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Organic micropollutants in the Yangtze River: Seasonal occurrence and annual loads

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HIGHLIGHTS

- The Yangtze River drains 40% of China's mainland with 400 million inhabitants
- Monthly concentrations and annual loads of organic pollutants were determined
- Seasonality of loads of PAHs, most pesticides, and antiinfectives were concise
- In spite of low concentrations due to high water discharge, pollutant loads are considerable

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ABSTRACT

Twenty percent of the water run-off from China's land surface drains into the Yangtze River and carries the sewage of approximately 400 million people out to sea. The lower stretch of the Yangtze therefore offers the opportunity to assess the pollutant discharge of a huge population. To establish a comprehensive assessment of micropollutants, river water samples were collected monthly from May 2009 to June 2010 along a cross-section at the lowermost hydrological station of the Yangtze River not influenced by the tide (Datong Station, Anhui province). Following a prescreening of 268 target compounds, we examined the occurrence, seasonal variation, and annual loads of 117 organic micropollutants, including 51 pesticides, 43 pharmaceuticals, 7 household and industrial chemicals, and 16 polycyclic aromatic hydrocarbons (PAHs). During the 14-month study, the maximum concentrations of particulate PAHs (1–5 μg/g), pesticides (11–284 ng/L), pharmaceuticals (5–224 ng/L), and household and industrial chemicals (4–430 ng/L) were generally lower than in other Chinese rivers due to the dilution caused of the Yangtze River's average water discharge of approximately 30,000 m^3/s. The loads of most pesticides, anti-infectives, and PAHs were higher in the wet season compared to the dry season, which was attributed to the increased agricultural application of chemicals in the summer, an elevated water discharge through the sewer systems and wastewater treatment plants (WWTP) as a result of high hydraulic loads and the related lower treatment efficiency, and seasonally increased deposition from the atmosphere and runoff from the catchment. The estimated annual load of PAHs in the river accounted for some 4% of the total emission of PAHs in the whole Yangtze Basin. Furthermore, by using sucralose as a tracer for domestic wastewater, we estimate a daily disposal of approximately 47 million m^3 of sewage into the river, corresponding to 1.8% of its average hydraulic load. In summary, the annual amounts flushed by the Yangtze River into the East China Sea were 2.9×10^6 tons of dissolved and particulate organic carbon (DOC and POC), 369 tons of PAHs, 98 tons of pesticides, 152 tons of pharmaceuticals, and 273 tons of household and industrial chemicals. While the concentrations seem comparably moderate, the pollutant loads are considerable and pose an increasing burden to the health of the marine coastal ecosystem.

1. Introduction

The Yangtze is the largest river in Asia and the third largest river in the world in terms of length (6,300 km) and discharge (900 km^3/yr). It flows through several megacities of China, such as Chongqing, Wuhan, Nanjing, Wuxi, Suzhou, and Shanghai. The rapid economic

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growth and expansion of these cities have placed enormous environmental pressure on the Yangtze River, including overexploitation in terms of hydropower (Qiu, 2012), fishing, cargo ship traffic, the disposal of sewage and industrial waste (Dudgeon, 2010), and an inundation of polluted land (Zhang and Lou, 2011; Yang et al., 2012). At the same time, a rapidly increasing urban population depends on the Yangtze River as the sole source of drinking water, although the concentrations of many organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalates, pesticides, pharmaceuticals, and many other household, agricultural, and industrial chemicals, are increasing and threaten water security (He et al., 2011; Müller et al., 2008, 2012). Moreover, the cocktail of inorganic nitrogen, phosphorus, oil hydrocarbons, organic matter, and heavy metals is expected to fuel algae blooms and "red tides" (Li and Dag, 2004), and trace elements and persistent organic chemicals—especially those related to suspended particles—may accumulate in the food chain of this productive shelf region, thus increasing the threat to human health.

In the last decade, many studies have focused on the contamination of sediment in the Yangtze estuary by organic micropollutants including PAHs (Liu et al., 2000; Xu et al., 2001; Hui et al., 2009), aliphatic hydrocarbons (Bouloubassi et al., 2001), organochlorine pesticides (OCPs) (Liu et al., 2003, 2008), PCBs (Liu et al., 2003; Shen et al., 2006), and polybrominated diphenyl ethers (Chen et al., 2006; Shen et al., 2006).

Only a few studies have been conducted using sediment along the course of the Yangtze, as it is difficult to find representative locations that provide continuous sedimentation without erosion during flooding. The large shallow lakes are especially suitable for this purpose, and Z.F. Yang et al. (2011) showed that the deposition rates of PAHs of up to 3.9 mg m^{-2} yr^{-1} in the sediment of Donghu Lake near Wuhan trace the economic development and are the highest in China. Except for the lakes, the Yangtze River sections at Wuhan and Nanjing are the main research areas. Xu et al. (2000) investigated the persistent pollutants, including polychlorinated organic compounds (PCOCs) and PAHs, in sediment from the Nanjing section of the Yangtze and reported up to 10 ng/g of PCOCs and between 16 ng/g to 765 ng/g of PAHs. Surface sediment from the Yangtze and several tributaries in the vicinity of Wuhan were analyzed for PAHs by C.L. Feng et al. (2007), for pentachlorophenol (PCP) by Tang et al. (2007), for phthalic acid esters (PAEs) by Wang et al. (2008), and for PCBs by Yang et al. (2009). Compared to concentrations detected in other large rivers of the world, the concentrations of PCP and PCBs were relatively low, the concentration of PAEs was similar, and the concentration of PAHs was higher.

