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Occurrence and fate of emerging trace organic chemicals in wastewater plants in Chennai, India

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ABSTRACT

The presence of pharmaceuticals, hormones, pesticides and industrial contaminants collectively termed as trace organic compounds (TOrCs) in wastewater has been well-documented in USA, Europe, China and other regions. However, data from India, the second most populous country in the world is severely lacking. This study investigated the occurrence and concentrations of twenty-two indicator TOrCs at three wastewater treatment plants (WWTPs) in South India serving diverse communities across three sampling campaigns. Samples were collected after each WWTP treatment unit and removal efficiencies for TOrCs were determined. Eleven TOrCs were detected in every sample from every location at all sites, while only five TOrCs were detected consistently in effluent samples. Caffeine was present at greatest concentration in the influent of all three plants with average concentrations ranging between 56 and 65 μg/L. In contrast, the x-ray contrast media pharmaceutical, iohexol, was the highest detected compound on average in the effluent at all three WWTPs (2.1–8.7 μg/L). TOrCs were not completely removed in the WWTPs with removal efficiencies being compound specific and most of the attenuation being attributed to the biological treatment processes. Caffeine and triclocarban were well removed (>80%), while other compounds were poorly removed (acesulfame, sucralose, iohexol) or maybe even formed (carbamazepine) within the WWTPs. The effluent composition of the 22 TOrCs were similar within the three WWTPs but quite different to those seen in the US, indicating the importance of region-specific monitoring. Diurnal trends indicated that variability is compound specific but trended within certain classes of compounds (artificial sweeteners, and pharmaceuticals). The data collected on TOrCs from this study can be used as a baseline to identify potential remediation and regulatory strategies in this understudied region of India.

1. Introduction

Pharmaceuticals, personal-care products, hormones, and industrial compounds, are often collectively termed as trace organic compounds (TOrCs). These substances are generally ubiquitous in municipal wastewater. Several thousand pharmaceuticals are currently in circulation and their primary route into the environment is through human excretion into wastewater. Similarly, hormones enter wastewater through human excretion and concentrated animal feeding operations while industrial compounds can enter wastewater through point discharges and surface runoff. Thus wastewater can be considered as the important contributor of TOrCs to the aquatic environment with high potential to enter source and potable water (Lee et al., 2015).

The primary concern associated with TOrCs is potentially adverse effects to wildlife and aquatic systems at environmentally relevant concentrations (vom Saal and Hughes, 2005; Kidd et al., 2007; la Farre et al., 2008). Further, potential chronic effects associated with low dose, long-term human exposures and mixture toxicity through potable water contamination has not yet been characterized (Daughton and Ternes, 1999; Snyder, 2014). Many of these TOrCs are not completely removed by conventional water treatment processes, which were not designed for their attenuation (Westerhoff et al., 2005; Kosma et al., 2014). Consequently, TOrCs have been detected in wastewater effluents and receiving water bodies in many regions. Numerous studies have characterized the presence of TOrCs in wastewaters across North America, Europe, Asia, and Australia. A summary of concentrations reported in the literature across the world has been provided in Table 1. However, concentrations of TOrCs are known to vary among regions due to sales and usage patterns, water consumption and water treatment methods employed (Verlicchi et al., 2012; Alidina et al., 2014). Thus no generalized conclusions can be drawn from one region to another without empirical data.

India is the second most populous country in the world with an estimated average water demand of 710 billion cubic meters. The study area, Chennai is the fourth most populous city in India with a population

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Table 1
TOrCs reported in studies around the world.

Contaminants	Country	Concentration range (μg/L)^	Samples*	Matrix	References
Pharmaceuticals	USA	nd-5.2	50	Wastewater Effluent	Batt et al. (2008), Sui et al. (2011), Bijlsma et al. (2012), Alidina et al. (2014), Kosma et al. (2014), Kostich et al. (2014), Kwon and Rodriguez (2014)
		nd-2.95	7	Wastewater Effluent	
		0.066–3.91	3	Wastewater Influent	
		nd-1.32	3	Wastewater Effluent	
	Greece	nd-96.6	32	Wastewater Influent	
		nd-1.07	32	Wastewater Effluent	
	Saudi Arabia	nd-3.2	4	Wastewater Effluent	
	China	nd-0.8	4	Wastewater Influent	
		nd-0.2	4	Wastewater Effluent	
	Netherlands	nd-3.70	5	Wastewater influent	
		nd-0.994	5	Wastewater effluent	
Hormones	Spain	nd-0.004	1	Wastewater Influent	Carballa et al. (2004), Chang et al. (2011), Sapozhnikova et al. (2011)
	USA	0.027–0.179	2	Wastewater Influent	
		nd-0.024	2	Wastewater Effluent	
	China	nd-3.7	7	Wastewater Influent	
		nd-0.012	7	Wastewater Effluent	
Pesticides	Spain	nd-1.94	5	Wastewater Effluent	Barco-Bonilla et al. (2010), Singer et al., (2010)
	Switzerland	nd-1.01	–	Wastewater Effluent	
Perfluorinated compounds	Japan/Thailand	nd-0.574	13	Wastewater Effluent	Sinclair and Kannan (2006), Shivakoti et al. (2010), Llorca et al. (2012)
	USA	nd-1.05	6	Wastewater Effluent	
	Germany/Spain	nd-0.50	5	Wastewater Effluent	
Artificial sweeteners	USA	~17.0–30.0	9	Wastewater Effluent	Buerge et al. (2009), Oppenheimer et al. (2011), Alidina et al. (2014)
	Saudi Arabia	0.415–28.0	4	Wastewater Effluent	
	Switzerland	2.0–65.0	10	Wastewater Influent	
		nd-46.0	10	Wastewater Effluent	

