Ecotoxicology and Environmental Safety 117 (2015) 132–140

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Occurrences of pharmaceuticals in drinking water sources of major river watersheds, China

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ARTICLE INFO

Article history:
Received 26 September 2014
Received in revised form
26 March 2015
Accepted 27 March 2015
Available online 5 April 2015

Keywords:
Pharmaceutical
Drinking water
Occurrence in China
Causality analysis

ABSTRACT

Pharmaceuticals in drinking water sources (DWSs) have raised significant concerns for their persistent input and potential human health risks. Currently, little is known about the occurrence of pharmaceuticals in DWSs in China. In this study, a survey for multi-class pharmaceuticals in DWSs of five major river watersheds in China was conducted from 2012 to 2013. Samples were collected from 25 sampling sites in rivers and reservoirs. 135 pharmaceuticals were analyzed using solid-phase extraction and ultra-performance liquid chromatography tandem mass spectrometry. The results showed that a total of 70 pharmaceuticals were present in the samples, and the most frequently detected ones included sulfonamides, macrolides, antiepileptic drugs, anti-inflammatory drugs, and β-blockers, etc. Amongst these, maximum concentrations of lincomycin, sulfamethoxazole, acetaminophen and paraxanthine were between 44 ng/L and 134 ng/L, and those of metoprolol, diphenhydramine, venlafaxine, nalidixic acid and androstenedione were less than 1 ng/L. Concentrations of the two that were most persistent, DEET and carbamazepine, were 0.8–10.2 ng/L and 0.01–3.5 ng/L, respectively. Higher concentrations of cotinine were observed in warm season than in cold season, while concentrations of lincomycin were the opposite. In a causality analysis, the occurrence of pharmaceuticals in DWSs depends mainly on the detection limits of the methods, their usage and the persistence in the aquatic environment.

1. Introduction

Pharmaceuticals are so-called “pseudo-persistent” contaminants in aquatic environments because of their consistent consumption, and their polar and non-volatile properties (Daughton, 2003). Pharmaceuticals include diverse groups, such as antibiotics, antiepileptics, non-steroidal anti-inflammatory drug (NSAIDs), blood-lipid regulators, antihistamines, β-blockers, anti-ulcer agents, anti-asthma drugs, serotonin re-uptake inhibitors and steroidal hormones. These compounds, together with their metabolites/transformation products, primarily enter aquatic environments via the effluents of municipal wastewater treatment plants (Nikolaou et al., 2007), discharges of sewage sludge (Li et al., 2013), livestock waste (Luo et al., 2011), and aquaculture activities (Zou et al., 2011). In receiving waters, certain pharmaceuticals, such as carbamazepine and diethyltoluamide (DEET), are resistant to natural degradation or transformation processes, resulting in their detection in rivers (de Jongh et al., 2012; Kolpin et al., 2002), lakes (Kleywegt et al., 2011) and reservoirs (Kim et al., 2007). The concentrations of detected pharmaceuticals normally occur at the ng/L level, but the concentrations of several pharmaceuticals, such as acetaminophen, caffeine and its metabolite paraxanthine, can exceed 1 μg/L (Kolpin et al., 2002). Due to the bio-activity of vast majority of pharmaceuticals, they could cause long-term adverse impacts to the aquatic organisms even at very low concentrations (Fent et al., 2006).

Drinking water sources (DWSs) are of great importance to human health. Multiple-classes of pharmaceuticals have been detected in DWSs in countries such as the United States (U.S.) (Benotti et al., 2009; Focazio et al., 2008), Canada (Kleywegt et al., 2011) and several European countries (de Jongh et al., 2012; Kuch

Abbreviations: DEET, diethyltoluamide; DWS, drinking water source; GPS, global positioning system; MDL, method detection limit; MQL, method quantification limit; NSAID, non-steroidal anti-inflammatory drug; U.S., United States; MRM, multiple reactions monitoring

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http://dx.doi.org/10.1016/j.ecoenv.2015.03.032
0147-6513/

and Ballschmiter, 2001; Mompelat et al., 2011; Valcárcel et al., 2013; Vulliet et al., 2011). In a national survey performed by the U.S. Geological Survey, several classes of pharmaceuticals, including antibiotics, prescription drugs, non-prescription drugs and other wastewater-related drugs, were detectable (Focazio et al., 2008), and the maximum concentrations of the detected pharmaceuticals ranged from 0.019 μg/L to 0.30 μg/L. Not all pharmaceuticals are completely removed during drinking-water treatment processes (Benotti et al., 2009; Huerta-Fontela et al., 2011; Stackelberg et al., 2007; Vulliet et al., 2011). As a result, several pharmaceuticals, such as carbamazepine, lincomycin, ibuprofen, acetaminophen, erythromycin, roxithromycin and metoprolol, are also detectable in distribution waters (Delgado et al., 2012; Stackelberg et al., 2004; Vulliet et al., 2011). In Germany, ethinylestradiol, the active ingredient in oral contraceptive pills, was detected in four out of 10 distribution water samples at the 0.15–0.50 ng/L level (Kuch and Ballschmiter, 2001). Ethinylestradiol may cause long-term endocrine disruption effects even at very low ng/L concentrations in distribution water (Vosges et al., 2008). The presence of various classes of pharmaceuticals in water may negatively affect the quality of drinking water and pose risks to human beings.

