Journal of Environmental Chemical Engineering 3 (2015) 2882–2891

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Mass loading and removal of pharmaceuticals and personal care products, including psychoactive and illicit drugs and artificial sweeteners, in five sewage treatment plants in India

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ARTICLE INFO

Article history:
Received 8 June 2015
Received in revised form 3 September 2015
Accepted 29 September 2015
Available online 9 October 2015

Keywords:
Pharmaceuticals
Antibiotics
Psychoactives
Illicit drugs
Artificial sweeteners
Sewage treatment plants
Sewage sludge

ABSTRACT

Despite the high consumption of pharmaceuticals, mass loading and removal of these compounds in sewage treatment plants (STPs) in India have not been investigated. In this study, 43 pharmaceuticals and personal care products as well as 13 of their metabolites were analyzed in five domestic STPs (wastewater influent, effluent, and sludge) and in raw domestic sewage collected in open sewerage channels in residential areas in India. The mean concentrations of amphetamine in two of the five STPs (mean: 4300 ng/L and 4720 ng/L) were the highest ever reported for wastewater influents, globally. Among artificial sweeteners, saccharin was the most abundant compound in influents (mean: 303,000 ng/L, df: 100%), followed by cyclamate [3460 ng/L, detection frequency (df): 75%] and sucralose (1460 ng/L, df: 100%). Elevated mean concentrations of an antimicrobial (triclocarban = 6180 ng/L), analgesic (ibuprofen = 2320 ng/L), antihypertensive (atenolol = 3180 ng/L), illicit drug (amphetamine = 984 ng/L), and saccharin (419,000 ng/L) were found in the Cooum River in Chennai. The median removal efficiencies of pharmaceuticals and personal care products (PPCPs) ranged from 5% (norcocaine) to 100% (triclosan) for the five STPs. On the basis of the concentrations measured in influents, the mass loadings of PPCPs were estimated to range from 0.1 (norquetiapine) to 77,800 (saccharin) mg/d/1000 people. An estimated 2.55 kg of triclocarban, 3.24 kg of carbamazepine, 6.93 kg of amphetamine, and 252 kg of saccharin were discharged from a typical STP with an average flow rate of 20.7 million liters per day (serving a population of 325,000) in India.

1. Introduction

Pharmaceuticals and personal care products (PPCPs), released mainly through human excretion or flushed down the drain, are introduced into the sewage treatment plants (STPs) via the sewerage systems [1–3]. STPs are, in turn, a source of PPCPs to the environment, when effluents and sludge from the facilities are discharged to water bodies and farmlands [1]. The extent of environmental contamination by PPCPs is presumably significant in developing countries, where the capacity for the treatment of wastewater is far below the quantity of sewage generated by the populations. In India, only 31% of the total sewage produced (~38,254 million liters per day; MLD) in 908 cities, whose STPs serve a population of 258 million, was treated in 2008 [4]. Further, the existing STPs are not effectively utilized or maintained; ~39% of existing STPs do not comply with the prescribed environmental regulations prior to discharge of effluents into the streams. In many small towns and rural areas, STPs do not even exist. Thus, the environmental emission of PPCPs can be expected to be high in

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http://dx.doi.org/10.1016/j.jece.2015.09.031
2213-3437/

India; however, little is known on the occurrence and fate of PPCPs in sewerage systems and STPs in India [5].

India is a major global market for pharmaceuticals. The current market is valued at more than US $21.7 billion and is estimated to be US$36.7 billion in 2015 [6]. Apart from human excretion, industrial discharges can contribute to pharmaceutical contamination in the environment [7]. Few studies have reported the occurrence of select antibiotics and non-steroidal inflammatory drugs in wastewater [8–10], river water [11,12,5], and drinking water [8] in India. However, no earlier studies have reported the occurrence or removal of different classes of psychoactive pharmaceuticals, illicit drugs, or artificial sweeteners in STPs in India.

Estimation of mass loadings of PPCPs in a STP on the basis of prescription records may underestimate the actual load, as ~64% of Indian patients purchase medications without a prescription [11]. Based on the measured concentrations in wastewater, an estimated loading of antibiotics in a STP in India was reported to range from 15.4 to 1395 g/day [11]. Inadvertent use of antibiotics in India has led to an increase in the occurrence of drug resistant microorganisms (i.e., superbugs) in the Indian environment [13]. Further, little is known on the ecosystem level effects of PPCPs in the environment [14–16]. One study reported that tadpoles and zebrafish exposed to 0.2% effluents from STPs showed a 40% reduction in growth [17]. Another study showed that egg production was decreased in Japanese medaka (*Oryzias latipes*) following exposure to 0.5 mg/L of propranolol [18].