Analyzing sediment is an excellent tool to document the temporal development of pollution concentrations, but it requires undisturbed and uniform deposition. Yet, combining the analysis of water samples and suspended particulate matter with water discharge data, allows the quantification of current concentrations and loads. Frequent measurements permit one to establish the seasonality, ways of transport, and possible decomposition in the environment, as well as to trace sources. Relatively few studies using this method have been performed in the Yangtze River so far, and they have mostly focused on distinct classes of compounds. The Three Gorges Reservoir is currently receiving attention; several articles reviewing research on POPs in the reservoir have been published recently (Wolf et al., 2013; Wang et al., 2012).

In the vicinity of Nanjing (Jiangsu province), PCOCs were sampled at four locations in May 1998 by Jiang et al. (2000), who determined concentrations in the lower ng/L range. Sun et al. (2002) detected 18 PCOCs in monthly water samples from December 1998 to October 1999 upstream of Nanjing City in concentrations less than 3 ng/L. Unfortunately, the loads were not quantified, but the concentration ranges of PCOCs that were determined 10 years earlier by Bao and Zhang (1990) were approximately 50 times higher, which might be due to the prohibition of the use of these chemicals 20 years ago. Pentachlorophenol residues were detected by Tang et al. (2007) in samples of suspended particles at Wuhan even though the production and application of this class of chemicals are banned in China. Phthalates at Wuhan exceed the water quality criteria of China (Wang et al., 2008), and the high concentrations of PAHs in the Wuhan section of the Yangtze have been mainly attributed to the burning of coal and wood (C.L. Feng et al., 2007). Semi-volatile compounds in the river water at Nanjing were studied in January 2007 by Wu et al. (2009), who allocated 44% to 65% of the input to industrial and domestic sewage. He et al. (2011) analyzed samples for persistent toxic substances (such as OCPs, PAHs, PCBs, and phthalates) collected from five sections of the Yangtze River around Nanjing and compared the concentrations with other rivers in China and other countries. Generally, concentrations of organic micropollutants were low in comparison with other rivers due to the large dilution by the enormous amount of water in the Yangtze.

While the concentration of a chemical in river water may be relevant for the toxicity and accumulation in the food chain, only the quantification of loads allow for comparisons of the pollution at different times and different locations, as well as emission rates and the quantification of sources and sinks. In spite of the past high-quality analytical investigations, there is an obvious lack of long-term monitoring data of organic pollutants and their distribution between water and suspended particulate matter, which would allow for the characterization of seasonality and the estimation of annual loads.

In November 2006, Müller et al. (2008) studied the middle and lower part of the Yangtze River from the Three Gorges Dam downstream to Shanghai and presented a snapshot overview of the longitudinal distribution of water constituents and anthropogenic chemicals. These authors screened for organic pollutants with limits of detection of 0.1 to 0.5 μg/L for dissolved compounds and 0.1 to 5 μg/g for particle-associated compounds, thereby detecting only the most notorious pollutants due to the high water discharge of the Yangtze. In a follow-up paper, Müller et al. (2012) characterized seasonality, the anthropogenic contribution to inorganic compounds and long-term temporal trends, and estimated annual loads using monthly measurements at Datong from May 2009 to June 2010.

The present study investigated the abundance, seasonality, and annual loads of organic micropollutants during a full hydrological year at Datong (Anhui province), the location of the lowermost hydrological station of the Yangtze River not influenced by the sea. We screened our water samples for 268 household chemicals, pharmaceuticals, pesticides, biocides, industrial chemicals, and associated metabolites. We also quantified bulk dissolved organic carbon (DOC) and particulate organic carbon (POC). The comprehensive dataset allowed us to accomplish the following objectives:

- Make accurate estimations of annual loads and discuss the seasonality. Persistent household chemicals allowed us to estimate the size of the population disposing their wastewater into the river. We were able to estimate the proportion of untreated wastewater in the Yangtze using selectively degradable compounds.
- Reflect on activities related to the use of chemicals in one of the world's largest catchments, which is home to one-third of China's population and is an integration point of the environmental impacts of this fast-growing economy.
- Provide a database and a reference point for future assessments of changes in water quality.

2. Materials and methods

2.1. Sampling

Water samples from the Yangtze River were collected monthly from May 2009 to June 2010 about 12 km upstream of the Station of Datong, approximately 600 km from the East China Sea (see Fig. 1). At this location, the Yangtze drains a catchment area of 1.7 million km^2 (Zhang et al., 2006). Three samples were collected from a ship in the cross-section of the river (geopositions Y1: N 30°46 53 , E 117°37 33 ; Y2: N