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Research article

Terrestrial humic-like fluorescence peak of chromophoric dissolved organic matter as a new potential indicator tracing the antibiotics in typical polluted watershed

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ABSTRACT

Natural surface waters are threatened globally by antibiotics pollution. In this study, we analyzed antibiotics and CDOM (Chromophoric dissolved organic matter) fluorescence in different water bodies using HPLC method and Excitation Emission Matrix- Parallel factor analysis, respectively. A combination of field studies in the Yinma River Watershed were conducted in rivers, reservoirs and urban rivers, and 65 CDOM and antibiotic samples were taken in April, May, July, and August 2016. EEM-PARAFAC analysis identified two components; a humic-like (C1) component and a tryptophan-like (C2) component. The redundancy analysis (RDA) demonstrated that CDOM could explain 38.2% (two axes) of the five antibiotics in reservoirs ($N = 31$), and 26.0% (two axes) of those in rivers and urban water ($N = 30$). Furthermore, the Pearson correlation coefficient between Sulfamethoxazole and C1 in reservoir water was 0.91 (*t*-test, 2-tailed, $p < 0.01$), and that between Sulfamethoxazole and C2 was 0.68 (*t*-test, 2-tailed, $p < 0.01$). This indicated that the humic-like component of CDOM PARAFAC fluorescence could detect Sulfamethoxazole contamination levels in the homogenized reservoir waters. Our results identified Sulfamethoxazole and Quinolones (Norfloxacin, 16.5 ng L^{-1}; Enrofloxacin, 0.3 ng L^{-1}; Ciprofloxacin, 30.9 ng L^{-1}) at mean concentrations of 369.5 ng L^{-1} and 15.9 ng L^{-1}, respectively, which were the higher levels in natural surface waters. The FTIR spectroscopy of the mixture of humic acid and sulfamethoxazole showed that the absorbance at 3415 cm^{-1} linked to OH stretching of OH groups and at 1386 cm^{-1} because of OH bending and vibration of COOH groups became weaker, indicating that COOH groups of humic acid can adsorb and react with –NH_2 of sulfamethoxazole. The CDOM PARAFAC components can be adapted for online or *in situ* fluorescence measurements as an early warning of Sulfamethoxazole distribution and contamination in similar aquatic environments.

1. Introduction

Antibiotics, a class of pharmaceuticals that kill pathogenic bacteria, have been extensively used in human and veterinary medicine, and agricultural industries to treat and prevent the spread of costly and harmful diseases, and as a feed additive to increase the lifespan of livestock to several decades (Chen and Zhou, 2014; Kümmerer, 2009a, b). With the excessive use of antibiotic products, the parent antibiotic or its metabolites are excreted urine and feces, and they can reach aquatic environments through direct sewage or wastewater treatment plants if removal methods are insufficient (He et al., 2016; Karthikeyan and Meyer, 2006; Wu et al., 2015). Even at small concentrations, the use of antibiotics or active metabolites could accelerate the development of antibiotic-resistant bacteria and genes through continual exposure (Kümmerer and Henninger, 2003; Pruden et al., 2006). Most antibiotics could have direct toxic and indirect adverse effects on environmental and human health (Ashbolt et al., 2013; He et al., 2016; Palmiotto et al., 2018; Xin et al., 2018). Moreover, antibiotics could be resistant to

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biodegradation, and interact with other pollutants and heavy metals (Stepanauskas et al., 2006). The increased prevalence of resistant strains of bacteria has become a concern, thus there is a need to discern the occurrence, fate, and transformation of antibiotics, particularly once they reach the natural environment.

Many studies analyzing antibiotics have been frequently conducted in natural surface waters (Bayen et al., 2014; Czekalski et al., 2015; Fick et al., 2009; Jiang et al., 2013; Tamtam et al., 2009; Wang et al., 2016) in regions including the US (Cahill et al., 2004; Karthikeyan and Meyer, 2006), Europe (Megraud et al., 2013), Switzerland (McArdell et al., 2003), France (Tamtam et al., 2008), and China (Boreen et al., 2005; Jiang et al., 2013; Luo et al., 2010; Wang et al., 2016; Wu et al., 2015), etc. With the increasing importance of global antibiotic monitoring, the objective of rapid monitoring and spatial mapping is insufficient in spite of the knowledge and monitoring technology has been resolved. Particularly, Luo et al. (2010) identified antibiotics at concentrations of up to a few μg L^{-1} in Hai River Basin, China, which were consistent with the concentrations in municipal sewage. With the increase of water pollution and reduction of usable water resources, the traditional methods of detecting antibiotics are mainly by collecting the individual samples in watershed, and then they were detected by High Performance Liquid Chromatography (HPLC) and Gas Chromatography-Mass Spectrometry (GC-MS), etc. These methods require fixed sampling points, precise experimental processes, and continuous monitoring, and can be time-consuming, expensive, and sensitive to high pollutant concentrations. To facilitate and monitor antibiotics from natural surface waters, a rapid, sensitive monitoring approach is required.

