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Source contributions and mass loadings for chemicals of emerging concern: Chemometric application of pharmaco-signature in different aquatic systems

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ABSTRACT

To characterize the source contributions of chemicals of emerging concern (CECs) from different aquatic environments of Taiwan, we collected water samples from different aquatic systems, which were screened for 30 pharmaceuticals and illicit drugs. The total estimated mass loadings of CECs were 23.1 g/d in southern aquatic systems and 133 g/d in central aquatic systems. We developed an analytical framework combining pollutant fingerprinting, hierarchical cluster analysis (HCA), and principal component analysis with multiple linear regression (PCA-MLR) to infer the pharmaco-signature and source contributions of CECs. Based on this approach, we estimate source contributions of 62.2% for domestic inputs, 16.9% for antibiotics application, and 20.9% for drug abuse/medication in southern aquatic system, compared with 47.3% domestic, 35.1% antibiotic, and 17.6% drug abuse/medication inputs to central aquatic systems. The proposed pharmaco-signature method provides initial insights into the profile and source apportionment of CECs in complex aquatic systems, which are of importance for environmental management.

1. Introduction

The contamination of freshwater ecosystems by synthetic chemicals is increasing worldwide. As the global population increases and economies in many regions show considerable growth, the production of chemicals is also predicted to increase. Anthropogenic compounds, such as pharmaceuticals, antibiotics, UV filters, and illicit drugs, are collectively referred to as chemicals of emerging concern (CECs). Due to their large production volumes and continuous usage, some of these compounds have become “pseudo-persistent” in the environment (Hernando et al., 2006; Postigo et al., 2010). The occurrence of these compounds has been reported in most aquatic systems (Jiang et al., 2014; Loos et al., 2013; Luo et al., 2014; Vidal-Dorsch et al., 2012). Although CECs usually occur at low environmental concentrations, many are of toxicological concern, particularly when they occur with the combined effects of multiple contaminants (Hoerger et al., 2014; Schwarzenbach et al., 2006); consequently, the potential environmental risks of residual CECs should not be ignored.

Despite treatment, the wastewater from households and industry is a major source of CECs entering the aquatic environment (Michael et al., 2013; Phillips et al., 2010). Additionally, untreated wastewater can also be discharged via sewer overflow or leaks. As a consequence of these sources and pathways for CECs, many can be

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found in freshwater ecosystems, particularly in densely populated regions (Heeb et al., 2012). Attention has generally been focused on investigating the occurrence and behavior of CECs in aquatic environments (Bu et al., 2013; Carmona et al., 2014; Gonzalez et al., 2012; Hoerger et al., 2014; Verlicchi et al., 2012; Xue et al., 2013). However, available information on the sources and mass loadings of CECs in densely populated regions remains very limited, especially for the megacities in Taiwan, which is the 17th most densely populated country globally (647 people km^{-2}), with a population of 23 million (UNWPP, 2013).

With appropriate analysis, pollutant profiles reflect the present CEC status of particular water sources and can infer pharmaco-signature and relative contributions. The present study addresses the challenge of accounting for source contribution of CECs by characterizing their fingerprint in aquatic systems. The purpose of this study is to: (1) examine the occurrence and spatial patterns of common CECs, (2) investigate mass loadings of CECs in different aquatic systems, and assess associated ecological risks via risk quotients (RQs), and (3) demonstrate and compare significant source contributions and the pharmaco-signatures of CECs via multivariate analysis including unsupervised pattern recognition (hierarchical cluster analysis, HCA) and receptor model (principal component analysis-multiple linear regression, PCA-MLR) in different aquatic systems. The results indicate that the proposed method can reliably estimate source contribution of CECs in aquatic environments.

