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Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China

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ABSTRACT

The occurrence and removal of 13 pharmaceuticals and 2 consumer products, including antibiotic, antilipidemic, anti-inflammatory, anti-hypertensive, anticonvulsant, stimulant, insect repellent and antipsychotic, were investigated in four wastewater treatment plants (WWTPs) of Beijing, China. The compounds were extracted from wastewater samples by solid-phase extraction (SPE) and analyzed by ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC–MS/MS). Most of the target compounds were detected, with the concentrations of 4.4 ng L^{-1}–6.6 μg L^{-1} and 2.2–320 ng L^{-1} in the influents and secondary effluents, respectively. These concentrations were consistent with their consumptions in China, and much lower than those reported in the USA and Europe. Most compounds were hardly removed in the primary treatment, while their removal rates ranging from −12% to 100% were achieved during the secondary treatment. In the tertiary treatment, different processes showed discrepant performances. The target compounds could not be eliminated by sand filtration, but the ozonation and microfiltration/reverse osmosis (MF/RO) processes employed in two WWTPs were very effective to remove them, showing their main contributions to the removal of such micro-pollutants in wastewater treatment.

1. Introduction

With the progress of sensitive analytical techniques, the frequent detection of various pharmaceuticals in the aquatic environment has received global concerns of both the academic community and the public (Daughton and Ternes, 1999; Jones et al., 2005). After intake by humans or animals, the pharmaceuticals will be partially converted to metabolites, however, partially excreted unchanged or as conjugates, and finally delivered to the wastewater treatment plants (WWTPs). As there is no unit specifically designed to remove these compounds, the elimination by most WWTPs seems to be inefficient (Ternes, 1998; Castiglioni et al., 2006; Lishman et al., 2006; Nakada et al., 2006; Santos et al., 2007; Vieno et al., 2007b; Xu et al., 2007; Gulkowska et al., 2008; Paxeus, 2004). Together with treated wastewater, these compounds are released to the aquatic environment, and consequently found to contaminate the receiving water bodies (Lindqvist et al., 2005; Kasprzyk-Hordern et al., 2009), or even raw water sources of drinking water treatment plant (Ternes et al., 2002; Vieno et al., 2007a; Radjenovic et al., 2008). Meanwhile, results of toxicology studies have revealed that some pharmaceuticals are suspected to have direct toxicity to certain aquatic organisms (Ferrari et al., 2003; Jjemba, 2006; Grung et al., 2008; Quinn et al., 2008). Besides, their continual but undetectable effects could accumulate slowly, and finally lead to irreversible change on wildlife and human beings (Daughton and Ternes, 1999). Therefore, the occurrence and behavior of pharmaceuticals in the WWTPs, which are both the sink and source of the compounds, should be focused on. So far, concentrations of pharmaceuticals from various therapeutic classes in the WWTPs have been well documented in the

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North America (Thomas and Foster, 2005; Lishman et al., 2006), Japan (Nakada et al., 2006) and some European countries (Ternes, 1998; Castiglioni et al., 2006; Santos et al., 2007; Vieno et al., 2007b; Jones et al., 2007; Paxeus, 2004). Reported species and concentrations of pharmaceuticals varied from country to country, and plant to plant, owing to the different usage patterns. Meanwhile, the removal efficiencies of pharmaceuticals also varied much (Nakada et al., 2006; Gulkowska et al., 2008), indicating that the removal could be affected by both the compound-specific properties, and the factors concerning specific WWTPs, such as types of treatment processes, solids retention time (SRT), hydraulic retention time (HRT), temperature, etc. In recent years, very few studies about the situation in China have been reported. Only one specific therapeutic class, antibiotics, has been investigated by limited previous studies (Xu et al., 2007; Gulkowska et al., 2008; Chen et al., 2008). Therefore, it is necessary and important to investigate the occurrence and removal of pharmaceuticals from different therapeutic classes in the WWTPs of China.

Due to the low efficiency of conventional wastewater treatment processes, some advanced treatment technologies have been evaluated. Ozonation was found to be effective to remove pharmaceuticals in real municipal WWTPs of Japan (Nakada et al., 2007; Okuda et al., 2008) and Germany (Ternes et al., 2003). Nanofiltration (NF) and reverse osmosis (RO) membrane filtration, the well-proven technologies to remove pharmaceuticals from different kinds of waters, have also been applied at bench, pilot and full scale (Khan et al., 2004; Nghiem et al., 2005; Drewes et al., 2005; Al-Rifai et al., 2007; Watkinson et al., 2007; Comerton et al., 2008; Radjenovic et al., 2008). Retention behavior of pharmaceuticals during the processes associated with physicochemical properties of pharmaceuticals, membranes as well as the solution chemistry, and mechanisms of pharmaceutical rejection have been discussed in Kimura et al. (2004), Nghiem et al. (2005), Nghiem and Coleman (2008) and Comerton et al. (2008). Recently, considering the requirement of reclaimed water, several advanced treatment facilities have been installed in the WWTPs of Beijing. However, the removal efficiency of micro-pollutants, such as pharmaceuticals, has not been evaluated yet.

