Ecotoxicology and Environmental Safety 150 (2018) 297–304

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Fate of pharmaceutical active compounds (PhACs) from River Yamuna, India: An ecotoxicological risk assessment approach

Pravin K. Mutiyar[a,b,*], Sanjay Kumar Gupta[a], Atul Kumar Mittal[a]

[a] Environmental Engineering, Department of Civil Engineering, Indian Institute of Technology Delhi, India
[b] National Mission for Clean Ganga, Ministry of Water Resources, River Development and Ganga Rejuvenation, Delhi, India

ARTICLE INFO

Keywords:
Pharmaceutical residues
Yamuna river
Hazard quotient
Ecotoxicity
Risk assessment

ABSTRACT

The river Yamuna is a major tributary of river Ganges and is a major source of freshwater in the National Capital Territory (NCT) catering 16.8 million people. This is the first report on occurrence, fate and ecotoxicological risk assessment of various pharmaceuticals active compounds (PhACs) in the Yamuna river. In this study, spatial and temporal distribution of nine PhACs "aspirin, ibuprofen, paracetamol, caffeine, ranitidine, diclofenac, carbamazepine, codeine, and diazepam", belonging to different therapeutic groups have been reported. Nine PhACs were analyzed in all the samples collected from the NCT stretch of river Yamuna. No specific trend in the distribution of the pharmaceutical residues was observed, however, the results revealed comparably higher PhACs contamination at YMN-2 (downstream Wazirabad, at this point, Najafgarh drain joins river Yamuna). Ecotoxicological risk assessment was carried out using Hazard quotients (HQ) for normal and worst case scenarios. The HQ showed that the levels of PhACs present in the samples were insufficient to cause acute toxicity to the flora and fauna of the river Yamuna. However, such residues could possibly cause chronic toxicity to the aquatic life and human beings as a huge amount of water of the river Yamuna is used for the drinking purposes in the NCT Delhi, the state capital of India.

1. Introduction

Pharmaceutical active compounds are frequently detected in different environmental compartments, owing to their mass production and consumption. The effluents from pharmaceutical manufacturing facilities and domestic sewage may have high levels of PhACs (Larsson et al., 2007; Mutiyar and Mittal, 2014) The human body usually does not retain the entire quantity of drug consumed, and a major fraction is excreted in parent form or in the form of active metabolites through urine and faeces (Beaumont et al., 2014). After administration, drugs are transformed to one or more of their metabolites and are excreted as a mixture of metabolites, major drug conjugates, and parent compounds. However, the excretion of drugs are highly compound specific (Lienert et al., 2007). For example, in case of ibuprofen, around 15% of the ingested dose is excreted in form of parent compound, and ~79% is excreted as conjugates (von Bruchhausen et al., 1994); but on the other hand, amoxicillin is excreted up to 80–90% as the consugated parent compound from the human body (Hirsch et al., 1999). Detailed pharmaco-kinetics data revealed that human excretion rates of unchanged drugs exceeded over ~50% and the rest is excreted as metabolites in conjugate forms. Once excreted, these pharmaceutical residues along with domestic sewage get transported to the sewage treatment plant (STP), where PhACs are partially removed during treatment (Ternes et al., 2007; Subedi et al., 2015, 2017). Due to microbial conjugate cleavage and inefficient removal during treatment in STPs, the pharmaceutical residues may be present at alarming levels in the treated effluents (Comeau et al., 2008; Akiba et al., 2015). Reports on the detection of these compounds in different water matrices, have received public attention as the residues are widely reported in, sewage (Ternes, 1998; Ying et al., 2009; Mutiyar and Mittal, 2013), rivers (Wiegel et al., 2004), groundwater (Sacher and Thomas, 2001) and lakes (Daneshvar et al., 2010). STPs are considered as major point sources for the release of these molecules in the aquatic environment (Gómez et al., 2007; Prabhasankar et al., 2016). The presence of PhACs in rivers is of growing concern and various studies have been conducted to determine their contamination levels in different rivers of the world. Their contamination in the aquatic matrices have been reported from many countries such as Germany (Ternes, 1998), Greece (Koutsouba et al., 2003), Switzerland (Golet et al., 2003), Sweden (Andreozzi, 2003), Italy (Zuccato et al., 2005), Canada (Lissemore et al., 2006), UK (Ellis, 2006), China (Peng et al., 2008), Taiwan (Chen et al., 2008), the USA (Yu and Chu, 2009), Pakistan (Scheurell et al., 2009), Korea (Sim et al., 2010), Spain (Valcárcel et al., 2011), Singapore (Xu et al., 2011) and Australia (Ying et al., 2009; Kookana et al., 2011). Environmental

