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Occurrence and fate of most prescribed antibiotics in different water environments of Tehran, Iran

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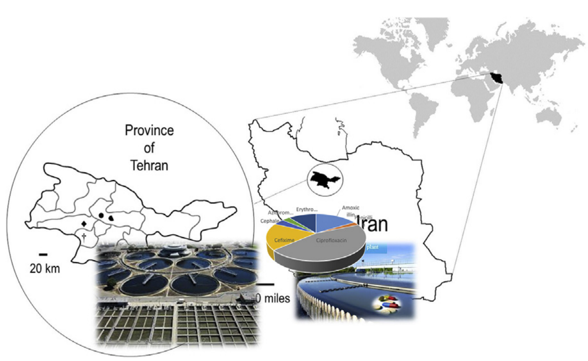
HIGHLIGHTS

- Most prescribed antibiotics in Iran were found in two rivers as well as the influent and effluent.
- There was a large variation in antibiotic removal from negative removal to 100% in WWTPs.
- Negative removal was observed for macrolides.
- A significant difference between antibiotics concentration in effluents and rivers were observed.
- The target antibiotics were not detected in any of the analyzed ground, source and treated water samples.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of most prescribed antibiotic compounds from four therapeutic classes (β-lactam, cephalosporins, macrolides, fluoroquinolones) were studied at two full-scale WWTPs, two rivers, thirteen groundwater resources, and five water treatment plants in Tehran. Analytical methodology was based on high performance liquid chromatography/tandem mass spectrometry after solid-phase extraction. Samples were collected at 33 sample locations on three sampling periods over four months from June to August 2016. None of the target antibiotics were detected in groundwater resources and water treatment plants, while seven out of nine target antibiotics were analyzed in two studied river waters as well as the influent and effluent of wastewater treatment plants at concentrations ranging from <LOQ to 926.32 ng/L. Ciprofloxacin predominated in all analyzed influent (552.6–796.2 ng/L) and effluent (127–248.7 ng/L) samples of WWTP A, whereas cephalosporins including cephalexin (523.3–977.7 ng/L) and cefixime (278.65 to 422.1 ng/L) were the most abundant detected antibiotics in the influent and effluent of WWTP B. Aqueous phase removal efficiencies were assessed and ranged from 339.83% to 100% for the seven detected antibiotics. “Negative removals” were observed for erythromycin, azithromycin, and cefixime due to the deconjugation of conjugated metabolites via biological transformation in the studied WWTPs. From a statistical point of view, significant differences ($p < 0.05$) were observed in the

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concentrations of cefixime, cephalexin, azithromycin, and erythromycin in the effluent of both studied WWTPs. Ciprofloxacin and cephalexin were the most abundant detected antibiotics in the two studied river waters. Statistical results revealed that there were significant differences in the concentrations of ciprofloxacin, azithromycin, and erythromycin ($p < 0.05$) in Firozabad ditch (receiving WWTP effluent) and Kan River (non-receiving WWTP effluent) which demonstrated that WWTPs discharges could be an important source of antibiotics being released in water bodies.

1. Introduction

Antibiotics are one of the most important groups of pharmaceutically active compounds (PhACs), which have been widely used in both human and veterinary medicine (Dinh et al., 2011; Kümmerer, 2009b). After administration, 5–90% of antibiotics may be excreted as metabolites or parent compounds depending on their chemical properties (Dinh et al., 2011; Jjemba, 2002; Kümmerer, 2009a; Sarmah et al., 2006). Thus, a large amount of antibiotics enter the aquatic environment directly via wastewater treatment plant effluents or via aquaculture activities (Dinh et al., 2011). Various groups of antibiotics have frequently been detected in hospital wastewater (Chang et al., 2010; Duong et al., 2008), wastewater treatment plant (WWTP) effluents (Gibs et al., 2013; Yan et al., 2014), groundwater (Barnes et al., 2008; Batt et al., 2006; Wolf et al., 2012), drinking water (Focazio et al., 2008; Padhye et al., 2014), and surface water (Dinh et al., 2011; Feitosa-Felizzola and Chiron, 2009; Yang et al., 2011). They have attracted scientific attention worldwide not only due to their potential adverse effects on non-target organisms but also due to their role in the development of antibiotics resistance via the selection of antibiotic-resistant bacteria and genes in the environment. That is why they were classified as a priority risk group (Gao et al., 2012; Hernando et al., 2006; Huang et al., 2011; Zhu et al., 2013). On the other hand, they are regarded as "pseudo persistent" contaminants because of their continuous introduction into the ecosystem and permanent presence (Hernando et al., 2006). Considerable fractions of administered antibiotics are excreted in metabolized and unmetabolized forms through urine and feces of humans and animals (Yan et al., 2014). These antibiotics are delivered into the wastewater collection system and finally reach WWTPs. Sewage treatment plants are not designed to deal with these emerging contaminants. Rather, they are designed to remove biodegradable carbon, nitrogen, and phosphorous compounds. Hence, antibiotics cannot be effectively removed from wastewater, and in some cases, they were found to exist in higher concentrations in effluents than they do in influents (Gao et al., 2012; Jelic et al., 2011; Yan et al., 2014). At the end, the effluent and sludge of wastewater treatment plants containing antibiotics are discharged into the aquatic environment and reused for irrigation or used as soil amendment. In addition, the presence of antibiotics can also endanger the reuse of treated wastewater, which may increase human exposure to these emerging contaminants (Kim and Aga, 2007; Yan et al., 2014). Therefore, WWTPs discharges are considered as the principal pathway for the entry of antibiotics into the water bodies (Jelic et al., 2011; Yan et al., 2014).