In the present study, we investigated the contamination levels of 13 pharmaceuticals and 2 consumer products from 8 classes (i.e. antibiotic, antilipidemic, anti-inflammatory, antihypertensive, anticonvulsant, stimulant, insect repellent and antipsychotic) in four WWTPs of Beijing, China, which have different advanced treatment units, and evaluated the elimination efficiencies of the target pharmaceuticals. To the best of our knowledge, this is the first report on the occurrence and removal of pharmaceuticals and consumer products from multiple classes in the WWTPs of China, especially for the situation during the advanced treatment processes.

2. Materials and methods

2.1. Chemicals

All the standards including chloramphenicol (CP), nalidixic acid (NA), trimethoprim (TP), bezafibrate (BF), clofibric acid (CA), gemfibrozil (GF), diclofenac (DF), indometacin (IM), ketoprofen (KP), mefenamic acid (MA), metoprolol (MTP), carbamazepine (CBZ), caffeine (CF), *N*,*N*-diethyl-meta-toluamide (DEET) and sulpiride (SP) (Appendix) were of analytical grade (>90%), and purchased from Sigma–Aldrich (Steinheim, Germany). Isotopically labeled compounds, used as internal standards, were ^{13}C-phenacetin obtained from Sigma–Aldrich, and ^{3}D-mecoprop from Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade methanol, acetone, dichloromethane, hexane, as well as formic acid were provided by Dikma (USA), and ultra-pure water was produced by a Milli-Q unit (Millipore, USA). Stock solutions of individual compound were prepared in methanol and mixture standards with different concentrations were prepared by diluting the stock solutions before each analytical run. All the solutions were stored at 4 °C in the dark.

2.2. Sample collection

Four full-scale municipal WWTPs, referred as A, B, C and D, were selected in our study. These WWTPs employ similar conventional treatment processes: primary treatment to remove particles coupled with secondary biological treatment. For the secondary biological treatment processes, WWTPs A and D employ anaerobic/anoxic/oxic (A^2/O) activated sludge process, anoxic/oxic (A/O) activated sludge process is adopted in WWTP B, and WWTP C employs oxidation ditch (OD). Other detailed information on each WWTP, such as inhabitants served, daily flow, HRT and SRT are shown in Table 1. Part of the secondary effluents was further treated in WWTPs A, B and D, by the processes of ultrafiltration (UF)/ozone, sand filtration (SF) and microfiltration/reverse osmosis (MF/RO), respectively. In WWTP A, a dead-end ultrafiltration system (Zenon GE) is used. The whole system has 6 trains of Zee-Weed 1000 membrane. Each train contains 9 cassettes of 57–60 modules per cassette. The membrane, with the pore size of 0.02 μm, is made by PVDF. The module is operated in an outside/in configuration at a constant flow of 23 L $(m^2\,h)^{-1}$ and the total treatment capacity reaches 80,000 $m^3\,d^{-1}$. The membrane is hydraulically backwashed at a constant flow rate of 34 $(m^2\,h)^{-1}$, and 29 times per day. The backwash phase lasts for 1 min. Maintenance cleaning is conducted once per day. Membranes are soaked in the sodium hypochlorite solution (50 mg L^{-1}) for 25 min. For the ozonation process, gaseous ozone is generated from an ozone generator (Mitsubishi Electric). The ozone dosage and contact time in the reaction tank is 5 mg L^{-1} and 15 min, respectively. The pH of the wastewater before ozonation ranges 6.5–8.0 and shows no significant change after ozonation. As the heart of the advanced treatment in WWTP D, a spiral-wound crossflow module is employed for the reverse osmosis (RO) membrane filtration. The RO membrane (Filmtec, DOW) is made from a thin-film composite polyamide material. Each module is designed to operate at a water flux of 1.3 $m^3\,h^{-1}$, and a product water recovery of 75–80%. The trans-membrane pressure is between 0.04 and 0.06 MPa, and the salt rejection remained at the level of 99%. Every 3–6 months, normally when the trans-membrane pressure reaches above 0.06 MPa, the membrane is cleaned with 0.1%(w) sodium hydroxide solution (for organic foulants), 2%(w) citric acid (for inorganic foulants) and 0.5%(w) formaldehyde (as biocide). Schematic diagram of treatment processes in the four WWTPs is shown in Fig. 1.