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# Occurrence, spatial distribution, and seasonal variation of emerging trace organic pollutants in source water for Shanghai, China

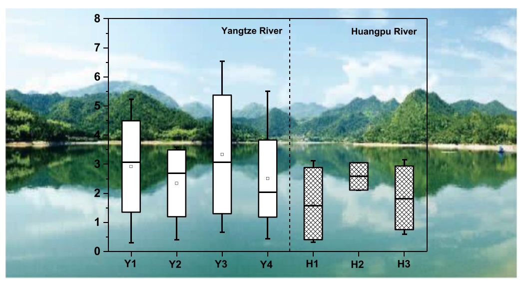
Sainan Sun, Yanan Chen, Yujin Lin, Dong An *

*Department of Environmental Science & Engineering, Fudan University, 220 Handan Road, Shanghai 200433, PR China*
*Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, PR China*

## HIGHLIGHTS

- 65 emerging trace organic pollutants were investigated for their occurrence in Shanghai's source water, China.
- The spatial distribution and seasonal variation of selected CECs were discussed.
- The concentration change of selected CECs in the reservoirs was described.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The long-term low concentrations of trace "contaminants of emerging concern" (CECs) can have potential toxic effects on human health and serious risks to the ecological environment. This study investigated the occurrence, spatial distributions, and seasonal variations of 65 target CECs, including 35 pesticides, 17 antibiotics, 7 microcystins, 5 estrogens, and 1 plasticizers in Shanghai's source water. The detected pesticides and antibiotics of sulfonamides and macrolides were relatively ubiquitous in source water of Shanghai, with levels decreasing in the following order: pesticides (average (avg.) 0.0003–1.67 μg/L) > antibiotics (avg. 0.1–14.1 ng/L). While microcystins, estrogens, and plasticizers (ng/L) were non-ubiquitous, with detected species of below 50%, and detection frequencies of mostly below 50%. Pesticide concentrations did not show obvious variations in the water from the inlets of the two rivers. Compare to all other water sources of Shanghai, the much higher concentrations of antibiotics found in the Y3, H2 reservoir and H3 were mainly from roxithromycin and sulfapyridine, roxithromycin and sulfadiazine, and sulfamethazine and roxithromycin, which accounted for 69.5%, 88.1% and 70.8% of the total concentration in corresponding water source, respectively. Pesticide concentrations in the Huangpu River were higher in the wet season than in the flat season, while the concentration decreased in the Yangtze River during the wet season. In Y1, Y3 and Y4, there were relatively large differences in pesticide levels in the wet season, and flat season when the maximal contribution of the pesticide concentration was from acephate, which accounted for about 67% of the total pesticide concentration. The levels of antibiotics in the flat season were higher than those in the wet season in both water sources. Overall, improvement of raw water quality was observed after entering the reservoir except for microcystin.



## 1. Introduction

At present, there are over 40,000 organic compounds that are considered potential "contaminants of emerging concern" (CECs). The

* Corresponding author.
*E-mail address:* andong@fudan.edu.cn (D. An).

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number of CECs is expected to increase as our analytical ability continues to improve, our knowledge about their toxicity accumulation, and more man-made chemicals that are being introduced into our daily lives. CECs include, but are not limited to, pesticides, antibiotics, microcystins, endocrine disruptors containing estrogens, and plasticizers. The long-term low concentrations of most of these pollutants, which have biological activity and environmental stability in water, can pose serious risks to human health and to the ecological environment.

Exposure to pesticides can inhibit cholinesterase enzymes, which serves as a biomarker of exposure (Singh et al., 2011; Jacobsen-Pereira et al., 2018). Pesticide exposure can also increase the risk of development of neurodegenerative diseases and cancer (Rani et al., 2017), and can affect female reproduction through decreased fertility, spontaneous abortion, premature birth, low birth weight, developmental abnormalities, ovarian disorders, and endocrine disruption. The presence and spread of antibiotics in the environment has given rise to antibiotic resistance in bacteria (Auerbach et al., 2007), especially in wastewater treatment plants, where large varieties of antibiotics coupled with bacterial loads contributes to the bacteria acquiring resistance to those antibiotics (Berendonk et al., 2015; Zhu et al., 2018) and releasing their antibiotic resistance genes (ARGs) into the environment (Everage et al., 2014; Naquin et al., 2015). Through genetic transformation, these released ARGs can get easily be transferred to environmental bacteria and pathogens, posing serious risks to ecosystem and human health (Liu et al., 2012). Microcystin is among the most common toxins produced by cyanobacteria in natural waters (Babica et al., 2006; Rastogi et al., 2014), and can cause liver complications and damage to the nervous system if ingested (Falconer, 2004; Blaha et al., 2009; Walls et al., 2018). Endocrine-disrupting chemicals (EDCs) incorporate a variety of substances that interfere with any aspect of the endocrine system, thereby causing a plethora of adverse health effects which include neurodegenerative diseases, bone and immune diseases, disorders of the reproductive or metabolic system, and a variety of cancers in intact organisms or their progenies (Gore et al., 2015; Stolz et al., 2018). At present, the monitoring and research of emerging pollutants in various matrices has been gradually carried out. Lopez-Doval et al. (2017) demonstrated the presence and seasonality of pesticides, illicit drugs, pharmaceuticals, and endocrine disruptors in the Guarapiranga reservoir in Brazil. In addition, carbendazim, imidacloprid, and bisphenol A (BPA) presented risks to the biota in the studied period. Grenni et al. (2018) reported that fluoroquinolone (33.1–306.1 ng/L), macrolide (0–149 ng/L), and sulfonamide (0–2.39 ng/L) were detected in the Po River and Lambro River in Italy. Zhang et al. (2018) found that 13 of the 19 target antibiotics were detected at low levels in the surface water from coastal coral reef regions (CRRs), with concentrations ranging from 0.01–1 ng/L, and 5 of the antibiotics occurred in offshore CRRs (300–950 km from the mainland), with concentrations ranging from 0.01–0.1 ng/L. The presence of anthropogenic contamination with antibiotics in CRRs may be a potential risk to coral growth. Graham et al. (2004) studied samples from 241 lakes in Missouri, Iowa, northeastern Kansas, and southern Minnesota, USA, which represented a south-north latitudinal gradient with increasing trophic status, during the summers of 2000–2001, and found that microcystin was common throughout the study region. Furthermore, both presence and concentration increased moving northward along the gradient. Gu et al. (2016) collected 95 wild and 88 processed marine biota samples during June 2013 to December 2013 from eight coastal cities in the Yangtze River Delta area of the East China Sea. The predominant compound found in marine organisms was 4-nonylphenol, with the highest detected concentration of 19,890.50 ng/g. The remaining three alkylphenols and BPA were investigated and had concentrations from <LOQ (limit of quantification) to 100.86 ng/g.