According to the Chinese Medical Statistical Yearbook 2006–2007, the domestic production of pharmaceuticals was 1,011,361 t in 2006 (Fig. S1). The production of pharmaceuticals accounts for more than 20% of the global volume and increases annually (Liu and Wong, 2013). Two categories, i.e. antibiotics (93,375 t in 2006) and analgesics/antipyretics (84,371 t in 2006), are associated with relatively high production volumes in China, and the production volumes of several classes of pharmaceuticals, such as alimentary system agents, nervous system agents, antiparasitics and disinfectants, and urinary system drugs, exceed 5000 t (Fig. S1). Hence, multiple classes of pharmaceuticals in addition to antibiotics and analgesics/antipyretics should be considered in surveys of DWSs. According to recent reviews of pharmaceutical contamination in China (Bu et al., 2013; Liu and Wong, 2013), a few categories of pharmaceuticals (mainly antibiotics and hormones) and a limited number of sampling sites in specific geographical areas have been considered. The occurrences of multi-class pharmaceuticals in the DWSs of the major river watersheds in China have not been well documented.

To determine the levels of pharmaceuticals in DWSs, reliable and stable analytical methods with low detection limits are required. Recently, our research group developed an analytical method to determine multiple-classes of pharmaceuticals with method detection limits (MDLs) between 0.004 ng/L and 7 ng/L in drinking water samples. With this method, many substances presented in water could be detected due to the very low detection limits, especially in the case of the sulfonamides, most of the quinolones, most of the macrolides, most of the androgens, an antiulcer agent, anti-asthma drug, analgesic drug, antihistamine, a caffeine metabolite, a nicotine metabolite, a lipid regulating agent, a calcium channel blocker, β-blockers, tranquilizers and a lincosamide. The MDLs of these compounds were below 0.15 ng/L. In the present survey, the method was applied for the priority list of candidate contaminants in DWSs located across five major river watersheds in China. The targeted pharmaceuticals were selected based on their production and consumption volumes in China, on their ubiquity and frequent detection in aquatic environments, as reported in the literature, and on their potential ecological impacts. The results reported in this paper will also enable international comparisons.

2. Materials and methods

2.1. Chemicals and materials

The targets were categorized into different groups, including antibiotics (sulfonamides, quinolones, tetracyclines, macrolides, a lincosamide and others), hormones (estrogens, progestogens, androgens and corticoids), anti-inflammatory drugs, β-blockers, antiulcer agents, receptor stimulants, analgesic drugs, antihistamines, serotonin re-uptake inhibitors, antiepileptics, tranquilizers, a lipid-regulating agent and a calcium channel blocker. In addition, two metabolites, i.e., cotinine and paraxanthine, one antifungal and two antimicrobials were also included.

2.2. Sampling collection

Brown glass bottles were used for sampling. To avoid contamination, all of the glassware used in the experiment was cleaned by being washed with detergent, rinsing with deionized water, and being heated at 110 °C for at least 2 h. Glass-fiber filters were heated at 450 °C for 2 h before use.

Samples were taken from stations of five major river watersheds, namely, those of the Yangtze River (S1–S5), the Huai River (S6–S9), the Yellow River (S10–S14), the Hai River (S15–S19) and the Liao River (S20–S25), which represented the most important watersheds in China (Table S1). A total of two sampling campaigns were conducted, one in 2012 and the other in 2013. The sampling campaigns for both the Huai River and the Yellow River watersheds were conducted during the cold seasons (fall and winter) of 2012 and the warm season (summer) of 2013, respectively. The surveys in the Liao River were conducted during the summer of both years. The surveys in the Hai River watershed were sampled during the fall of both years. The sampling campaigns for the Yangtze watershed were conducted during the winter of 2012 and fall of 2013. A total of 25 sampling sites were selected, based on the information provided by the Ministry of Water Resources of the People's Republic of China (Fig. 1), from the most important DWSs in these river watersheds, consisting of a total of 13 reservoirs and 12 rivers that serve as the source waters for local drinking water systems for populations ranging from 0.8 million to 23 million individuals. All of the sampling sites were located within close proximity to municipal drinking water treatment plants, with varying land uses in the surrounding watersheds (i.e., cropland, forest and urban area). Most river-water locations were surrounded by land used for residential or cropland purpose, and most reservoir-water locations were located in well-preserved surroundings. One sample was collected for each site during the 2012 sampling campaign. Two samples were collected for each site during the 2013 sampling campaign (Table S1). A global positioning system (GPS) was used to locate the sampling sites (GPS locations are given in Table S1). Water quality parameters were measured in situ (Table S2). The total organic carbon concentrations of the water samples were analyzed in laboratory (Teledyne Tekmar, Mason, OH, U.S.) (Table S2).

2.3. Sample extraction and instrumental analysis

The water samples were transported to the laboratory in a cool condition (with ice) and stored under a cool condition (4 °C) within three days. Sample volumes were 2 L. The water samples were filtered through 0.7 μm glass-fiber filters. The filtered water samples were extracted by solid-phase extraction (SPE) with tandem cartridges: Oasis WAX (150 mg; 6 mL) weak anion exchange mixed-mode cartridge coupled with Oasis HLB (500 mg; 6 mL) hydrophilic–lipophilic balance cartridges. Before extraction, the samples were added with Na_2EDTA, adjusted to pH 6. All the