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Source estimation of pharmaceuticals based on catchment population and in-stream attenuation in Yodo River watershed, Japan

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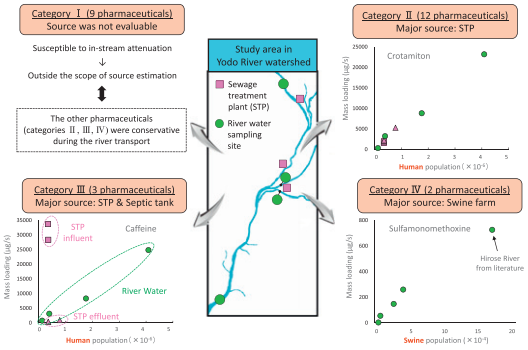
HIGHLIGHTS

- In-stream attenuation of pharmaceuticals was observed by a mass balance approach.
- Source was estimated based on populations for pharmaceuticals conservative in river.
- STPs were major source of 12 pharmaceuticals in this extensively-sewered watershed.
- Treatment facilities of swine urine were major source of two veterinary drugs.
- Three pharmaceuticals were substantially affected by household septic tanks.

GRAPHICAL ABSTRACT



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ABSTRACT

Fifty-five pharmaceuticals were monitored at four rivers and inlets and/or outlets of three sewage treatment plants (STPs) in Yodo River watershed, Japan over 17 sampling events. Twenty-six quantified pharmaceuticals were classified by source and fate. The load per person (LPP) of nine pharmaceuticals, including six with observed mass balance in studied river stretch of <80%, was appreciably lower in river water (RW) than in the effluent (EF) of STPs (RW/EF <0.5), indicating that they were susceptible to in-stream attenuation in the study area, while the others were relatively conservative. The LPP of 12 pharmaceuticals in RW were within ±50% of that in EF. Because their mass loadings in rivers were correlated with human population in the catchment and most people use the sewer system, the major source of the 12 pharmaceuticals was considered to be STPs. The LPP of the three most labile pharmaceuticals in STPs (caffeine, theophylline, and acetaminophen) was >1.5 in RW/EF and <1.0 in RW/influent (IF) of STPs. Poorly treated sewage discharged from households without using the sewer system was considered to be influential source of the three pharmaceuticals. The LPP (RW/EF) of caffeine, a pharmaceutical contained in food and beverage, was considerably higher than that of the other two, and this is attributable to untreated gray water discharged at households using the night-soil treatment system. The LPP of two veterinary drugs (sulfamonomethoxine and lincomycin) were >1.5 (RW/EF) and >1.0 (RW/IF). Their mass loadings in rivers showed a positive correlation with swine population in the catchment, although sulfamonomethoxine is equally used in both cattle and swine farming. This was attributable to application of cattle excrement as manure, and lability of sulfamonomethoxine during composting processes. The major source of the two veterinary drugs was considered to be on-site treatment facilities of swine urine.

Abbreviations: STP, sewage treatment plant; CV, coefficient of variation; LPP, load per person; RW, river water; IF, influent; EF, effluent.

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1. Introduction

Pharmaceuticals are one of the most noticeable emerging contaminants due to their potential risks to aquatic organisms (Boxall et al., 2012), and they have been widely detected in surface waters (Kasprzyk-Hordern, Dinsdale, & Guwy, 2008; Kolpin et al., 2002; Nakada et al., 2008). Since the use of pharmaceuticals cannot be restricted due to their advantages, source control is necessary to reduce their risks to aquatic organisms. Therefore, source identification and mass loading prediction should be conducted to develop pharmaceutical reduction strategies.

Pharmaceuticals may enter surface water via sewage treatment plants (STPs), and non-point sources such as septic tanks and runoff of land-applied biosolids and manure (Heberer, 2002). To determine their sources, several studies have linked the spatiotemporal distribution of pharmaceutical concentrations with land use (Barber, Murphy, Verplanck, Sandstrom, Taylor, & Furlong, 2006; Bernot, Smith, & Frey, 2013; Fairbairn et al., 2016a, 2016b; Gómez, Herrera, Solé, García-Calvo, & Fernández-Alba, 2012), wastewater discharge (Conley, Symes, Schorr, & Richards, 2008; Dai, Wang, Huang, Dong, Deng, & Yu, 2015; Jia, Hu, Wu, Peng, Wu, & Dong, 2011; Karpuzcu et al., 2014; Lin, Yu, & Lin, 2008; Shimizu et al., 2013), and environmental factors (Bernot et al., 2013; Kolpin, Skopec, Meyer, Furlong, & Zaugg, 2004; You et al., 2015). However, most studies only reported qualitative outcomes for non-point sources. To provide quantitative source characterization, the spatial distribution of pharmaceutical concentrations should be linked with human or livestock populations in catchment areas. Such information could provide more reliable source identification and advance our understanding on mass loading prediction at sources.

After entering a surface water body, pharmaceuticals may be attenuated by physical, chemical, and/or biological processes. Studies on in-stream attenuation suggest rapid removal is possible for some pharmaceuticals (Azuma et al., 2015; Gurr & Reinhard, 2006; Hanamoto, Nakada, Yamashita, & Tanaka, 2013; Kunkel & Radke, 2012; Lin, Plumlee, & Reinhard, 2006). Therefore, the in-stream attenuation of pharmaceuticals should be evaluated to provide quantitative source characterization. However, discussions on the sources of pharmaceuticals based on their natural attenuations are quite limited. Because the reported attenuation of pharmaceuticals often differs between rivers (Acuña et al., 2015; Aymerich et al., 2016; Li, Sobek, & Radke, 2016), in-stream attenuation should be observed in individual watersheds.