Organic matter fluorescence has been considered as a potentially viable approach to trace and monitor anomalous changes in water quality and pollutant levels (Stedmon and Markager, 2005; Stedmon and Bro, 2008; Stedmon et al., 2011). Chromophoric dissolved organic matter (CDOM), which is the colored fraction of dissolved organic matter, could also produce, carry, and transmit carcinogenic substances (Zhang et al., 2011; Zhou et al., 2016). The chemical structure, composition, and abundance of CDOM are optically dynamic due to their complexity and heterogeneity, which are dependent on their origins (Zhang et al., 2011). Nonetheless, optically active components of CDOM can emit fluorescence after absorbing light at certain wavelengths. It is difficult to isolate hydrophobic from hydrophilic acids by using Amberlite XAD ionexchange resins. Some optically active components of CDOM can emit fluorescence after absorbing light at certain wavelengths (Zhang et al., 2011). As is noted, these Characteristics of CDOM make it is provided with advantages that could be estimated by remote sensing (absorption) and portable fluorescence spectrum analyzer (fluorescence) (Zhu et al., 2014). Therefore, absorption characteristic and fluorescence spectroscopic techniques can be used to provide detailed information about the source and composition of CDOM. Three-dimensional excitation-emission matrix (EEM) fluorescence is a simple and effective method of determining the composition and source of CDOM (Stedmon et al., 2011; Zhang et al., 2011). Fluorescence spectroscopy has recently been used to characterize the composition of CDOM using EEM data and a parallel factor model with an *in-situ* fluorescence sensor, which is relatively cost-efficient (Kowalczuk et al., 2010; Stedmon et al., 2011). This method could separate the various overlapping fluorophores into signal components. Many researchers found that CDOM fluorescence associated with chemical oxygen demand, standard five-day Biochemical Oxygen Demand, dissolved organic carbon, point source pollution and the compositional changes of CDOM in waters (Hudson et al., 2008; Niu et al., 2014; Zhang et al., 2011; Zhou et al., 2016, 2017). Likewise, there have been many attempts to use fluorescence spectra of organic matter as a supportive tool to understand the influence of various natural and anthropogenic factors on water quality. Particularly, for the drinking water, the fluorescence of CDOM is low, and opposite results for highly polluted waters (Zhou et al., 2016, 2017). To date, few have used CDOM fluorescence to investigate and monitor antibiotics in natural surface waters. Different water types, such as drinking or urban water, could have different fluorescence intensities due to their compositions and sources. Large water bodies provided different CDOM and antibiotic concentrations. Thus, the development of continual ranges for detecting antibiotics by CDOM fluorescence is desirable. It exhibited significant advantages that could effectively help to understand and manage our aquatic environment and water resources.

As a typical polluted watershed in China, the Yinma River Watershed includes the heavily polluted tributaries of the Songhua Fluvial System, according to the 2014 Chinese environmental state bulletin. Amounts of pollutants mainly were discharged into rivers, withstand intensive agriculture (65%) and urban development (12%) in this watershed (Li et al., 2016). The main polluted rivers including Yinma River (flowing through STKM) and Yitong River (flowing through XLC), and the latter is Urban water mainly consisted of the section of the Yitong River that flows through the Changchun city. Then the urban Yitong River also serves as the ultimate recipient of urban wastewater. Furthermore, the Shitoukoumen (STKM) and Xinlicheng (XLC) Reservoirs are protected by the local government as they supply drinking water to approximately 9 million residents in Changchun City (the capital city of Jilin Province, with 23 million residents). These can exacerbate existing levels of pollution, and will empoison environment and foods to cause widespread heath problems. In this study, water samples from the reservoirs, rivers, urban water bodies, and landscape lakes located in this typical polluted watershed were analyzed. The purpose of this study was to (1) document the seasonal occurrence of various, commonly used human and veterinary antibiotics in rivers, reservoirs and urban river, (2) assess the seasonal CDOM absorption and fluorescence characteristic, and analyze the influence of the optical characteristics of CDOM on antibiotics, and 3) demonstrate the use of CDOM fluorescence to detect antibiotics in natural surface waters.

2. Materials and methods

2.1. Study site and water sampling

The studies watershed is located in a northern temperate, subhumid, continental monsoon climate zone, with a mean annual temperature of 5.3 °C (Song et al., 2013). In the winter, lakes, and rivers often freeze period from November to the April of the following year. During this period, the river and reservoir are heavily polluted, most of which originates from point-sources. In the spring (March to May), increasing ice-melt and surface runoff at the onset of the spring thaw causes an increase in antibiotic concentrations of surface waters as rainwater discharges allochthonous and accumulated antibiotics into rivers and reservoirs. In the summer (June to August), this watershed enters the rainy season, which is most intense in July and August. The average annual precipitation ranges from 370 to 668 mm, and the average annual evaporation is 1438.4 mm (Li et al., 2016). In the autumn (September to November), the temperature and rainfall decrease.

Sampling sites were selected at crucial and import tributaries, areas downstream of enterprise and domestic sewage outlets, and the reservoir entrance. Four riverine samples, including the Yitong, Shuangyang, Yinma, and Chalu Rivers, were selected because they were located in the upstream of the Shitoukoumen and Xinlicheng Reservoirs, and approximately 8 million people reside in the entire basin. The Yitong (YT) and Yinma River (YM) sections are state-controlled, and the Shuangyang (SY) and Chalu River (CL) sections are provincial-controlled. As the main tributaries, samples from these rivers were collected from the domestic sewage and agricultural effluent in the upstream region, and from bulk import to the reservoirs. The main land use types surrounding the four sample rivers were upland fields (Chalu, Shuangyang, Yitong, and Yinma), poultry plants (Chalu), aquaculture farms (Yitong, Shuangyang), and villages (Yinma) (Fig. 1). Shitoukoumen (STKM) reservoir is 35 km away from Changchun City, and provides over 80% of the city's drinking water. Xinlicheng (XLC)