in excess of 4.5 million. The annual wastewater treatment capacity of the city is estimated at 571 million liters per day (MLD) while projected daily water requirement is between 710 and 900 MLD (Vedachalam, 2012). With this shortage between demand and supply, the city will be forced to consider alternate strategies for water replenishment including water reuse. While several studies have analyzed bulk water parameters like pH, total organic carbon, total nitrogen, and others very few studies have measured individual organic contaminants in India (CPCB, 2004). Recently, work on analyzing pesticides has been performed in some regions of the country (Dsikowitzky et al., 2014), and TOrCs have been detected in surface waters (Ramaswamy et al., 2011; Selvaraj et al., 2014; Shanmugam et al., 2014). Larsson et al. looked at the presence of pharmaceuticals in a wastewater effluent servicing over 90 pharmaceutical manufacturers in a town in India and reported some of the highest concentrations seen in the world (Larsson et al., 2007). However, no data on a large variety of indicator TOrCs is available for WWTPs in the region of study (South India). While, developed countries are swiftly adopting advanced treatments like ozone and high pressure membranes to attenuate TOrCs from water (Wert et al., 2009; Yang et al., 2011), the overwhelming majority of plants in India adopt only secondary treatment before discharge (CPCB, 2004). Thus, with potential growth in water reuse schemes in the country, studies on occurrence, and fate of TOrCs in water is critical.

The aim of this study was to characterize the concentrations of a suite of indicator TOrCs that represent a larger category of organic contamination in three diverse wastewater treatment plants (WWTPs) in Chennai influenced by domestic waste, farming and point source discharges that are typical of the country. Three sample campaigns were conducted at the three WWTPs that varied in treatment capacity, type and size of population served and treatment train. Further, removal efficiency of the three WWTPs were calculated after each treatment stage and average WWTP effluent concentrations were compared to those in the USA and other countries. Diurnal variability of TOrCs at a small wastewater plant serving a unique community was also studied to compare with results from other regions in the world. This is the one of the first studies looking at TOrC concentrations in South India in wastewater and will serve as a guideline for potential regulatory action in the country.

2. Experimental

2.1. Materials

All standards and reagents were procured at the highest purity that was practically feasible. The TOrC standards were acquired from a variety of vendors and have been described in previous literature (Anumol et al., 2013; Anumol and Snyder, 2015). Water and acetonitrile (both LC-MS grade) were purchased from Burdick & Jackson (Muskegon, MI), while formic acid (>95%) and acetic acid (>99%) were purchased from Sigma-Aldrich (St. Louis, MO).

2.2. Methods

UV absorbance and fluorescence spectroscopy was analyzed with a Horiba Aqualog spectrophotometer. Light scattering and inner filter effects were corrected as described previously (Lakowicz, 2007). Biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids, ammonia, total phosphate and nitrate were analyzed as per the Standard Methods for the analyses of water and wastewater (APHA, 2012). Total nitrogen was measured using TOC analyzer equipped with total nitrogen module (Shimadzu, Japan). Two methods using fully-automated online solid phase extraction with an Agilent Flexcube module and large volume direct injection were used to analyze the 22 TOrCs in this study (Table 2). All TOrC analyses were performed on an Agilent (Santa Clara, USA) LC-MS/MS system and quantification was performed using MassHunter software (Ver. 06.00). The instrument operation conditions for both methods are provided in the supplementary materials. Details of the methods including compound transitions, mass spectrometer conditions, MRLs and QA/QC have been published earlier (Anumol and Snyder, 2015; Anumol et al., 2015).

2.3. Study area

Samples were collected from three WWTPs, in Chennai city that discharge into the Adyar River. WWTPs 1 and 2 have 54 and 40 million liters per day (MLD) treatment capacity. Both plants employ conventional treatment units including activated sludge (AS) process with WWTP 1 having a nitrification process and consequently longer sludge