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Potential environmental implications of emerging organic contaminants in Taihu Lake, China: Comparison of two ecotoxicological assessment approaches

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HIGHLIGHTS

- Most water areas were at significant risk for adverse effects based on HQ indexes.
- Compounds were ranked and hormones were regarded as the greatest hazards.
- The firstly applied EIBR in field suggested Zhushan Bays as the most stressful place.
- Both approaches, HQ and EIBR, are mutually consistent, with good positive linear correlation.

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ABSTRACT

In this study, the hazard quotient (HQ) and a novel enhanced integrated biomarker response (EIBR) were applied to indirectly/directly estimate the ecotoxicological risk of emerging organic contaminants in Taihu Lake. Nine out of sixteen target compounds were detected in most sampling points at comparable concentrations (1.58–206.95 ng/L). Simultaneously, changes in multi-biomarkers were measured in caged fish for 28 days. The 0HQ results preliminarily indicated that most water areas were at significant risk for adverse effects to aquatic organisms (HQ > 10). The prioritisation was then ranked and 17α-ethinylestradiol, diethylstilbestrol and 17β-estradiol were regarded as the greatest hazards. The EIBR, covering multi-biomarkers and their weighting, was applied to field study, and Zhushan Bay was suggested as the most stressful place, followed by Meiliang Bay. The HQ showed significant positive linear correlation with the EIBR ($r = 0.848$, $P < 0.001$), suggesting mutual consistency between the two approaches based on laboratory and field study in ecotoxicological risk assessment.

1. Introduction

The occurrence and implication of emerging organic contaminants in aquatic environments have recently become a matter of concern. These contaminants from municipal wastewater treatment plants, concentrated livestock farming operations, decentralised on-site treatment systems, manufacturing and hospital effluents, and urban and agricultural runoff enter the environment (Daughton and Ternes, 1999; Fenech et al., 2013; Kolpin et al., 2002; Liu and Wong, 2013; Swartz et al., 2006; Verlicchi et al., 2012) and have been detected in different aquatic environments, such as wastewater, surface water, ground water, and even drinking water throughout the world (Benotti et al., 2009; García-Galán et al., 2011; Stuart et al., 2012; Zhang et al., 2013a).

The concentrations of these compounds are generally found in the ng/L–μg/L range in natural waters, and these low concentrations are thought to cause detrimental effects on both aquatic biota and human health due to their biological activities. For instance, Purdom et al. (1994) found extremely high plasma vitellogenin (Vtg) concentrations in caged fish living downstream from sewage treatment plants in the UK due to the presence of estrogenic chemicals in the effluents. Kidd et al. (2007) indicated that vanishingly low levels of 17α-ethynylestradiol (5–6 ng/L) in a Canadian lake led to the feminisation of male fathead minnows (*Pimephales promelas*), ranging from the inappropriate synthesis of Vtg to the presence of intersex individuals and, ultimately, the collapse of the population of the fish species. The mixtures of carbamazepine, fenofibric acid, propranolol, sulfamethoxazole and trimethoprim in the Douro River estuary also caused increases in Vtg, hepatic mass, cytoplasmic eosinophilia and cytochrome P450 1A immunoreactivity in male zebrafish liver (Madureira et al., 2012). The near extinction of Asian vultures following exposure to diclofenac is a key example where exposure to pharmaceuticals caused a population-level impact on non-target wildlife (Cuthbert et al., 2011).

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Given that emerging organic contaminants are referred as "pseudo-persistent" contaminants due to their wide production in daily life and continuous release into the aquatic environment (Daughton, 2002), there is an urgent need to conduct a comprehensive risk assessment to better understand and predict the negative consequences of these emerging contaminants. Diverse approaches have been developed to directly/indirectly assess the ecotoxicological risks of these compounds in the environment, such as the water quality index (Pesce and Wunderlin, 2000), the toxic unit concept (López-Doval et al., 2012), the integrative tissue pollutant index (Marigómez et al., 2013), the aquatic macroinvertebrate diversity indexes (Ginebreda et al., 2010) and the fish plasma model (Du et al., 2014; Huggett et al., 2003). The hazard quotient (HQ), a ratio between the predicted or measured environmental concentrations (PEC or MEC, respectively) and their non-observed effect or predicted non-effect concentrations (NOEC or PNEC, respectively) estimated from laboratory study, can provide a general characterisation of the chemical risks of contaminants according to the European Medicines Evaluation Agency (EMEA) guidelines on risk assessment, and ranking compounds of environmental concern for both regulatory and monitoring purposes in many investigations has proven beneficial (Cristale et al., 2013; García-Galán et al., 2011). It is a single-value estimate for screening-level risk assessment at early stages based on laboratory toxicity data. However, the HQ does not necessarily reflect the real ecosystem situation because many extra concurrent contaminations can be present, causing interactive or even synergistic effects on biota under certain environmental conditions.

