average flow rate of 319 m^3/s. Plenty of the remaining wastewater and effluents are directly discharged into the Huangpu River every day. Sampling locations were homogenously distributed through the course of the river from its source to its mouth and were close to the tributary of interchange (Fig. 1). The stations are representative of the effects of human pressure in its different aspects (agriculture, industry, urbanization, infrastructures).

Surface water samples were taken at the end of October 2014. Grab water samples (4 L) were collected in clean amber glass bottles, from the middle of the river width at 0.5 m depth using standard equipment (organic glass barrel with the package lead weight at the bottom to keep vertical drop and there is a thermometer inside). Before sample collection, each bottle was thoroughly pre-rinsed with Milli-Q water at the laboratory and then, rinsed with sample water prior to sample collection. Frankly, the active