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Effects of the summer holiday season on UV filter and illicit drug concentrations in the Korean wastewater system and aquatic environment☆

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ABSTRACT

Seasonal variations in the concentrations of eight ultraviolet (UV) filters and 22 illicit drugs including their metabolites in the Korean aquatic environment were investigated. Seawater samples from three beaches, water samples from two rivers, and influents and effluents from three wastewater treatment plants were analyzed. The UV filter concentrations in the seawater, river water, and effluent samples were 39.4–296, 35.4–117, and 6.84–51.1 ng L^{-1}, respectively. The total UV filter concentrations in the seawater samples were 1.9–4.4 times higher at the peak of the holiday season than outside the peak holiday season. An environmental risk assessment showed that ethylhexyl methoxy cinnamate (EHMC) could cause adverse effects on aquatic organisms in the seawater at the three beaches during the holiday period. Seven of the 22 target illicit drugs including their metabolites were detected in the wastewater influent samples, and the total illicit drug concentrations in the influent samples were 0.08–65.4 ng L^{-1}. The estimated daily consumption rates for *cis*-tramadol (*Cis*-TRM), methamphetamine (MTP), meperidine (MEP), and codeine (COD) were 25.7–118.4, 13.8–36.1, 1.36–12.6, and 1.75–8.64 mg d^{-1} (1000 people)$^{-1}$, respectively. In popular vacation area, the illicit drug consumption rates (*Cis*-TRM, MTP and MEP) were 1.6–2.6 times higher at the peak of the summer holiday season than at the beginning of the summer.

1. Introduction

Numerous pharmaceuticals and personal care products have been found to be ubiquitous in the environment because of human activities (Jiang et al., 2015). These compounds are found in environmental media in different concentration at different times. The fates of pharmaceuticals and personal care products are often related to their use and physicochemical properties (Liu and Wong, 2013; Rodil and Moeder, 2008). Seasonal and spatial variations have been found in the concentrations of many pharmaceuticals and personal care products in environmental media. For example, Li et al. (2007) found that the UV filter concentrations in reclaimed wastewater influent in China were two times higher in July than in February. In a study in Hong Kong, UV filter concentrations were found to be 30% higher during the wet season (May to August) than during the dry seasons (February and November) (Tsui et al., 2014).

The presence of illicit drugs in water environment is also of emerging concern. Seasonal and spatial variations have been found in the concentrations of illicit drugs in environmental media, and this has been linked to increased drug consumption during holidays in urban areas, at festivals, and at weekends (Bijlsma et al., 2009; Jiang et al., 2015; Kasprzyk-Hordern et al., 2009; Lai et al., 2012). As in studies elsewhere, UV filters and illicit drugs have been found in the Korean environment (Ekpeghere et al., 2016; Kim et al., 2014, 2015), and higher UV filter concentrations have been found in summer than at other times (Ekpeghere et al., 2016).

Especially in Korea, about 10 million people visit Korean beaches during the summer for recreation. Pollution caused by increased use of UV filters and recreational drugs in the holiday season could pose risks to the environment. UV filters may cause endocrine disruption and systemic circulation problems in humans, other mammals, amphibians, and fish exposed to them (Blüthgen et al., 2014; Fent et al., 2010; Jurado et al., 2014; Krause et al., 2012;

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Schlumpf et al., 2004). Illicit drug consumption rates in Korea have been estimated, but the samples used to make these estimates were collected in December, and seasonal and regional variations need to be studied.

Therefore, the aim of this study was to determine the concentrations and distributions of UV filters and illicit drugs in Korean aquatic systems before and after the summer holidays. Risk assessments for aquatic organisms were performed using the concentrations found, and illicit drug consumption rates for before, during, and after the holiday season were also calculated in this study.

2. Materials and methods

2.1. Chemicals and reagents

Standards of eight organic UV filters were used. Benzophenone (BP), benzophenone-3 (BP-3), 2-ethylhexyl 4-dimethylaminobenzoate (OD-PABA), 2-ethylhexyl salicylate (EHS), isoamyl benzoate (IAMB), and benzyl cinnamate (BC) standards were supplied by Sigma-Aldrich (Steinheim, Germany), and 4-methylbenzylidene camphor (4-MBC) and ethylhexyl methoxy cinnamate (EHMC) standards were supplied by Merck (Darmstadt, Germany). All the UV filter standards had purities ≥98%. Benzophenone-d_{10} (99%; Sigma-Aldrich) and phenanthrene-d_{10} (100%; Accustandard, New Haven, CT, USA) were used as internal and recovery standards, respectively, for the UV filter analyses. A total of 22 illicit drugs including their metabolites were analyzed. These compounds were cocaine, benzoylecgonine, cocaethylene, norcocaine, ecogonine methyl ester, amphetamine types of stimulants (amphetamine (AMP), methamphetamine (MTP), 3,4−methylenedioxy methamphetamine (MDMA), 3,4−methylenedioxyethamphetamine (MDEA), 3,4−methylenedioxy amphetamine (MDA)), buprenorphine, meperidine (MEP), heroine, cis−tramadol HCl (cis−TRM), morphine (MOR), hydrocodone (HCD), hydromorphone, oxymorphone, 6−acetylmorphine, oxycodone, methadone, ketamine, 2−ethylidene−1,5−dimethyl−3,3−diphenylpyrrolidine (EDDP) and codeine (COD). These compounds were purchased from Cerilliant (Round Rock, TX, USA). Methadone-d_3, cocaine-d_3, codeine-d_3, morphine-d_3, ketamine-d_4, and amphetamine-d_6, also purchased from Cerilliant, were used as surrogate standards for the illicit drug analyses.