This is a pilot study to elucidate the occurrence and removal of 43 widely used PPCPs (two antimicrobials, four antibiotics, an antimycotic, four analgesics, an antihistamine, an antiplatelet, a UV-filter, a stimulant, two antischizophrenics, six sedative-hypnotics-anxiolytics, four antidepressants, four antihypertensives, eight illicit drugs, and four artificial sweeteners) and 13 of their metabolites in five STPs in India. In addition, PPCPs also were determined in raw sewage collected in open sewerage channels (i.e., ditches) near residential areas. The mass loadings of PPCPs to STPs, removal rates, and environmental emissions through the discharge of wastewater effluents and sludge were estimated based on the measured concentrations of PPCPs in limited samples of wastewater and sludge.

2. Materials and methods

2.1. Reagents and chemicals

Target analytes include two antimicrobials (triclosan and triclocarban), four antibiotics (sulfamethoxazole, trimethoprim, clindamycin, and lincomycin), an antimycotic (miconazole), four analgesics (ibuprofen, ketoprofen, codeine, and oxycodone), an antihistamine (diphenhydramine and its metabolite 2-diphenylmethoxy acetic acid), an antiplatelet (clopidogrel and its metabolite clopidogrel carboxylic acid), an UV-filter (oxybenzone), a stimulant (caffeine), two antischizophrenics (aripiprazole and quetiapine and their respective metabolites dehydro-aripiprazole and norquetiapine), six sedative-hypnotic-anxiolytics [alprazolam, α-hydroxyalprazolam (a metabolite of alprazolam), lorazepam, diazepam, oxydiazepam, nordiazepam, and carbamazepine], four antidepressants [venlafaxine, sertraline, norsertraline (a metabolite of sertraline), bupropion, citalopram, and *N*-desmethylcitalopram (a metabolite of citalopram)], four antihypertensives [verapamil, norverapamil (a metabolite of verapamil), diltiazem, desacetyl diltiazem (a metabolite of diltiazem), propranolol, and atenolol], eight illicit drugs [cocaine, three metabolites of cocaine (benzoylecgonine, cocaethylene/benzoylecgonine ethyl ester, and norcocaine), amphetamine, methamphetamine, methadone, EDDP (a metabolite of methadone: 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine), morphine, MDA (3,4-methylenedioxyamphetamine), MDEA (3,4-methylenedioxyethylamphetamine), MDMA (3,4-methylenedioxymethamphetamine)], and four artificial sweeteners (acesulfame, cyclamate, saccharin, and sucralose). Analytical standards of individual PPCPs and their metabolites, as well as corresponding isotopically labeled internal standards were purchased from commercial vendors, as described elsewhere [19–22]. The purity of all of the standards was ≥95%. All organic solvents (HPLC grade) and ammonium hydroxide (29.5% as ammonia) were purchased from Mallinckrodt Baker (Phillipsburg, NJ). Ultrapure water was prepared using a Milli-Q ultrapure system (Barnstead International, Dubuque, IA). All standard stock solutions were stored at −20° C.

2.2. Sample collection and preparation

Wastewater influent and effluent samples were collected from five STPs in India during July and August 2012: Saidpur (STP_{SP}), Beur (STP_{BU}), Coimbatore (STP_{CO}), Udupi (STP_{UP}), and Manipal (STP_{MP}). Saidpur and Beur are in Bihar state, Northern India, whereas Udupi and Manipal are in Karnataka state and Coimbatore is in Tamil Nadu state, Southern India. All STPs used activated biological treatment and received only domestic discharges. Aerobically digested sludge samples were collected from STP_{SP}, STP_{BU}, STP_{CO}, and STP_{UD}; however, samples from STP_{MP} was not be analyzed due to the lack of that sample. The activated sludge samples from all STPs were the combined sludge produced after primary and secondary treatments. Detailed information on STPs, including daily wastewater inflow, total treatment capacity, population served, and the sludge production rate are provided in Table 1. In addition to samples from STPs, raw sewage samples also were collected from sewerage channels near residential areas in Patna (Patna Sewage), Cooum River (two locations: at the Napier bridge near river mouth and at the mid-section near Spurtank Bridge, Chennai) and Sanganur Pallam (Mettupalayam Road, Coimbatore). A landfill leachate sample was collected from the Vellalore solid waste landfill facility in Coimbatore. All samples were collected as one-time grab samples in pre-cleaned 250 mL polypropylene bottles, shipped frozen to the laboratory in Albany, New York, and stored in a freezer at −20° C until extraction.

The detailed procedure for the extraction of wastewater and sludge has been described elsewhere [19–22]. Unfiltered wastewater samples (50 mL) were spiked with a mixture of labeled internal standards of the target analytes (25 or 50 ng) prior to

Table 1
Characteristics of five sewage treatment plants (STP) studied in India.

	Saidpur STP (STP_{SP})	Beur STP (STP_{BU})	Coimbatore STP (STP_{CO})	Udupi STP (STP_{UD})	Manipal STP (STP_{MP})
Inflow (capacity) (MLD)	19 (45)	20.9 (35)	22.5 (50)	2.0	2.0
Population served	350,000	275,000	350,000	10,000	12,000
Sludge production (tons/y ww)	60.7	67.0	12.0	–	–