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Technical Note

Mass flows and removal of antibiotics in two municipal wastewater treatment plants

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ABSTRACT

The mass flows and removal of 20 antibiotics of seven classes in two wastewater treatment plants (WWTPs) of Hong Kong were investigated in different seasons of a whole year, using bihourly 24 h flow proportional composite samples. Antibiotics were detected at concentrations of 3.2–1718, 1.3–1176 and 1.1–233 ng L^{-1} in influents, secondary and disinfection effluents. Total daily discharges of all the detected antibiotics from effluents of Shatin and Stanley WWTPs were 470–710 and 3.0–5.2 g d^{-1}, respectively. Ampicillin, cefalexin, sulfamethoxazole, sulfadiazine, sulfamethazine, chlortetracycline and vancomycin were effectively (52–100%) eliminated by activated sludge process while ampicillin and cefalexin were effectively (91–99%) eliminated by disinfection. Bihourly variation analysis showed that concentrations of the major antibiotics in influents varied more significantly in Stanley WWTP which served small communities.

1. Introduction

In recent years, the occurrence, fate and potential toxic effects of antibiotics in the environment, including surface water, ground water and soils have drawn great attention all over the world (Kümmerer, 2001; Xiao et al., 2008). Although the antibiotics residue in the environment is at subinhibitory concentration, usually at ng L^{-1} to μg L^{-1} level in natural water (Xu et al., 2007b; Tamtam et al., 2008) and wastewater (Watkinson et al., 2007; Li et al., 2009), and μg kg^{-1} to mg kg^{-1} level in soil (Golet et al., 2002; Schlüsener et al., 2003) and sludge (Golet et al., 2003), they are still considered to be emerging pollutants due to the following reasons. Firstly, antibiotics at subinhibitory concentration may inhibit human embryonic cells/zebrafish liver cells proliferation in vitro (Pomati et al., 2006, 2007) and influence both the structure and the function of algal communities (Wilson et al., 2003) combining with other pharmaceuticals. Secondly, they might result in the development/maintenance/transfer/spread of antibiotics resistant bacteria and antibiotics resistant genes in the long-term (Göbel et al., 2005a; Hernando et al., 2006; Knapp et al., 2008; Martínez, 2008). Reuse of treated wastewater also increases the opportunity of antibiotics introduced into the drinking water systems and thus human exposure to antibiotics has escalated (Kim and Aga, 2007). Considering these potential toxic effects, one antibiotic, erythromycin has been selected to the Drinking Water Contaminant Candidate List formulated by US Environmental Protection Agency (USEPA, 2010). In addition, due to their continual input into the environment and permanent presence, antibiotics are also considered to be "pseudopersistent" contaminants (Daughton and Ternes, 1999; Hernando et al., 2006).

Human-use antibiotics from three major sources, i.e. industry, hospital and household, are discharged into sewage (with or without in situ pretreatment) and then get into the municipal wastewater treatment plants (WWTPs) (Giger et al., 2003). However, many studies have shown that conventional WWTPs cannot remove antibiotics completely (McArdell et al., 2003; Miao et al., 2004; Göbel et al., 2005a,b) and they will finally enter into the environment via effluent and sludge. Therefore, WWTPs will act as one of the dominant point pollution sources and principal pathways for human-use antibiotics during their transfer process into environment (Gulkowska et al., 2008). Up to now, most studies on antibiotics in WWTPs focused on their detection methods and concentrations in influent, effluent and sludge using grab samples (Batt et al., 2007; Spongberg and Witter, 2008; Kasprzyk-Hordern et al., 2009; Watkinson et al., 2009) or composite samples (Karthikeyan and Meyer, 2006; Ternes et al., 2007; Zorita et al., 2009). A few researchers have investigated the mass flows of multiple antibiotics discharged from WWTPs (McArdell et al., 2003; Göbel et al., 2005a; Lindberg et al., 2005; Minh et al., 2009) based on short-term samplings. However, the long-term samplings in different seasons are essential to monitor the real daily mass flows of antibiotics discharged into environment, considering the seasonal changes of winter/summer consumption patterns and wet/dry sewage flow rates. Some researchers (McArdell et al., 2003; Goossens et al., 2005) have found that seasonal fluctuations of antibiotics mass

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flows were very high between winter and summer. Antibiotic mass flows in winter may be two times higher than that in summer (McArdell et al., 2003). Additionally, most of previous researches calculated the "overall" removal efficiency (RE) of antibiotics based on the concentrations in influent and effluent of WWTPs, as "black boxes". The REs of different treatment processes, such as the biological treatment and the chlorination, are very limited. Moreover, the situation in Hong Kong is much more complicated and unique as some WWTPs (e.g. Shatin WWTP) treat saline sewage resulting from the practice of seawater toilet flushing. Thus, the aims of this study were (1) to detect 20 antibiotics of seven classes in influent, secondary effluent and disinfection effluent from two WWTPs of Hong Kong, using bihourly 24 h flow proportional composite (FPC) samples in different seasons of a year; (2) to investigate the bihourly variation of antibiotic concentrations in influent; (3) to evaluate the elimination of antibiotics in activated sludge (AS) and disinfection processes, respectively; and: (4) to reveal the antibiotic consumption patterns and estimate daily load discharged into environmental water body by calculating the mass flows in influent and effluent.