2.2. Sample collection

The sampling sites were two rivers (Songjeong Stream and Suyeong River), three wastewater treatment plants (WWTPs) and three beaches (Gwangalli, Haeundae, and Songjeong). Gwangalli, Haeundae, and Songjeong are famous beaches in southeast Korea. All three beaches are open from 1 June to 10 September, but recreational activities at the beaches only commence fully from mid-July. The Korean summer holiday period normally runs from late July to mid-August, and between one and 10 million people visit beaches during this period (TOUR.GO, 2013), as shown in Supplementary Table S2. The WWTPs were WWTP1, which is in a semi-rural area, WWTP2, which is in a residential area, and WWTP3, which is in a vacation area. Details of the sampling sites are shown in Supplementary Figure S1.

Three sampling campaigns were conducted in this study. The samples were collected between 8 and 10 July 2013 (before the main holiday period), between 1 and 3 August 2013 (in the peak holiday period), and between 12 and 14 September 2013 (after the main holiday period). UV filter concentrations were measured in WWTPs effluents, river water and sea water samples. In each sampling campaign, by using the grab sampling method, the effluent and sea water samples were collected for two times during two days (one time a day) at each site but river water was collected for one time. Especially, at each beach, a seawater sample was collected from each of five points 3−20 m from the coastline. A total of 2 L (400 mL at each point) were collected using a grab sampler, and then the sample was poured into a 2 L amber bottle, leaving no headspace. For illicit drugs, the 24 h composite influent samples were collected using a time proportional method with an auto sampler (WS700, Global Water) at a sampling rate of 50 mL h^{-1} for two days. The 24 h composite sample was then transferred to a polyethylene bottle and immediately acidified to pH 2 by adding 1 N HCl. In total, 14 samples for UV filter analysis and six samples for illicit drugs were collected in each sampling campaign.

2.3. Sample preparation and analysis

2.3.1. UV filters

A 400 mL aliquot of each sample was acidified to pH 3 by adding 6 N sulfuric acid. Benzophenone-d_{10} (20 μL of a 10 μg mL^{-1} solution) was spiked into each sample to act as an internal standard. Each spiked samples was extracted using a solid phase extraction system (SPE-DEX 4790; Horizon Technology, Salem, NH, USA) containing an Empore C_{18} extraction disk (47 mm diameter; 3 M, Eagan, MN, USA). Each disk was conditioned with 5 mL of a 1:1 mixture of methylene chloride and ethyl acetate for 1.5 min, 5 mL methanol for 1.5 min, and 5 mL water for 1.5 min. All the reagents used for conditioning the disks were purchased from J.T. Baker (Phillipsburg, NJ, USA). Each sample was loaded onto a conditioned disk, then the disk was washed with water for 1 min and dried for 8 min. The disk was then eluted sequentially with 5 mL methylene chloride for 1.5 min, 5 mL ethyl acetate for 1.5 min, and 5 mL of a 1:1 mixture of methylene chloride and ethyl acetate for 1.5 min. Water was removed from each eluted sample using sodium sulfate, then the sample was evaporated to 500 μL. Phenanthrene-d_{10} was added to each extract as a recovery standard.

2.3.2. Gas chromatography-mass spectrometry analysis and quantification of UV filters, and quality assurance

The UV filters in the extracts described above were determined by gas chromatography-mass spectrometry (using a Agilent 7890 GC/MSD; Agilent Technologies, Santa Clara, CA, USA). Separation was achieved using a HP-5MS column (30 m long, 0.32 mm i.d., 0.25 μm film thickness; Agilent Technologies). A 2 μL aliquot of a sample was injected in splitless mode. The inlet temperature was 280 °C, the carrier gas was helium, and the constant flow rate was 1.0 mL min^{-1}. The oven temperature program started at 90 °C (held for 1 min), then increased at 20 °C min^{-1} to 160 °C, and then increased at 5 °C min^{-1} to 270 °C. The interface line temperature was 300 °C. The mass spectrometer was used in electron impact positive ionization mode and selected ion monitoring mode, and the ionization energy was 69.9 eV.

The UV filter calibration curve correlation coefficients (r^2) were all >0.99. The limit of detection was defined as the concentration of the calibration standard giving a signal-to-noise ratio of three. The accuracy of the method was determined by analyzing triplicate river water samples spiked with all of the target compounds, and the recoveries were 79%−118%. The limit of detection, accuracy, and other quantification information for each target UV filter are shown in Supplementary Table S3. Procedural blanks were included with each batch of 10−15 samples to identify any contamination that occurred during the sample preparation process. The internal standard recoveries for the real samples were 50%−130%. The relative percentage differences for duplicate real river water and wastewater samples were 14%−20% and 1%−26%, respectively.