The Yangtze River Delta encompasses many population centers, sensitive ecosystems, and important farming regions. The combination of these factors highlights the importance of obtaining a better understanding of the occurrence of CECs in treated water resources, and the contributions to contamination in the natural and agricultural ecosystems. However, very few data are available on CECs in drinking water sources in Shanghai, China. In this work, a comprehensive study on CECs in source water samples in Shanghai was conducted in order to investigate the occurrence, spatial distribution, and seasonal variation of 65 target contaminants, including pesticides, antibiotics, microcystins, estrogens, and plasticizers, as well as to identify the processes for elimination of these substances in source water.

## 2. Materials and methods

### 2.1. Site selection and sampling

The source water was sampled at 11 sites as shown in Fig. 1. (1) 7 sites along the Yangtze River, namely Y1 (the first monitoring point flowing into Shanghai from the Yangtze River), Y2 (southwest of Chongming Island)-Inlet and Y2-outlet, Y3 (east of Luojing Town, Baoshan District in Shanghai)-Inlet and Y3-outlet, and Y4 (northwest of Changxing Island)-Inlet and Y4-outlet. (2) 4 sites along the Huangpu River, namely H1 (Wujiang District of Suzhou in Jiangsu Province), H2 (Qingpu District in Shanghai)-Inlet and H2-outlet, H3 (southeast of Songjiang District in Shanghai). The designed residence time was 7–10 days for all reservoirs. Samples were collected from 2016 to 2017 in the specific months of July and October of 2016, and April and July of 2017. All samples were stored in pre-cleaned amber glass bottles and were kept in the dark at 4 °C before use.

### 2.2. Chemicals

For the 65 targeted compounds, pesticide, estrogen, and plasticizer standards were purchased from Absolute Standards (Hamden, CT, USA), and antibiotic and microcystin standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany) and Abraxis (USA), respectively. To correct for losses during the analysis, 4 $^{13}$C- or $^{15}$N-labeled standards were used as internal standards and were all obtained from Cambridge Isotope Laboratories (Andover, MA, USA).

Organic solvents, such as acetonitrile, methanol, isopropanol, and formic acid, were of P.R. grade purity, and were supplied by Merck (Darmstadt, Germany). Sulfuric acid (Guaranteed Reagent) and ethylenediaminetetraacetic acid disodium salt ($Na_2$EDTA, Analytical Reagent) were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium fluoride was purchased from Sigma-Aldrich (St. Louis, MO, USA). Nanopure water was generated by a lab water purification system (Millipore, Bedford, USA).

### 2.3. Determinations

#### 2.3.1. Sample pretreatment

All samples were filtered through a 0.45 μm membrane prior to analysis. Individual sample pretreatment methods were as follows:

(1) Antibiotics (Ben et al., 2017; Du et al., 2017)

Filtrate samples were adjusted to pH 3.0 with 40% sulfuric acid, and 0.5 g/L $Na_2$EDTA was added prior to extraction. Filtrate samples were introduced into activated dual-SPE cartridges of Dikma ProElut PLS (500 mg/6 mL) and Water Oasis HLB (6 cm$^3$/500 mg) with a flow of approximately 2 mL/min to concentrate antibiotics in the water samples. Elution was performed with 3 mL of methanol three times. The collected extract was concentrated to approximately 200 μL under a gentle nitrogen stream, and 50% methanol was added in 200 μL of the concentrated extract to a volume of 1 mL. Then, samples were spiked with an internal standard mixture.

(2) Microcystins (Landsberg, 2010)