2. Experimental section

2.1. Chemicals and standards

The standards of antibiotics, including 6 β-lactams (ampicillin, oxacillin, ceftazidime, cefazolin, cefotaxime and cefalexin), 3 sulfonamides (sulfamethoxazole, sulfadiazine and sulfamethazine), 3 fluoroquinolones (norfloxacin, ciprofloxacin and ofloxacin), 3 tetracyclines (tetracycline, oxytetracycline and chlortetracycline), 2 macrolides (roxithromycin and erythromycin), 1 glycopeptides (vancomycin) and 2 others (trimethoprim and chloramphenicol) were all purchased from Sigma–Aldrich. All the standards were of the highest purity available. Except for vancomycin (⩾80%) and ceftazidime (⩾90%), the purities of all other standards were ⩾95%. Other chemicals, such as isotopically labeled $^{13}C_3$-caffein, acetonitrile, ultrapure water, formic acid, disodium ethylenediamine tetraacetate, ascorbic acid, sodium hydroxide, sulfuric acid solution and 0.2 μm cellulose nitrate membrane were the same as those reported previously (Li et al., 2009).

2.2. Sample collection

Samplings were conducted in March, June, October 2009 and January 2010 at Shatin and Stanley WWTPs, which treat saline sewage and freshwater sewage, respectively. In Supplementary Material (SM), Table SM-1 shows details of the two WWTPs. Bihourly 24 h FPC samples were collected from influent (after the screen), secondary effluent and disinfection effluent (for Stanley WWTP only) using automatic samplers (Liquiport 2000, Endress + Hauser) equipped with cooling systems to cool samples down to 12 ± 2 °C. For disinfection effluent, 0.5 mM ascorbic acid was added as quenching agent at sampling to avoid oxidation of antibiotics by disinfection residual.

2.3. Analytical methods

Pretreatment, including centrifugation, filtration (0.2 μm cellulose nitrate membrane) and solid phase extraction, was conducted within 24 h. Then Acquity ultra performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS, Waters) was applied to analyze antibiotics using the positive electrospray ionization multiple reaction monitoring mode. All experiments were carried out in duplicate. The detailed information on pretreatment and UPLC-MS/MS were reported previously (Li et al., 2009).

2.4. Calculation of mass flows

To investigate the antibiotics usage and examine the dissolved daily environmental loads (total amounts of antibiotics discharged into environment via effluent), mass flows of individual antibiotics were calculated by multiplying the measured concentration at the specific sampling point and the daily flow. For comparison reasons, the results were normalized to 1000 population equivalents (PE) and named as average daily mass flow.

3. Results

3.1. Occurrence of antibiotics in influent and effluent

The detailed occurrence information of β-lactams, sulfonamides, fluoroquinolones, tetracyclines, macrolides, glycopeptides and others are summarized in the SM. Table SM-2 shows that totally 15 and 14 antibiotics of all the seven classes were detected in the influents (3.2–1718 ng L^{-1}) and secondary effluents (3.6–1176 ng L^{-1}) of Shatin WWTP, respectively. For Stanley WWTP, 13, 12, and 10 antibiotics belonging to six out of seven classes (except for glycopeptides) were detected in influents (4.2–530 ng L^{-1}), secondary effluents (1.3–285 ng L^{-1}), and disinfection effluents (1.1–233 ng L^{-1}), respectively (Table SM-3). To sum up all these data, concentrations of the same antibiotic in different WWTPs varied considerably, sometimes by 1–2 orders of magnitude. The significant variation of antibiotics in influent could be due to many reasons, including antibiotics consumption pattern, seasonal and bihourly fluctuation, and effect of WWTP scale. As to concentration variations in effluent, in addition to different sampling procedures and different treatment technologies (AS process and chlorination process), the inorganic matters in sewage (Ca^{2+} and Mg^{2+}) can also affect the concentration significantly in most cases because the Ca^{2+} and Mg^{2+} with relative high concentrations in saline sewage (about 120 and 300 mg L^{-1}, respectively) can decrease the REs of some specific antibiotics significantly.

3.2. Mass flows of antibiotics

It should be noted that antibiotics in sludge were not analyzed and thus only mass flows in influent and effluent were investigated in this study.

3.2.1. Influent

Average daily mass flows of antibiotics in influents are shown in Fig. 1. There are no pharmaceutical industries or livestock husbandries in Hong Kong and thus average daily mass flow, which was normalized to 1000 PEs could partially reflect the antibiotic usage consumed by human in an area, assuming that the attenuation of an antibiotic during its transportation from toilets to WWTPs was the same in different areas. Kümmerer (2009) pointed out that the regional and local consumption may be different within the same country, let alone different countries. Actually, as shown in Fig. 1, even in different districts of a big city, like Hong Kong, the consumption patterns varied greatly. The usages of cefotaxime, cefalexin, ciprofloxacin, ofloxacin, tetracycline, oxytetracycline, and vancomycin in Shatin area were much greater than the corresponding usage in Stanley area. While for ampicillin and sulfamethoxazole, their consumptions in Shatin district were much lower than those in Stanley area. The consumptions of sulfamethazine, norfloxacin, chlortetracycline, roxithromycin, erythromycin-H_2O, and trimethoprim in two WWTPs serving areas