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Short Communication

Pay attention to non-wastewater emission pathways of pharmaceuticals into environments

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HIGHLIGHTS

- The importance of emission of antibiotics via non-wastewater pathways was evaluated.
- Non-wastewater pathways accounted for approximately 30–80% of the total emission.
- Disposal with domestic waste could be important for antibiotics into environments.

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ABSTRACT

Pharmaceuticals have been widely detected in the aquatic environment and demonstrated to be potential risks to humans and the environment. Understanding emission pathways of pharmaceuticals is essential to the control of pharmaceutical contamination for environmental management. The present study is aimed at testing the hypothesis that non-wastewater pathway is also significant to the emission of pharmaceuticals into the environment. To this end, we compared the actual production with the amount of 12 antibiotics obtained by back calculation from sewage concentrations in Beijing, Guangzhou and Chongqing. The results showed that for over a half of investigated antibiotics, the emission through non-wastewater pathways accounted for approximately 30–80% of the total emission, varying with individual antibiotics. It was revealed that non-wastewater emission pathways could be of significance for pharmaceuticals emitted into the environment, of which disposed by household waste could be among the most important non-wastewater pathways.

1. Introduction

With the rapid development of medical science and industry, the production and consumption of human-use pharmaceuticals increased significantly. The increasing use and the subsequent release of pharmaceuticals have led to high residual levels in various environments (Besse and Garric, 2008; Brausch and Rand, 2011; Bu et al., 2013; Daughton, 2010, 2016; Hoyett et al., 2016; Liu and Wong, 2013; Verlicchi et al., 2012). The presence of pharmaceuticals has raised concerns due to their deleterious effects in organisms and aquatic ecosystem (Fent et al., 2006; García et al., 2014; Overturf et al., 2015).

There are multiple possible emission pathways of pharmaceuticals into the environment (Bound and Voulvoulis, 2005). However, effluents of wastewater treatment plants (WWTPs) were generally recognized as the major emission pathway of pharmaceuticals into the environment (Kümmerer, 2001; Ramirez et al., 2009). This is mainly due to the fact that (i) some pharmaceuticals were excreted from human body only slightly transformed or even unchanged into WWTPs (Heberer, 2002), and (ii) in general WWTPs are designed to remove solids and nutrients and to reduce the biological oxygen demand of the effluent. Studies on the occurrence of pharmaceuticals in WWTP influents and effluents have shown that the current treatment processes do not always remove pharmaceuticals completely (Dong et al., 2016; Kaplan, 2013; Mohapatra et al., 2016; Paxeus et al., 2016; Sui et al., 2010,

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2011). And just because of this, occurrence data of pharmaceuticals in WWTP influents and effluents were extensively used as the foundation to estimate the use volume in many studies (Bones et al., 2007; Lai et al., 2013; Ort et al., 2014; Zuccato et al., 2005).

Bound and Voulvoulis (2005) proposed that the household disposal could be an emission pathway for pharmaceuticals entering into the aquatic environment in the United Kingdom. More recently, Massoud et al. (2016) pointed out that most of respondents in their survey disposed unwanted medicines through domestic solid wastes. Consequently, there is a strong possibility that non-wastewater emission pathways may play an important role for pharmaceutical pollution in the environment. However, the contribution of these pathways has not yet been investigated and evaluated. In a previous study (Bu et al., 2016), we compared the amount of antibiotics obtained by back calculation from sewage concentrations using human excretion rates with actual production. It was found that for most antibiotics, use estimates from the back calculation were generally compared or lower than those from our proposed model. Reasons for this discrepancy could be due to uncertainty in the estimation, incomplete inclusion of emission pathways in the back calculation method, or both.

In the present study, a dataset for antibiotics as representative pharmaceuticals was compiled and updated based on the previous study (Bu et al., 2016), to re-interpret the discrepancy between both methods. We hypothesized that the non-wastewater pathway is also significant to the emission of pharmaceuticals into the environment.

2. Materials and methods

2.1. Use estimation

2.1.1. Back calculation

In this calculation we assume that the wastewater is the main pathway of antibiotics into the environment. If this assumption is valid, the back calculation estimates would be comparable to the production-based model. Use estimates were back calculated according to the following equation:

$$HUV_{\mathrm{backcal}} = \frac{C_{\mathrm{inf}} \times Q \times 365}{e\%} \times \frac{P_{\mathrm{t}}}{P_{\mathrm{ser}}} \times 10^{-9} \quad (1)$$

where HUV_{backcal} is the back calculated human use volume of a pharmaceutical (kg year^{-1}); C_{inf} is the concentration of a pharmaceutical in the influent of WWTPs (ng L^{-1}); Q is the sewage treatment capacity of the WWTPs (m^3 d^{-1}); $e\%$ is the excretion rate of a pharmaceutical by humans unchanged after administration; P_{ser} and P_{t} refer to the service population of one specific WWTP and the total population of the studied region, respectively.

