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Mass loading and removal of pharmaceuticals and personal care products including psychoactives, antihypertensives, and antibiotics in two sewage treatment plants in southern India

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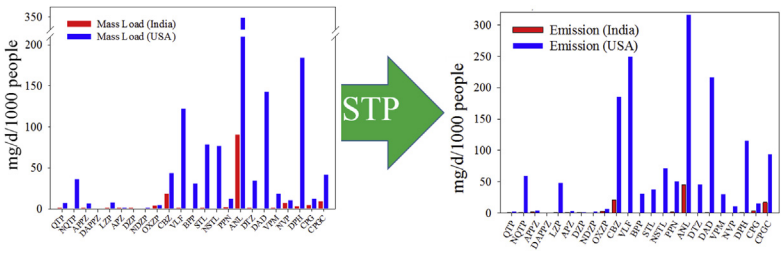
HIGHLIGHTS

- 29 PPCPs and 6 metabolites were detected in two STPs in India.
- Atorvastatin, mefenamic acid and paraxanthine found for the first time in Indian STPs.
- Metabolites were found 7 times higher than their parent drugs.
- Conventional STP did not remove carbamazepine, diazepam and clopidogrel.
- First study in India to report mass loading and emission of PPCPs into the environment.

GRAPHICAL ABSTRACT



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ABSTRACT

Environmental contamination by pharmaceuticals and personal care products (PPCPs) is barely studied in India despite being one of the largest global producers and consumers of pharmaceuticals. In this study, 29 pharmaceuticals and six metabolites were determined in sewage treatment plants (STPs) in Udupi (STP_U: population served ~150,000) and Mangalore (STP_M: population served ~450,000); the measured mean concentrations ranged from 12 to 61,000 ng/L and 5.0 to 31,000 ng/L, respectively. Atorvastatin (the most prescribed antihypercholesterolemic in India), mefenamic acid, and paraxanthine were found for the first time in wastewater in India at the mean concentrations of 395 ng/L, 1100 ng/L, and 13,000 ng/L, respectively. Select pharmaceutical metabolites (norverapamil and clopidogrel carboxylic acid) were found at concentrations of upto 7 times higher than their parent drugs in wastewater influent and effluent. This is the first study in India to report mass loading and emission of PPCPs and their select metabolites in STPs. The total mass load of all PPCPs analyzed in this study at STP_U (4.97 g/d/1000 inhabitants) was 3.6 times higher than calculated for STP_M. Select recalcitrant PPCPs (carbamazepine, diazepam, and clopidogrel) were found to have negative or no removal from STP_U while additional

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Removal efficiency
Wastewater
Sludge
Sewage treatment plant
India

treatment with upflow anaerobic sludge blanket reactor at STP_M removed (up to 95%) these PPCPs from STP_M. Overall, 5.1 kg of caffeine, 4.1 kg of atenolol, 2.7 kg of ibuprofen, and 1.9 kg of triclocarban were discharged annually from STP_U. The PPCP contamination profile in the Indian STP was compared with a similar study in the USA.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) enter the environment as parent drugs, their metabolites, and transformed products through industrial and/or domestic wastewater discharge as well as the farm application of sewage sludge from sewage treatment plants (STPs) (Halling-Sorensen et al., 1998). There is a concern over the ecological threats posed by "down-the-drain" chemicals including PPCPs in India; India is one of the top five emerging pharmaceutical manufacturing countries due to the recent relocation of global pharmaceutical industry from North America and EU to Asian countries (Rehman et al., 2015). India is one of the countries with largest drug consumption (Mathew and Unnikrishnan, 2012), and ranked 11th in the global consumption of over-the-counter drugs (Nagaraj et al., 2015).

In addition to the environmental discharge of significant amount of residual PPCPs through industrial effluent (Gunnarsson et al., 2009; Larsson et al., 2007), the treatment capacity of domestic sewage in India is far below the quantity of sewage generated from 1.3 billion people (Subedi et al., 2015). In 2008, only 31% of the total sewage produced (~38,254 million liters per day; MLD) in 908 cities were treated (CPCB, 2010). The shortage in demand and supply for the sewage treatment, inadequate maintenance of STPs, and sewage overflow every year for ~3–4 months of monsoon, consequently, can outweigh the estimated environmental emission of PPCPs. The majority of centralized wastewater treatment systems in developing countries consist of low-cost stabilization tank and septic ponds, while advanced secondary/tertiary treatments are common in developed countries (Kivaisi, 2001).

