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Ecological risks of home and personal care products in the riverine environment of a rural region in South China without domestic wastewater treatment facilities

Nai-Sheng Zhang [a,b], You-sheng Liu [b], Paul J. Van den Brink [a,c], Oliver R. Price [d], Guang-Guo Ying [b,*]

[a] Department of Aquatic Ecology and Water Quality Management, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands
[b] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[c] Alterra, Wageningen University and Research Centre, P.O. Box 47, 6700 AA Wageningen, The Netherlands
[d] Safety and Environmental Assurance Centre, Unilever, Colworth Science Park, Sharnbrook, Bedfordshire MK44 1LQ, UK

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ABSTRACT

Home and personal care products (HPCPs) including biocides, benzotriazoles (BTs) and ultraviolet (UV) filters are widely used in our daily life. After use, they are discharged with domestic wastewater into the receiving environment. This study investigated the occurrence of 29 representative HPCPs, including biocides, BTs and UV filters, in the riverine environment of a rural region of South China where no wastewater treatment plants were present, and assessed their potential ecological risks to aquatic organisms. The results showed the detection of 11 biocides and 4 BTs in surface water, and 9 biocides, 3 BTs and 4 UV filters in sediment. In surface water, methylparaben (MeP), triclocarban (TCC), and triclosan (TCS) were detected at all sites with median concentrations of 9.23 ng/L, 2.64 ng/L and 5.39 ng/L, respectively. However, the highest median concentrations were found for clotrimazole (CLOT), 5-methyl-1H-benzotriazole (MBT) and carbendazim (CARB) at 55.6 ng/L, 33.7 ng/L and 13.8 ng/L, respectively. In sediment, TCC, TCS, and UV-326 were detected with their maximum concentrations up to 353 ng/g, 155 ng/g, and 133 ng/g, respectively. The concentrations for those detected HPCPs in surface water and sediment were generally lower in the upper reach (rural area) of Sha River than in the lower reach of Sha River with close proximity to Dongjiang River ($P_{t\text{-test}} < 0.05$), indicating other input sources of HPCPs in the lower reach. Biocides showed significantly higher levels in surface water in the wet season than in the dry and intermediate seasons. Preliminary risk assessment demonstrated that the majority of HPCPs monitored represented low risk in surface waters. There are potentially greater risks to aquatic organisms from the use of TCS and TCC in the wet season than in dry and intermediate seasons in surface waters. This preliminary assessment also indicates potential concerns associated with TCC, TCS, DEET, CARB, and CLOT in sediments, although additional data should be generated to assess this fully. Thus future research is needed to investigate ecological effects of these HPCPs on benthic organisms in sediment of rural rivers receiving untreated wastewater discharge.

1. Introduction

A variety of organic compounds are used as the ingredients in home and personal care products (HPCPs) for diverse functions. For instance, biocides such as parabens, triclocarban (TCC) and triclosan (TCS) are widely used in personal hygiene products and cosmetics as preservatives or antimicrobials (Ramaswamy et al., 2011). Benzotriazoles (BTs) are used as anti-corrosives in dishwasher detergents and anti-icing fluids (Giger et al., 2006), while ultraviolet (UV) filters are commonly used in cosmetic formulation such as sunscreens, skin care, facial makeup and lip care products (Manova et al., 2013). After use, these chemicals are discharged with domestic wastewater into the receiving environment directly without any treatment or indirectly after sewage treatment processes. Therefore, it is essential to understand their occurrence, fate and ecological risks in the environment.

As emerging contaminants, HPCP ingredients have drawn considerable attention in recent years because of increasing

* Corresponding author. Fax: +86 020 85290200.
E-mail addresses: guangguo.ying@gmail.com, guang-guo.ying@gig.ac.cn (G.-G. Ying).

