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Occurrence of pharmaceuticals and perfluorinated compounds and evaluation of the availability of reclaimed water in Kinmen

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ABSTRACT

Emerging contaminants have commonly been observed in environmental waters but have not been included in water quality assessments at many locations around the world. To evaluate the availability of reclaimed water in Kinmen, Taiwan, this study provides the first survey of the distribution of thirty-three pharmaceuticals and five perfluorinated chemicals in lake waters and water from local wastewater treatment plants (WWTPs). The results showed that the target emerging contaminants in Kinmen lakes were at trace ng/L concentrations. In addition, most of the target compounds were present in the Jincheng and Taihu WWTP influents at ng/L concentrations levels, of which 5 compounds (erythromycin-H_2O (1340 ng/L), ibuprofen (1763 ng/L), atenolol (1634 ng/L), acetaminophen (2143 ng/L), and caffeine (3113 ng/L)) reached μg/L concentrations. The overall treatment efficiencies of the Jincheng and Taihu WWTPs with respect to these pharmaceuticals and perfluorinated chemicals were poor; half of the compounds were less than 50% removed. Five compounds (sulfamethoxazole, erythromycin-H_2O, clarithromycin, ciprofloxacin and ofloxacin) with risk quotient (RQ) values > 1 in the effluent should be further investigated to understand their effects on the aquatic environment. Additional and advanced treatment units are found necessary to provide high-quality recycled water and sustainable water resources.

1. Introduction

Kinmen, an outlying subtropical island of Taiwan (24 °30′N, 118 °25′E), is located on the west side of the Taiwan Strait. Kinmen covers a total area of 153.1 km^2 and has a total population of approximately 120,000 (http://www.kinmen.gov.tw/). The economic structure of Kinmen is dominated by agriculture, and the consumption of water for irrigation is approximately 9000 tons/day. Kaoliang Liquor is an economic mainstay of Kinmen and has resulted in agriculture and tourism development.

Water scarcity is a severe and urgent issue in Kinmen. Because urbanization has occurred rapidly in Kinmen in recent years, water consumption in Kinmen has increased. However, only a limited number of short and small rivers and streams exist in Kinmen, with rainfall mainly occurring from April to September. Furthermore, the annual evaporation (1684 mm/yr) is greater than the annual rainfall (1047 mm/yr) in Kinmen, which results in water shortages. Although several lakes and reservoirs are located in Kinmen, severe algal blooms and eutrophication have resulted in their poor water quality. Groundwater has played an important role in supplying a sufficient amount of water with up to 54% of water for domestic use, agricultural irrigation and industrial use (e.g., Kaoliang Liquor manufacturing process) obtained from groundwater sources. Accordingly, continuous and excessive groundwater pumping has led to decreased groundwater levels (a decrease of nearly 20 cm/yr) and groundwater salinization. To solve the urgent water scarcity problem, a project for the development of reclaimed water and alternative water sources in Kinmen has been implemented. Currently, treated water in Kinmen is recovered for non-potable reuse, such as agricultural irrigation and groundwater recharge, following conventional wastewater treatment processes. To improve the use and application of reclaimed water, emerging

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contaminants must remain part of the discussion because many emerging contaminants are not completely removed by conventional wastewater treatment processes and are, consequently, released into receiving aquatic environments and potentially threaten the ecosystem and human health [1–4].

Pharmaceuticals and personal care products (PPCPs), hormones and industrial compounds, such as perfluorinated compounds (PFCs), were the most commonly detected emerging contaminants. These compounds have been found at ng/L to μg/L concentrations around the world in many types of water matrices, including wastewater treatment plant (WWTP) influents and effluents, hospital wastewater, wastewater from pharmaceutical manufacturing companies, industrial wastewater and even surface water and groundwater. For example, nonsteroidal anti-inflammatory drugs (NSAIDs), antibiotics and other pharmaceuticals have commonly been detected in hospital wastewater and pharmaceutical manufacturing wastewater in Korea, Switzerland and the USA [5–7], with corresponding concentrations of up to μg/L. Regarding the removal efficiency of pharmaceuticals in WWTPs, Canadian researchers have indicated that many compounds are not effectively removed (e.g., diclofenac and gemfibrozil) and remain in effluents [8]. In addition, Spanish researchers have demonstrated that the removal efficiency of different pharmaceuticals varies greatly (6–93%) and differs among WWTPs [9]. In a nationwide reconnaissance conducted by the US Geological Survey [10], 95 pharmaceuticals, hormones, and other organic wastewater contaminants were investigated in 139 streams in the USA. The results of the reconnaissance indicated that many compounds may survive wastewater treatment processes and enter streams. A study from the UK [11] showed the frequent presence of low concentrations of pharmaceuticals in rivers (the most frequently detected compounds include erythromycin-H_2O, acetaminophen, trimethoprim, naproxen and ibuprofen). These pharmaceutical compounds have also been detected in groundwater [12]. In addition to pharmaceuticals, PFCs have generally been recognized as recalcitrant compounds, being detected in industrial wastewaters and their receiving water bodies in many countries (e.g., Japan, China, Thailand, Spain, Taiwan and Germany) [13–17]. In Taiwan, our previous work has demonstrated the occurrence of these emerging contaminants in many types of water matrices (e.g., WWTP wastewater, hospital wastewater, industrial wastewater, surface water and groundwater) [16–21]. Based on previous work, 38 of the most commonly occurring pharmaceuticals (including antibiotics, NSAIDs, lipid regulators, cholesterol lowering drugs, β-blockers, vasodilators, psychiatric drugs and psychostimulants) and PFCs were chosen as our target compounds and monitored for their occurrence on Kinmen Island.

