



Research article

Occurrence and discharge of pharmaceuticals and personal care products in dewatered sludge from WWTPs in Beijing and Shenzhen

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ABSTRACT

This study mainly focused on the occurrence of pharmaceutical and personal care products (PPCPs) in sewage dewatered sludge and their discharges through sludge disposal from wastewater treatment plants (WWTPs). The data were obtained and calculated from seven PPCPs in dewatered sludge collected from 12 WWTPs in two typical cities, Beijing and Shenzhen in China. Four of seven PPCPs, diclofenac acid, carbamazepine, mefenamic acid and N,N-diethyl-m-toluamide were detectable in dewatered sludge from Beijing and Shenzhen with concentration up to 4240, 11,060, 92 and 219 µg/kg respectively. While, the other three compounds, trimethoprim, chloramphenicol and bezafibrate were not detected in collected samples from these two cities. The highest discharge of diclofenac acid and carbamazepine were 1023 g/d and 494 g/d respectively. In addition, the total discharge of these four detected PPCPs from each plant ranged from 5 to 1092 g/d in Beijing and 4–497 g/d in Shenzhen. Thus, PPCP discharge through sludge disposal cannot be neglected, and further research on transfer of PPCPs during sludge disposal onto agriculture land and influence of sludge application is required and essential.

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1. Introduction

Pharmaceutical and personal care products, namely PPCPs, have received considerable attention recently all over the world. As ever-increasing use leads to continuous emission into the environment, they are regarded as “pseudo persistent” contaminants [1]. Although their concentrations range from ng/L to µg/L, they can exist in various environmental media including aquatic environment, soil, plants and so on, having potential adverse effects on the ecosystem and human health [2,3]. Previous research on risk quotients containing digested sludge and digested sludge

amended-soil shows that chronic effects can occur due to continuous environment exposure of pharmaceuticals, in spite of the risk quotient values below 1 for most compounds [3,4].

PPCPs, designed primarily to improve human health and for veterinary use, can be discharged into the environment through many pathways in the original or metabolized form [5]. PPCPs typically enter surface waters through WWTPs, aquaculture facilities and runoff from fields, and also into soils through sludge and manure application. At present, WWTPs are widely considered as the main discharge source of PPCPs [2]. Since traditional WWTPs are not originally designed for removing PPCPs, their capacities for eliminating such compounds are limited [6]. Biodegradation and sorption onto sludge are known as the two main removal mechanisms in WWTPs [3]. As sludge contains various nutrient elements and organic compounds, its application to agriculture is regarded as a way of recycling resources [7]. Unfortunately, this process introduces PPCPs to the environment again and has potential risks to human health. Consequently sewage sludge plays as a sink for PPCPs [8] and becomes a potentially nonpoint source of PPCPs into the environment [9].

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Although many studies [10–12] have been performed on PPCP content in sludge, the analytical method still remains challenging due to its complex matrix effect. More and more countries like United States and some Western European countries are currently applying sewage sludge as fertilizers in agriculture [13]. Also, the proportion of sludge applied in agriculture is increasing [13]. Similarly, the presence of PPCPs in sludge becomes an important issue in China which applied about 40% sludge total generated (10 Mt wet sludge annually) to agriculture use [14].

Dewatered sludge is the final form of sludge transferred from WWTPs to environment. The research on dewatered sludge is rather limited in terms of how much PPCPs entering into environment through its discharge and application. As a result, the present study was undertaken to investigate the occurrence of PPCPs in dewatered sludge in two typical cities of China to observe the extent of PPCP pollution in sludge. The discharge of PPCPs through sludge disposal from WWTPs is also determined. It is hoped that by estimating the PPCP content in dewatered sludge and subsequently total discharge quantity, information obtained may be useful to regulatory agency for control and management of the adverse effect of PPCPs on environment.

2. Experimental

2.1. Chemicals and materials

Based on the priority list of pharmaceuticals in the water environment of China established by Sui et al. [15], 7 PPCPs with different priority levels were studied. The analytical standards of 7 PPCPs containing diclofenac acid (DF), carbamazepine (CBZ), chloramphenicol (CP), mefenamic acid (MA), trimethoprim (TP), N,N-diethyl-m-toluamide (DEET) and bezafibrate (BF) were purchased from Sigma-Aldrich (Steinheim, Germany). Among them, TP and CP are anti-infection agents. MA and DF are antipyretic analgesics. CBZ, DEET and BF belong to anti-epileptic agent, anopheluge and lipid regulator. The properties of target compounds are listed in Table 1.