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concerns over their potential adverse impacts on human health and aquatic organisms (Brausch and Rand, 2011; Gago-Ferrero et al., 2012; Liu and Wong, 2013). Parabens may have narcotic and endocrine disrupting effects on medaka (*Oryzias latipes*), fathead minnow (*Pimephales promelas*), as well as acute/chronic toxicity on cladoceran (*Daphnia magna*), and green algae (*Psuedokirchneriella subcapitata*) (Dobbins et al., 2009; Yamamoto et al., 2011). TCS and TCC were reported to produce cytotoxic, genotoxic, and endocrine disruptor effects (Ahn et al., 2008; Bedoux et al., 2012; Hinther et al., 2011; Schebb et al., 2011). They can be accumulated in algae (Coogan et al., 2007), snails (Coogan and La Point, 2008), and wetland plants (Stevens et al., 2009; Zarate et al., 2012) with relatively significant toxicity at the concentration range of 100–100,000 ng/L (Dussault et al., 2008; Ishibashi et al., 2004; Orvos et al., 2002). Exposures with frequent or prolonged topical applications of DEET, an insect repellent, may result in central nervous system toxicity in some individual humans (Antwi et al., 2008) and inhibit growth or even cause mortality of algae, crustacean, and fish (Harada et al., 2008; Weeks et al., 2012; USEPA, 2013). Benzotriazole (BT) and methylbenzotriazole (MBT) may inhibit growth and vitality of algae and duckweed, and affect reproduction of daphnids (Cornell et al., 2000; Seeland et al., 2012). Some UV filters (e.g. 3-benzylidene camphor and benzophenone-2) were demonstrated to show oestrogenic and additional hormonal activities, thus possibly resulting in decreased fecundity and reproduction of fish (Fent et al., 2006; Kunz et al., 2006; Weisbrod et al., 2007). Acute and chronic toxicity of UV filters on *D. magna* were also reported by Fent et al. (2010). In addition, 2-(2′-Hydroxy-5-methylphenyl) benzotriazole (UV-P) and BT were found to have significant antiandrogenic activity (Fent et al., 2014).

HPCPs have been reported worldwide at relatively high concentrations in the effluents of wastewater treatment plants (WWTPs) and their receiving environments (Halden and Paull, 2005; Kolpin et al., 2002; Liu et al., 2012; Weiss et al., 2006; Zhao et al., 2010). TCS and TCC are listed as top 10 common detected wastewater compounds for frequency and concentration, and they were detected in surface water at concentrations up to 2300 ng/L and 1425 ng/L, respectively (Brausch and Rand, 2011). Parabens and an insect repellent DEET were also detected in surface water with maximum concentrations of 400 ng/L and 660 ng/L, respectively (Brausch and Rand, 2011). Giger et al. reported a maximum concentration of 6300 ng/L for benzotriazole in the rivers and lakes of Switzerland (Giger et al., 2006). TCS and TCC, which are hydrophobic with logarithmic distribution coefficients (log D) of 4.90 and 4.93 at pH7, respectively, were also reported in sediment of the rivers receiving WWTP effluents in China at concentrations up to 705 ng/g and 1956 ng/g, respectively (Wang et al., 2014).

Most reported studies focus on the wastewaters from municipal WWTPs and their impacted riverine environments, while little research has been carried out on HPCPs in subtropical rural riverine environments that receive untreated sewage discharges in China, although several similar studies have been performed in other countries, e.g. USA and Japan (Bernot et al., 2013; Karpuzcu et al., 2014; Tamura et al., 2013). In developing countries, rural regions have low wastewater treatment rates, with most of the domestic wastewaters being discharged into rivers without any treatment. In 2013, the rural regions in China have a population of 762 million distributed in 2.65×10^6 villages, 59.7% of the total population. Compared to the high sewage treatment volumes (1.51×10^8 m^3/d) and treatment rate (percentage of sewage coverage, 78.47–89%) in urban regions, low wastewater treatment rates in rural regions are resulted from limited WWTPs (MHURD, 2014). For instance, among the 145,000 villages in Guangdong Province, only 274 WWTPs were built up with a sewage treatment volume of 3.6×10^4 m^3/d (Ling et al., 2009).