Over the past decade, research determining sources and overall fates of PPCPs through STPs, and their distribution in multiple environmental matrices including biota (Subedi et al., 2012), wastewater (Metcalfe et al., 2010; Radjenovic et al., 2009), surface water (Kolpin et al., 2002), drinking water (Benotti et al., 2009), and sludge (Subedi et al., 2013) were studied in developed countries. However, the frequency and concentration of PPCPs can vary depending on the consumption pattern of drugs and the effectiveness of wastewater treatment strategies (Kolpin et al., 2002). The fates of PPCPs in STPs in India are poorly reported (Anumol et al., 2016; Subedi et al., 2015). Moreover, the reported PPCPs fate studies focused only on parent drugs (Anumol et al., 2016; Prabhasankar et al., 2016; Singh et al., 2014). Environmental fate studies are particularly important because 30–90% of the administered dose of drugs is typically excreted through urine or feces (Halling-Sorensen et al., 1998), and metabolites of pharmaceuticals can be as much pharmacologically active as their parent drugs (Schwartz et al., 1985). A pilot study reported recently by our research group was the first to estimate mass loadings, removal efficiency, and environmental emission of wide-range of PPCPs and their select metabolites including illicit drugs and artificial sweetener in India (Subedi et al., 2015). We found ng/L to μg/L levels of PPCP residues including some of the highest reported concentrations in wastewater and sludge from Indian STPs.

PPCPs are capable of exerting toxic effects at relatively low concentrations through specific modes of action, and can affect non-target organisms at different trophic levels (Rehman et al., 2015). Antipsychotics, antidepressants, and antibacterials are the three most toxic classes of pharmaceuticals in the environment (Fent et al., 2006; Asimakopoulos and Kannan, 2016). For instance, at environmentally relevant concentrations, carbamazepine altered the ultrastructural cellular reactions in liver, kidney and gills of *Oncorhynchus mykiss* (rainbow trout) and *Cyprinus carpio* (common carp) (Triebskorn et al., 2007); diazepam inhibited polyp regeneration of *Hydra vulgaris* (Pascoe et al., 2003), and metoprolol and verapamil significantly changed the heartbeat of *Daphnia magna* (Villegas-Navarro et al., 2003). Therefore, studies on the environmental occurrence of fate of PPCPs are important. A detailed discussion on the toxicity of pharmaceutical residues in various test organisms has been compiled by Halling-Sorensen et al. (1998).

In this study, occurrence and removal of 29 PPCPs and nine metabolites including antischizophrenic, sedative-hypnotic-anxiolytic, antidepressant, antihypertension, antimicrobial, antibiotic, analgesic, antihistamine, antiplatelet, antihypercholesterolemic, UV-filter, and stimulant were determined in two STPs located at Udupi and Mangalore in southern India. Profiles of occurrence of PPCPs in wastewater influent in India were also compared with that in wastewater influents in the USA. This is the first study to determine mass loading of a wide-range of PPCPs in STPs from a week-long sampling event, removal efficiency, and environmental emission of these chemicals from Indian STPs.

2. Material and methods

2.1. Reagents and chemicals

Standard stock solutions (100 or 1000 μg/mL) of individual pharmaceuticals, metabolites, and their corresponding isotopically-labeled standards were purchased from commercial vendors, as described elsewhere (Subedi et al., 2015; Subedi and Kannan, 2015). Purity of all of the standards were ≥95%. Formic acid (98.2%) was from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure Deionized water was prepared with the Barnstead ultrapure system (Barnstead International, Dubuque, IA, USA). All standard stock solutions were stored at −20 °C.

2.2. Sample collection and preparation

Wastewater samples including raw wastewater (influent), treated wastewater (effluent), and sludge were collected over a seven-day period, from Sunday, May 19, 2013 to Saturday, May 25, 2013, consecutively from two STPs located in Udupi (STP_U) and Mangalore (STP_M) in the State of Karnataka, southern India. The wastewater influents were collected after the initial treatment that included screening of large-sized debris followed by grit removal. The wastewater effluents were collected at an outlet after the treatment processes prior to discharge into the Arabian Sea. STP_U involves a conventional aerobic biological treatment with activated sludge followed by final clarification and chlorine disinfection. STP_M involves upflow anaerobic sludge blanket reactor (UASBR),