To overcome this limitation, a suite of biomarkers that reflect exposure to various types of contaminants and provide reliable indications of effects are increasingly employed as early warning signals in monitoring programmes for the ecotoxicological risk assessment of contaminants. Because contaminants are usually present as complex mixtures, there is no single biomarker that can provide a complete interpretation of the current environment (Cazenave et al., 2009). The integrated biomarker response (IBR) index, an early multivariate response method that summarises multiple biomarker responses into a single value, has been frequently used in environmental risk assessment in various studies (Kim et al., 2010; Li et al., 2011). However, the conventional IBR calculation suffers from two weak points: (1) the IBR result is strongly dependent on the arrangement of the biomarkers on the star plot; and (2) it always overlooks the weighting of each biomarker deviating from the normal healthy state (Liu et al., 2013; Sanchez et al., 2013). To avoid mistakes due to the above weak points, Liu et al. (2013) extended the environmental toxicity of perfluorinated chemicals in mussels (*Perna viridis*) using an enhanced integrated biomarker response (EIBR) approach and demonstrated that perfluorononanoic acid (PFNA) could be as equally potent as perfluorooctanesulfonate (PFOS) in terms of integrative toxicity because PFNA induced a higher toxic response at the cellular level with higher ecological significance than PFOS.

Taihu Lake, the third largest freshwater lake in China, is located in the heart of Yangtze River Delta and has a surface area of 2338 km^2 and a mean depth of 1.89 m. It serves as an indispensable water source for drinking water, agriculture and industry for a population of 20 million in several important cities in Eastern China, including Shanghai, Suzhou, and Wuxi. However, with the extraordinary economic development, population growth and urbanisation, increasing amounts of anthropogenic pollutants have been continuously discharged into the whole basin (Liu et al., 2009; Zhang et al., 2012). Taihu Lake is famous for its severe eutrophication, which has deteriorated the water quality and threatened the water supply. Additionally, the occurrence of emerging organic contaminants, such as polybrominated diphenyl ethers and synthetic musks, has been detected in the sediment and native fish from the lake (Yu et al., 2012; Zhang et al., 2013b). Our previous studies detected some pharmaceuticals and endocrine disrupting chemicals in different regions of the lake (Lu et al., 2011, 2013; Yan et al., 2012). However, almost all studies have focused on the biological effects based on the conventional IBR approach but have overlooked biomarkers' weightings and thus could be biased and misleading. Moreover, previous studies failed to prioritise the health risks of those contaminants. In addition, public concern over the chemical and ecological quality of the lake requires a comprehensive chemical and biological assessment of the ecotoxicological risk in water bodies. Therefore, the goals of this study are to provide a more comprehensive method to assess the potential ecotoxicological risk of 16 emerging organic contaminants in Taihu Lake and to help distinguish the potential hazard factors. HQ was employed as an indicator to provide a general identification and indirect estimation of the chemical status in the lake based on laboratory study, and the EIBR approach was applied in the field study as an early warning signal to directly assess the ecological effects. Moreover, relationships between HQ and EIBR based on the laboratory and field studies were also discussed in different sampling points of Taihu Lake.

2. Materials and methods

2.1. Sampling points and water sampling

According to the characteristics of the lake, the locations of eight sampling points in the northern section of Taihu Lake are illustrated in Fig. 1. These points were located in Gonghu Bay (P1, P2 and P3), Meiliang Bay (P4 and P5), Zhushan Bay (P6 and P7) and Lake Centre (P8). Water samples were collected twice from each sampling point during November 21–December 17, 2011 using a stainless steel bucket from 50 cm below the water's surface and were immediately transferred to an amber glass bottle that was pre-rinsed with methanol. All sampling equipment was rinsed with the sample before sampling. The water samples were immediately transferred to the laboratory in an ice-packed container and stored at 4 °C for a maximum of 6 h before extraction.

A total of 16 emerging organic contaminants were determined in this study based on the information found in the literature on their occurrence in surface water as well as their high usage and consumption in China (Luo et al., 2010; Zhao et al., 2009). These contaminants comprised five hormones (17α-ethinylestradiol, 17β-estradiol, diethylstilbestrol, estrone and estriol), four antibiotics (sulfamethoxazole, norfloxacin, ofloxacin and chloramphenicol), two anti-inflammatory analgesics (diclofenac and ibuprofen), two β-blockers (atenolol and propranolol), one antibacterial (triclosan), one stimulant (caffeine) and one plasticiser (bisphenol A). The purity and source of all analytical compounds are listed in the Supplementary material (Table S1).

2.2. Sample extraction and analysis

After filtering through 0.45 μm glass fibre filters, the water samples (500 mL) were spiked with 100 ng of each surrogate standard and were passed through Oasis HLB solid phase extraction cartridges (200 mg, 6 mL, Waters, Milford, USA) that were pre-conditioned with 6 mL of methanol and 6 mL of ultrapure water. After further rinsing with 10 mL ultrapure water, the cartridges were dried under vacuum for at least 30 min and eluted twice with 5 mL of methanol. The internal standards (100 ng each) were added into the extracts before final evaporation to 1 mL under a gentle nitrogen stream. The final extract was stored in a 2 mL amber glass vial at −20 °C for further chemical analysis.

Identification and quantification of the 16 target compounds were performed with a 1260 UHPLC instrument equipped with a 6460QQQ triple quadrupole mass spectrometer with electrospray ionisation (Agilent Technologies, Palo Alto, USA) operating in the multiple reactions monitoring (MRM) mode (Yan et al., 2012; Lu et al., 2013). Sulfamethoxazole, norfloxacin, ofloxacin, atenolol, propranolol and caffeine were measured in the positive ion mode, and the remaining 10 compounds were measured in the negative ion mode. The recovery, relative standard deviation and method detection limits for the different investigated compounds are summarised in the Supplementary material