* Corresponding author.

https://doi.org/10.1016/j.ecoenv.2017.12.041
Received 10 August 2017; Received in revised form 15 December 2017; Accepted 19 December 2017
Available online 04 January 2018

concentration of PhACs has already shown toxic effects to the non-target organisms (Contardo-Jara et al., 2011), so it is crucial to assess the possible risk toward the aquatic organisms. Gleaning the literature revealed that hardly any report is presently available on PhACs from the rivers of Ganga basin in India, the most densely populated river basin in the world. The present study was conducted to determine the distribution and fate of some of the commonly used pharmaceuticals, in the Delhi stretch of river Yamuna, which is a part of the Ganga River basin. It was also contemplated to assess the ecotoxicological risk of the selected pharmaceutical residues to the aquatic organisms.

The water quality of Yamuna river remains good (CPCB river classification), throughout the length from its origin at Yamunotri in the Himalayas up to upstream Wazirabad in Delhi. The Yamuna enters Delhi at Wazirabad in the north and leaves at Okhla in the south. This stretch of river Yamuna (Wazirabad to Okhla) is one of the most polluted river stretches in India. This stretch, which is less than 2% of the total length of the river, receives 71% of its total wastewater load (Mutiyar and Mittal, 2014). Delhi has the highest number of working STPs with the highest sewage treatment capacity in India. The major objectives of this study were (i) comprehensive evaluation of the distribution pattern of selected PhACs in the river Yamuna at Delhi, (ii) ecotoxicological risk assessment of commonly used selected pharmaceuticals in river Yamuna for Delhi stretch.

2. Materials and methodology

2.1. Sampling sites and sample collection

Sewage and industrial discharge are brought to river Yamuna by 17 drains in Delhi stretch. Depending on the location at which these drains discharging the wastewater into the river, six sampling sites were selected over a 25 km river stretch (Fig. 1). Selected sites were: (1) YMN-1 (at Palla, Wazirabad) i.e. upstream to the city. This site does not have any domestic or industrial discharge in the close vicinity and hence the pollution load was mainly from the agricultural runoff. The water quality at this point is important, as it is used as raw water (feed-water) for the water treatment plants supplying potable water in Delhi; (2) YMN-2 (downstream Wazirabad, at this point, Najafgarh drain joins river Yamuna). Najafgarh drain is the largest drain, having an average discharge of about 25.65 m^3 s^{-1} (http://www.cpcb.delhi.nic.in/annual-report2000–01); (3) YMN-3 (Old Bridge downstream); (4) YMN-4 (Nizamudeen Bridge), (5) YMN-5 (Okhla Barrage, where the sewage and industrial discharge from Ghaziabad city is also mixed with the river. The treated sewage from Okhla STP is also discharged at this site). The last site was (6) YMN-6, at Okhla, the downstream. The sampling was done as per standard protocol (APHA, 2010). Due precautions were followed to avoid any loss of organics during the sampling, handling or transport. Sampling was carried out during three different seasons of the year, i.e. winter (November 2010), summer (April 2011) and monsoon (July 2011). Samples were collected in 5 L amber (dark) colored, virgin quality HDPE plastic bottles. The collected sample bottles were kept in dark, airtight large plastic ice-cold containers and were transported to the laboratory within 2–4 h of collection.