This study aimed to provide quantitative source characterization of pharmaceuticals in the Yodo River watershed in the Kansai region of Japan. Fifty-five pharmaceuticals were selected from broad therapeutic categories, including those for both human and veterinary uses (Supplementary Information (SI) Table S1). We monitored the pharmaceuticals at four rivers and inlets and/or outlets of three STPs in the watershed over five months. In-stream attenuation of pharmaceuticals in the study area were quantified through a mass balance approach. The sources of pharmaceuticals were evaluated by discussing their mass loadings in rivers with catchment populations, flow rates, and their behavior in rivers and STPs.

2. Materials and methods

2.1. Site description

Yodo River watershed (8240 km^2) comprises residential area (21%), agricultural land (25%), forest (47%), and others (7%). The annual average rainfall in the watershed is approximately 1800 mm. The population is approximately 12,000,000, of which approximately 95% use the sewer system in the watershed. Field surveys were conducted in the middle basin of the watershed (Fig. 1). The travel time between Kuze Bridge (site R_1) and Hirakata Bridge (site R_4, 34°48′51″N, 135°37′57″E) is approximately 16 h, and the river depth along the stretch ranges from 0.4 to 1.5 m under annual average flow conditions. The studied river stretch directly receives water from three STPs (A, B and C). Although there are some additional inflows from tributaries other than the sampling sites, mass loading from the tributaries were minor for most pharmaceuticals (see SI Fig. S1). The STPs employ an activated sludge and chlorine disinfection system to treat wastewater from 779,600 (STP A), 345,400 (STP B), and 353,200 (STP C) residents. The treatment process is same for most STPs located upstream of sites R_{1-3}. The catchment of STP A, a part of Kyoto city, uses a combined sewer system, while that of STPs B&C and most cities located upstream of sites R_{1-3} use separate sewer systems. Biosolids generated from the STPs are mostly recycled into construction materials such as raw materials for cement and not extensively applied to agricultural land (Ministry of the Environment, 2010a). The study area (Fig. 1) is mostly urbanized with high sewer coverage and low livestock populations, whereas the catchment areas of sites R_{1-3} have relatively low sewer coverage and more livestock population. For households located beyond the coverage of sewer facilities, black water is treated in on-site septic tanks or night-soil treatment plants, whereas a part of gray water is discharged to the aquatic environment without treatment. Livestock waste is mostly used as manure or treated at on-site treatment facilities (SI Table S2). Human and livestock population, and flow rates of river water sampling sites (sites R_{1-4}) are summarized in Table 1.

2.2. Field study

River water, treated wastewater, and raw sewage samples (Fig. 1) were collected approximately weekly between October 2009 and February 2010, yielding a total of 17 sampling events. Samples were collected using a grab in a stainless steel bucket at rivers (sites R_{1-4}), and outlets of STP A ($A_{EF1,2}$), and automatic water samplers (stationary automatic sampler, NKS Co., Ltd., Osaka, Japan) at inlets and outlets of STPs B&C for 24-h composite samples ($B\&C_{IN,EF}$). The samples were stored in amber glass bottles with 1.0 g/L ascorbic acid in darkness and taken to the laboratory. Ascorbic acid was added to remove residual chlorine, present especially in samples collected at STP outlets. The flow rates of water at rivers, STP A, and STPs B&C on each sampling day were obtained from the Ministry of Land, Infrastructure and Transport, Kyoto City Waterworks Bureau, and Kyoto Prefecture Sewer Office, respectively. Rainfall within 12 h before the sampling events were low (<3.5 mm) at Kyoto city, which uses a combined sewer system, indicating that collected samples would not be significantly affected by combined sewer overflow. Rainfall within three days before the sampling events were 0–26.5 mm, resulting in moderate changes of river flow rates among sampling days (see Table 1).

2.3. Analysis

Details on the sample treatment and analytical method applied can be found in Okuda, Yamashita, Tanaka, Matsukawa, and Tanabe (2009). In brief, samples were filtered through a 1-μm glass fiber filter (GF/B, Whatman, UK). The 55 selected pharmaceuticals in the dissolved phase were concentrated by solid-phase extraction using an Oasis HLB cartridge (200 mg, 6 cm^3, Waters, USA) within 3 days. The selected pharmaceuticals were measured by ultra-performance liquid chromatography (ACQUITY, Waters, USA) coupled to a tandem mass spectrometer (Quattro micro API, Waters, USA). A BEH C_{18} column (1.7 μm, 2.1 mm × 100 mm, ACQUITY, Waters, USA) was used for separation. The selected pharmaceuticals were quantified by the absolute calibration method. Recovery rate was determined (for each sample) from the difference in concentration between samples spiked with and without a mixture containing 50 ng of each pharmaceutical, and their concentrations were determined. Signal to noise ratios (S/N) of 3 and 10 were used as the detection and quantification limits. Twenty-six pharmaceuticals quantified frequently (>80%) at more than one river or STP outlet were considered in the discussion of mass loading, natural