Regarding the simultaneous occurrence of different classes of antibiotics in complex matrices such as wastewater, multiple-residue analytical methodologies for the measurement of multiple-classes of antibiotics are very important in providing reliable knowledge about their occurrence, behavior, and fate in the environment (Zhang and Zhou, 2007). With the improvements in advanced analytical technology and methodologies, antibiotics are detected in WWTP influents and effluents, groundwater, surface water, river water, and even drinking water at concentrations ranging from a few ng/L to μg/L level (Gros et al., 2013; Huerta-Fontela et al., 2011; Ibáñez et al., 2017) and most published analytical methods for antibiotics residue determination in environmental matrices are based on off-line solid phase extraction (SPE) and liquid chromatography followed by tandem mass spectrometry (SPE – LC/MS/MS) (Dinh et al., 2011; Gros et al., 2013; Yan et al., 2014). The fate and behavior of antibiotics in wastewater treatment plants and surface waters have been the subject of numerous studies (da Silva et al., 2011; Rossmann et al., 2014; Zhou et al., 2013; Zhou et al., 2011).

Zhou et al. (2013) found twenty-one antibiotics in the sewage sludge from two WWTPs at concentrations up to 5800 ng/g, with tetracycline, oxytetracycline, norfloxacin and ofloxacin being the predominant antibiotics. Ibáñez et al. (2017) reported that UHPLC-QTOF MS is a powerful technique for the screening and identification of metabolites and transformation products of pharmaceuticals. They detected 34 transformation products (TPs) and metabolites of pharmaceuticals in treated wastewater in Greece. Rossmann et al. (2014) studied the quantification of a combination of the most prescribed antibiotics including β-lactams and other highly interesting substances of all antibiotic classes in wastewater. All selected substances were found in wastewater samples in concentrations up to 6.2 μg/L. The process efficiency was found to be highly compound-specific and ranged from 20% for doxycycline to 134% for cefuroxime in the influent and from 31% for doxycycline to 171% for cefuroxime in the effluent samples. Zhou et al. (2011) investigated the occurrence of four classes of 17 commonly used antibiotics in the sediments of rivers in the north of China. Norfloxacin, ofloxacin, ciprofloxacin, and oxytetracycline in the three rivers were the most frequently detected ones with concentrations up to 5770, 1290, 653, and 652 ng/g, respectively. High frequencies and concentrations of the detected antibiotics were often found in the downstream of large cities and areas affected by feedlot and fish ponds. da Silva et al. (2011) reported that the dilution factor was the main factor by which the concentration of contaminants was affected in the studied rivers. Furthermore, the distribution of the contaminants between surface water and suspended solids is an important issue because some compounds with basic characteristics (pKa > 7) showed higher tendencies to bind to suspended solids.

Furthermore, most studies have focused on determining antibiotics in WWTPs as "black boxes" and the overall removal efficiency of antibiotics in the influent and final effluent have been calculated (Jia et al., 2012; Yan et al., 2014; Zhou et al., 2013). On the other hand, although the occurrence and fate of PhACs including antibiotics in the aquatic environment in developed countries within Europe, North America, and Australia have extensively been investigated and well documented (Jelic et al., 2012; Kasprzyk-Hordern et al., 2009; Rosal et al., 2010; Verlicchi et al., 2012), the risk of exposure to PhACs including antibiotics is greater in the developing world due to inappropriate consumption, uncontrolled disposal, and lack of well-enforced regulations in these countries.

Up to now, there are only a few studies in the literature which have investigated the occurrence of antibiotics in water environments in Iran, and their analytical methods have been based on high-performance liquid chromatography (HPLC) with the analysis of a single group of compounds (Javid et al., 2016; Shokoohi et al., 2017) or the evaluation of the predicted environmental concentration (PEC) instead of measuring environmental concentration (MEC) (Alighardashi et al., 2014). Employing a new analytical method for the analysis of antibiotics in water environments based on (LC/MS/MS), some of these studies reported the occurrence of antibiotics qualitatively rather than