The aim of this study was to investigate the occurrence of 29 HPCPs including 17 biocides, 4 BTs and 8 UV filters in the riverine environment of a rural region of South China and to assess their potential ecological risks to aquatic organisms by the risk quotient (RQ) approach. The study area is located in the Pearl River Delta (PRD) region, South China, with Sha River as the receiving environment for the domestic wastewater from the rural population. The results from this study provide initial information on the presence of HPCPs in rural riverine environments and help to identify future research priorities to better characterise the potential risks of HPCPs on the riverine ecosystem.

2. Materials and methods

2.1. Chemicals and materials

Twenty-nine HPCPs were selected as the target compounds in this study, with their physicochemical properties being listed in Table S1 (Supplementary Material). Authentic chemical standards and corresponding internal standards (ISs) were obtained from various international suppliers, i.e. AccuStandard (New Haven, USA), Dr. Ehrenstorfer GmbH (Augsburg, Germany), Tokyo Chemical Industry (Tokyo, Japan), International Laboratory (South San Francisco, USA), Toronto Research Chemicals (North York, Canada), Campro Scientific (Berlin, Germany), CDN Isotopes (Pointe-Claire, Canada), Cambridge Isotope Laboratories (Andover, USA), United States Pharmacopeia (Rockville, USA), Sigma Aldrich (Seelze, Germany), and Wako (Osaka, Japan). The chemicals involved in chemical analysis include 17 biocides and 9 corresponding ISs: methylparaben (MeP), ethylparaben (EtP), propylparaben (PrP), and butylparaben (BuP), triclosan (TCS), triclocarban (TCC), clotrimazole (CLOT), miconazole (MICO), fluconazole (FLUC), ketoconazole (KETO), itraconazole (ITRA), thiabendazole (THIA), carbendazim (CARB), DEET, climbazole (CLIM), icaridin (ICAR), 1,2-benzisothiazolinone (BIT), 4-hydroxybenzoate-2,3,5,6-D4 (methylparaben-D_4), $^{13}C_{12}$-triclosan, triclocarban-D_7, clotrimazole-D_5, fluconazole-D_4, ketoconazole-D_8, thiabendazole-D_6, imazalil-D_5, and octhilinone-D_{17}; 4 BTs and 1 corresponding IS: benzotriazole (BT, 99%), 5-methylbenzotriazole (MBT, 98%), 5-chlorobenzotriazole (CBT, 98%), 5,6-dimethylbenzotriazole (DMBT, 99%), and thiabendozole-D_6 (100%); 8 UV filters and 2 corresponding ISs: 3-(4-methylbenzylidene)camphor (4-MBC, 99%), octyl 4-methoxycinnamate (OMC, 95%), octocrylene (OC, 97%), UV-P (99%), UV-326 (97%), UV-327 (98%), UV-328 (98%), UV-329 (98%), metolachlor-D_6 (100%), and chrysene-D_{12} (100%).

Reagents of HPLC grade, i.e. methanol, acetonitrile, ethyl acetate (EtOAc), n-hexane, dichloromethane (DCM), and formic acid, were purchased from Merck (Shanghai, China), CNW Technologies (Dusseldorf, Germany), and Tedia (Cincinnati, USA). Oasis HLB cartridges (200 mg, 6 mL) and Oasis HLB cartridges (500 mg, 6 mL) were obtained from Waters (Milford, USA). Glass fibre filters (GF/F, pore size 0.7 μm) were purchased from Whatman (Maidstone, UK), 0.22-μm membrane filters from Anple (Shanghai, China), and cellulose filters (30 mm) from Dionex (Sunnyvale, USA). HPLC-grade water was obtained from a Milli-Q water purification system (Millipore, Watford). All glassware was hand-washed with detergent and tap water, rinsed with Milli-Q water, and then baked at 400 °C for 4 h before use. Silica gel (80–100 mesh) from Haiyang Chemical (Qingdao, China) and silica sand from Qiangsheng Chemical (Suzhou, China) were washed with methanol and dichloromethane each three times, and baked at 400 °C for 4 h prior to use.

Individual stock solutions of all target compounds and internal standards were prepared in methanol at a concentration of 100 mg/L. Mixed standard solutions and internal mixed standard solutions for analysis by high performance liquid chromatography-