2.2. Extraction of pharmaceutical residues

Extraction of the pharmaceutical residues was performed on the same day of collection, to avoid any further degradation. Solid phase extraction (SPE) process was performed for the extraction and preconcentration of the pharmaceutical residues from the samples. Hydrophilic-lipophilic balance (HLB) copolymer cartridges have already been reported to show better recoveries for the simultaneous determination of PhACs (Wiegel et al., 2004; Ferrer et al., 2010), thus

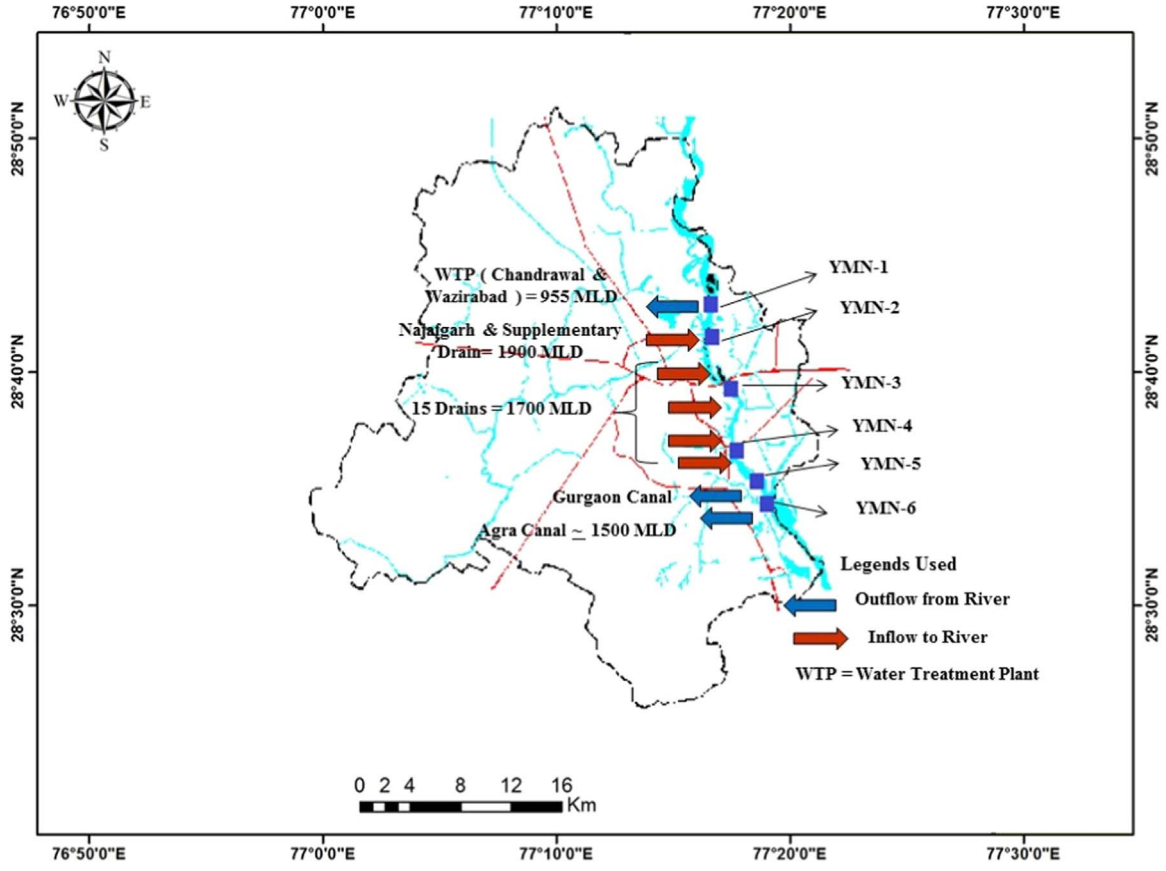

Fig. 1. Sampling sites along river Yamuna and major inflow and outflow of water from river Yamuna.