2.1.2. The production-based model

The use volume of a pharmaceutical was estimated from the production data according to our previous regression model (Bu et al., 2016). In brief, the allocation proportion for sub-region i (f_i, unitless) was firstly calculated according to our developed regression model. Then the production-based use volume (HUV_{reg}, kg year^{-1}) of drug j in any region i was calculated as

$$(HUV_{\mathrm{reg}})_{ji} = f_i \times HUV_{j\mathrm{T}} \quad (2)$$

where $HUV_{j\mathrm{T}}$ (kg year^{-1}) is the average total use volume of drug j in China during 2011–2014 (MIIT, 2012, 2013, 2014, 2015). Here we assumed that the total antibiotics were sold out by the end of year and were equivalent to the sum of antibiotics consumption in individual regions.

2.2. Data collection and statistical analysis

Concentrations of 12 antibiotics (i.e. norfloxacin, pipemidic acid, lomefloxacin, gatifloxacin, ofloxacin, erythromycin, roxithromycin, sulfadiazine, sulfamethazine, sulfamethoxazole, trimethoprim, and chloramphenicol) in influents of WWTPs from Beijing, Guangzhou, and Chongqing between 2005 and 2014 were retrieved by an extensive literature review. The three cities located in the northern, southeastern and southwestern China, respectively, which reflect broad geographical and demographical characteristics. Those data that satisfy the need of back calculation were compiled in Table S1. Excretion rates by humans after administration were from the online database RxList (www.rxlist.com) or Drugs (www.drugs.com) and listed in Table S2. The population data for the three selected regions were retrieved online from the China Statistical Yearbooks Database (CNKI, 2016).

For the regression model, statistical data for the corresponding region and year were obtained online from the China Statistical Yearbooks Database (CNKI, 2016) and the SOSHOO database of social development of China (SOSHOO, 2016). Production data of pharmaceuticals in China were obtained from China Medical Statistics (MIIT, 2012, 2013, 2014, 2015).

For the back calculation method, every parameter varies due to the interference of external confounding factors without control. Uncertainty analysis was conducted by assigning an uncertainty factor and distribution type based on best judgment to each input parameter. Input parameters considered include the following: C_{inf}, Q, P_{ser}, and $e\%$, designating as normal or uniform distribution, respectively (Table S3). The analysis was accomplished by using Oracle Crystal Ball (Version 11.2) add-in in Microsoft Excel 2013. The 95% upper and lower bound confidence interval is determined by the uncertainty analysis for HUV_{backcal}.

3. Results

Table 1 showed the best estimates and the 95% upper and lower bound confidence interval for HUV_{backcal}, as well as HUV_{reg}. It can be found that for most antibiotics HUV_{backcal} was lower than HUV_{reg}, which is in accordance with our previous calculation (Bu et al., 2016). The proportion of pharmaceuticals emitted through non-wastewater pathways can be inferred by the ratio (R) defined as follows:

$$R = \frac{HUV_{\mathrm{backcal}}}{HUV_{\mathrm{reg}}} \quad (3)$$

According to the assumption, $R = 1$ reflects the most ideal case that indicates the wastewater is the unique emission pathway. If R is significantly smaller than 1, it indicates that there are other non-wastewater emission pathways.

It can be found from Table 1 that R varied with antibiotics and locations, ranging from 0.01 (sulfamethazine in Beijing) to 3.84 (roxithromycin in Chongqing), while R values for over a half of investigated antibiotics were within the range of 0.20–0.70 (**bold entries** in Table 1). This indicates that emission through non-wastewater pathways accounted for approximately 30–80% of total emissions into the environment for different antibiotics. For the case of lomefloxacin in Beijing and chloramphenicol in Guangzhou, emission through wastewater could be the unique route as R values were very close to 1 and the 95% upper and lower bound confidence intervals were well within a factor of 2 compared to the best estimates (Table 1).

There are two exceptional cases that need further investigation. It should be noted that R values for some of investigated antibiotics (e.g. trimethoprim, pipemidic acid, and sulfamethazine in Beijing;