2. Material and methods

2.1. Chemicals and standards

Thirty CECs, including analgesics, antibiotics, lipid regulators, β-blockers, antiepileptic drugs, psychostimulants, ulcer healing compounds, UV filters, and illicit drugs, were selected as target compounds. Most of the selected CECs are frequently used in prescriptions, over-the-counter medications, human treatments, veterinary medicines, and illicit drugs in Taiwan. These CECs are also reported in many other researches worldwide (Jiang et al., 2014, 2015b; Kasprzyk-Hordern et al., 2008; Kolpin et al., 2002; Nakada et al., 2007; Thomas et al., 2012; Yoon et al., 2010; Zhu et al., 2013). The chemicals and standards used in this study (including suppliers, purities, and detailed physiochemical properties of the 30 target CECs) are described in Section S1 and Table S1 of the Supplementary Information.

2.2. Aquatic systems and sample collection

Samples were collected from two aquatic systems in Taiwan (Table 1). The locations of the sampling sites are shown in Fig. 1. In the southern aquatic system, we investigated three rivers and one canal in Tainan, which has a population of approximately 1.8 million and is located between the Yanshuei and Agongdian Rivers. The Yanshuei (Y1–Y6) and Erren Rivers (E1–E8) have drainage basins of 343.7 and 339.2 km^2 and lengths of 41.3 and 61.2 km, respectively. The Tainan Canal (C1–C5), which is 37 m in width and 5 km in length, flows through urban areas and is influenced mostly by domestic sewage. The Agongdian River (A1–A4) has a length of 38 km and a catchment area of 137 km^2. The most upstream site, Agongdian Reservoir, (at the head of Agongdian River) was used as a control site (A1). This site was chosen as it had little human activity or contamination. In the central aquatic system, two main rivers, namely, the Wu (W1–W8) and Zhuoshui Rivers (Z1–Z7), were chosen to characterize the city of Taichung. The Wu River, with an overall length of 117 km and a drainage area of 2026 km^2, flows through Taichung, which is the third most populous city in Taiwan (2.7 million inhabitants). Two small drainage systems (LIC and LYC), which receive direct discharges of domestic wastewater from surrounding residential areas, were also sampled. Constituting the longest river in Taiwan, the Zhuoshui River is a mountain stream (total length 187 km) that drains an area of 3155 km^2. From upstream to downstream, it flows through rural areas, industrial districts, agricultural, and animal husbandry areas. Detailed information on the sampling sites is given in Table S2 and Fig. S1 of the Supplementary Information.

Forty samples were collected in the two aquatic systems during August (central aquatic system) and November (southern aquatic system) 2010. All of the samples were collected approximately 0–50 cm below the surface using a stainless steel bucket from bridges at the centroid of the flow. Samples were immediately transferred to 1-L amber glass bottles that had been pre-cleaned successively with detergent, distilled water, and methanol and finally dried. Each bottle was rinsed with sample water prior to sampling. The samples were kept at 4 °C in a cold storage room before further treatment and analysis in the laboratory.

2.3. Analytical methods

The CECs were concentrated and analyzed using the following previously published method (Jiang et al., 2014, 2015b). Briefly, 1-L water samples were filtered through 0.45-μm glass fiber filters and

Table 1
Geographical information for the southern and central aquatic systems.

River	Length (km)	Drainage area (km^2)	Annual rainfall (mm)	Flow rate (m^3/d)[a]	Population per unit area (people/km^2)	Pig per unit area (pig/km^2)	WWTPs[b]
Southern aquatic systems							
Yanshuei River	41.3	343.7	1650	2,083,968	1955	209	–
Tainan Canal	5	NA	NA	NA	6410	NA	1 (Primary + Secondary treatment)
Erren River	61.2	339.2	1850	1,678,752	1006	649	–
Agongdian River	38	137	1730	819,936	1728	123	–
Central aquatic systems							
Wu River	117	2026	1800	3,620,160	4052	4	1 (Primary + secondary treatment)
Zhuoshui River	187	3155	2200	4,086,720	471	716	–

Data obtained from Taiwan Water Resources Agency and Council of Agriculture.
NA: Information was not available.
[a] Mean fluxes at each river.
[b] Wastewater treatment plants.

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