The objectives of this study are to (i) simultaneously analyze 38 emerging contaminants using solid-phase extraction (SPE) combined with liquid chromatography–tandem mass spectrometry; (ii) investigate the occurrence of the target compounds in Taihu and Lunghu Lakes (the main drinking water sources for Kinmen residents); and (iii) investigate the occurrence and removal of the target compounds at the Jincheng and Taihu WWTPs (the largest and second largest WWTPs in Kinmen) and evaluate the use of the treated discharge water as reclaimed water regarding the target emerging contaminants. Because water scarcity is an urgent problem in Kinmen, this study could be used by the Kinmen government to assist in the establishment of guidelines (e.g., evaluation of the availability of reclaimed water in Kinmen and the development of related reclaimed water policies in the future). To our knowledge, this is the first study of the distribution of emerging contaminants in the water matrices of Kinmen Island. The experience at Kinmen Island can be used as an example for islands that are similar and in need of reclaimed waters around the world.

2. Materials and methods

2.1. Sample collection, pretreatment and analysis

The sampling sites, including two lakes (Taihu Lake and Lunghu Lake) and two WWTPs (Jincheng WWTP and Taihu WWTP), are shown in Fig. 1. Water samples were collected as grab samples. Although the grab sample method can result in large uncertainties (because it involves sampling water at one point in time), the samples were collected based on the hydraulic retention times of the two WWTPs to minimize these uncertainties. In addition, all of the samples were collected during the daytime. Triplicate samples were collected and stored in 1-L amber glass bottles in ice-packed containers. All sample bottles (except those used for PFC analysis) contained 4 mL 0.125 M EDTA-2Na/L before sample collection. The samples were vacuum-filtered through 0.45 and 0.22 μm disk filter paper (ADVANTEC, Toyo Roshi Kaisha, Ltd., Japan), acidified to pH 4 using hydrochloric acid and stored at 4 °C until solid-phase extraction (SPE).

The samples were analyzed using SPE combined with liquid chromatography–tandem mass spectroscopy (LC–MS/MS). To obtain the most linear range and the best analytical signals with LC–MS/MS, the target compounds were classified into the following four categories: Group 1: sulfonamide antibiotics (sulfadiazine, sulfamethoxazole, sulfathiazole, sulfamethazine, sulfamonomethoxine and sulfadimethoxine), macrolide antibiotics (erythromycin-H_2O, clarithromycin, roxithromycin and tylosin), imidazole antibiotics (dimetridazole and metronidazole), quinolone antibiotics (nalidixic acid, flumequine, pipemidic acid, norfloxacin, ciprofloxacin and ofloxacin), non-steroidal anti-inflammatory drugs (acetaminophen), other antibiotics (trimethoprim), vasodilator (pentoxifylline), psychiatric drugs (carbamazepine) and psychostimulants (caffeine); Group 2: non-steroidal anti-inflammatory drugs (ibuprofen, naproxen and ketoprofen), lipid regulators and cholesterol-lowering drugs (clofibric acid, gemfibrozil and bezafibrate); Group 3: β-blockers (propranolol, atenolol, metoprolol and sotalol); and Group 4: perfluoroalkyl sulfonic acids (PFOS) and perfluorinated carboxylic acids (PFHxA, PFOA, PFDA and PFHpA). Based on the physicochemical properties and extraction efficiencies of the four groups, Oasis MCX cartridges (Waters, Milford, MA, USA) were utilized for negative-mode analytes, and Oasis HLB cartridges (Waters, Milford, MA, USA) were utilized for positive- and negative-mode analytes. The different target compound classes were extracted using the following three SPE methods.

2.1.1. Method 1 (for groups 1 and 2)

The HLB cartridges were preconditioned using 6 mL of methanol and 6 mL of DI water (pH = 4.0). Aliquots from 400 mL water samples (the pH was adjusted to 4.0 with hydrochloric acid) were spiked with 40 μL of an internal standard (1 mg/L of $^{13}C_6$-sulfamethazine, metronidazole-$^{13}C_2$, $^{15}N_2$, ciprofloxacin-d_8, erythromycin-$^{13}C,d_3$ and roxithromycin-d_7) and loaded into the cartridges at a flow rate of 3–6 mL/min. After sample passage, the cartridges were rinsed with 6 mL of DI water (pH = 4.0) and drained, and after drainage, the analytes were eluted with 3 mL of methanol and 3 mL of a 50% methanol-diethylether (v:v = 50:50) mixture. The eluents were collected, evaporated under a stream nitrogen and reconstituted to a volume of 0.4 mL with 25% aqueous methanol. The final solutions were passed through a 0.45-μm PVDF filter membrane prior to LC–MS/MS analysis.

2.1.2. Method 2 (for group 3)

The MCX cartridges were preconditioned with 6 mL of methanol and 6 mL of DI water (pH = 4.0). Aliquots from 200 mL water samples (the pH was adjusted to 4.0 using hydrochloric acid) were