The internal standards of D3-mecoprop, chloramphenicol-d5, DEET-d7 were purchased from Dr. Ehrenstorfer (Augsburg, Germany), C13-phenacetin and gemfibrozil-d6 were obtained from Sigma-Aldrich and Toronto Research Chemicals respectively. Methanol and acetonitrile were HPLC grade obtained from Dikma, USA. Ultra-pure water was made by a Milli-Q water purification system (Millipore, USA). Analytical grade citric acid-monohydrate with anhydrous sodium phosphate-dibasic to prepare buffer, aluminum oxide and diatomite were provided by Sinopharm Chemical Reagent Co., Shanghai, China.

0.45 μm glass fiber filters were purchased from Whatman, UK and 0.22 μm nylon syringe filters from Millipore, USA. Diatomite filters were obtained from Jitian Co., Beijing, China. Oasis HLB cartridges (500 mg, 6 cc) were purchased from Waters, USA.

2.2. Sampling sites and collection

Two typical cities, Beijing and Shenzhen, were selected in the present study. A total of 12 sewage sludge samples were collected directly from the outlet of dewatering facility from 7 WWTPs in Beijing and 5 WWTPs in Shenzhen (Fig. 1). The selected WWTPs contains different treatment scale from 3×10^4 to $100 \times 10^4 \text{ m}^3/\text{d}$, different wastewater treatment processes as activated sludge, membrane biological reactor, oxidation ditch, anaerobic-anoxic-oxic and cyclic activated sludge system, and different sludge treatment processes, including mesophilic digestion with dewatering and only dewatering. Three samples were taken from each WWTP and mixed as a composite sample. Then, they were kept in

hermetic bags stored in a sealed box with ice packs and transported to the laboratory. One aliquot sample was separated to characterize its moisture content (p), suspended solids (SS) and volatile suspended solids (VSS) using gravimetric method. And the remaining samples were stored at $-20 \text{ }^\circ\text{C}$ in refrigerator before analysis. Relevant parameters are listed in Table 2. The moisture content of most samples was among 60–88%. And the VSS/SS ratios of sludge samples from 12 WWTPs were different related to the wastewater and sludge treatment processes and wastewater characteristics.

2.3. Analytical methods

The analytical method was established based on the studies done by Chen et al. [16] and improved with special purification process described by Gago-Ferrero et al. [17]. Sludge samples were subjected to in-cell purification pressurized liquid extraction (PLE), solid phase extraction (SPE) and liquid chromatography-tandem mass spectrometry (LC-MS/MS), as shown in Supplementary Information (SI), Fig. S1.

The sludge sample transported to the lab was firstly frozen at $-20 \text{ }^\circ\text{C}$ for more than 24 h and then lyophilized at $-56 \text{ }^\circ\text{C}$. After that, the sample was grind by a mortar and pestle, and sieved to 0.125 mm for the subsequent extraction. Then, 0.1 g homogenized sample was extracted by PLE using acetonitrile/EDTA-McIlvaine buffer (1:1, v:v) using accelerated solvent extraction system (APLE2000) equipped with 22 mL capacity of stainless-steel cells. It was worth mentioning that the sludge sample was initially mixed with 1 g aluminium oxide to rid of impurity as reported by Gago-Ferrero et al. [17]. The collected extract was diluted to about 500 mL with Milli-Q water, filtered by 0.45 μm glass fiber filter, then passed through the SPE to be concentrated and finally eluted by 10 mL methanol. The elution was then concentrated by nitrogen gas to near dryness. After that, it was redissolved by 400 μL methanol/ultra-pure water (1:4,v:v) and filtered by 0.22 μm nylon syringe filter. At last, 10 μL sample was injected and analyzed by LC (Ultimate 3000, Dionex, Sunnyvale, CA) with electrospray ionization and tandem MS (API3200, AB Sciex, Framingham, MA). The operating parameters and conditions had been described by Chen et al. [16].

2.4. Quality assurance and quality control (QA/QC)

To assure quality of the method described above, experiments of spiking into blank samples and sludge samples to evaluate the method recovery were performed. The blanks were prepared using diatomite. The absolute recovery (AR) of the method was calculated as:

$$AR = \frac{A_{\text{spiked sludge}} - A_{\text{non-spiked sludge}}}{A_{\text{solvent}}} \times 100\% \quad (1)$$

where, $A_{\text{spiked sludge}}$, $A_{\text{non-spiked sludge}}$ and A_{solvent} are the peak areas of the compound in the spiked sludge samples, non-spiked samples and pure solvent samples, respectively.

The experiments results showed that the ARs of most compounds spiked into blank samples were 40–82%, and that in sludge samples were 24–74%, lower than the former. Because of the matrix effects taken into account in Eq. (1) and complex analytical procedure, the ARs were poor and some were lower than 50% which was the standard requirement for AR. Thus, the relative recovery was measured using the isotopically labeled compounds as internal standards. They were spiked into the samples at the same time to amend the result. The relative recoveries for most target compounds were 70–125%, which could meet the need basically. The detailed information of method recovery, compound retention

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