Organic micropollutants in the Yangtze River: occurrence and annual loads

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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 x 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 these concentrations seem comparably moderate, the pollutant loads are considerable and pose an increasing burden to the health of the marine coastal ecosystem.

Keywords: Yangtze River, organic micropollutants, pharmaceuticals, pesticides, household chemicals, polycyclic aromatic hydrocarbons

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 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 et al., 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; Müller et al., 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 et al., 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; Liu et al., 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 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 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 fewstudies 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 (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 Figure 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 30°46'11", E 117°37'48"; Y3: N 30°46'27", E 117°37'41") at 0.5 m below the surface using a stainless steel sampler. Samples were placed in precombusted (at 450° C for 4 hours) 250 mL glass bottles (for analysis of pesticides, pharmaceuticals, and household chemicals) or 4 L precleaned brown glass bottles (for analysis of PAHs). For the PAHs analysis, a known volume (4 L) of the water samples was filtered through preweighed glass-fiber filters (Millipore, 0.7 µm pore size, 142 mm diameter, preheated at 450° C for 4 hours). The filtered particle fraction was weighted and stored at -18° C for later analysis of the suspended particulate matter (SPM). The water samples for the analysis of pesticides, pharmaceuticals, and household chemicals were filtered through glass-fiber filters (Whatman, 0.7 µm pore size, 47 mm diameter), and an isotope-labeled internal standard (IS) solution was added before storage. The concentrations in the three samples (Y1, Y2 and Y3) were initially analyzed individually. The corresponding results were in agreement, indicating that the river was well mixed at the sampling location. Hence, for reasons of efficiency we decided to mix the three samples before analysis.

2.2. Analysis of DOC and POC

The determination of DOC was performed by combustion with a Shimadzu TOC-5000A total organic carbon analyzer. TOC was determined on the glass-fiber filters by thermic combustion after treatment with 3 M HCl. The blanks for each parameter were always below the limit of detection of 0.5 mg/L.

2.3. PAH analysis

After spiking the surrogate standards, 4 L of the filtered water samples were passed through a C18 cartridge (Supelco) for extraction. The PAHs were then eluted with a 10 mL mixture of 1:9 hexane and dichloromethane followed by 5 mL of hexane. Following freeze-drying and weighing, the samples of suspended particulate matter were spiked with surrogate standards and extracted instrumentally by accelerated solvent extraction (ASE300, Dionex) with a mixture of 1:1 hexane and acetone for 10 minutes in two static cycles. The extraction temperature was 120°C, and the pressure was 1500 psi. The elution and extract of each sample was concentrated, solvent-changed, and purified with a 1:2 alumina-to-silica gel ratio as previously reported (Mai et al., 2002). 2-fluorobiphenyl was added to the samples as an IS prior to instrumental analysis.

PAH concentrations were determined using an Agilent 7890A GC equipped with a 5975C mass selective detector under the selected ion monitoring mode. An HP-5 silica-fused capillary column (60 m × 0.32 mm inner diameter and 0.25 μm film thickness) was used with helium as the carrier gas. The operation parameters were previously reported by Qiao et al. (2006). QA and QC procedures included analysis of method blanks, matrix duplicated spikes, and sample duplicates. The recoveries of acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 for the water samples were 95±17%, 92±14%, 86%±17%, 72%±24%, respectively. Recovery rates for the samples of the suspended particulate matter were 88±21%, 95±16%, 105±27%, 95±17%, respectively. PAH concentrations were not corrected by the surrogate recovery data. The method detection limits (MDL) and relative standard deviation (RSD) for the PAHs were 3 to 7 ng/L and 0.4% to 10% in water samples, and 2 to 14 ng/g and 1% to 7% for the particulate samples.

2.4. Analysis of pesticides, pharmaceuticals, and household chemicals

The water samples were analyzed using a fully automated solid phase extraction (SPE) system, coupled directly to a liquid chromatography (LC) tandem mass spectrometer. The analytical method we used for applying 44 ISs for quantification has been reported elsewhere (Singer et al., 2010; Heeb

et al., 2012). For targets where no structurally identical ISs were available, the ISs with the most similar retention times were used for quantification. The limit of quantification was determined from the analyte concentration, producing a signal-to-noise ratio of at least 10:1 in the matrix sample. The average relative recoveries were between 80% to 120% for all compounds except for imidacloprid (71%) and metronidazole (65%).

3. Results and Discussion

3.1. Organic carbon in water and suspended particles

The DOC concentrations at Datong varied from 1.2 mg/L to 3.2 mg/L (Fig. 2), and the range compared well with previous measurements reported for the Yangtze River (Wu et al., 2007; Müller et al., 2008). During the dry season in the fall and winter, when water discharge can get as low as 12,000 m^3/s (Fig. 2a), DOC concentrations were higher (Fig. 2b) and decreased during the wet season, when the water discharge was up to 50,000 m^3/s. The DOC load (shown as bars in Fig. 2b), however, was highest during the wet season. The POC levels (Fig. 2b) fluctuated in direct correlation to the concentration of the suspended particles (Figs. 2a and 2b). The POC content of the suspended particles, however, remained relatively constant at 1.9% to 3.1%, indicating that the source of POC was mainly terrestrial (Sun et al., 2010; Xia et al., 2011).

The ratio of DOC/POC varied from 0.67 to 5.17 with a median value of 1.75. The minimum value occurred during the flood season, and the maximum value occurred in the dry season. The DOC/POC ratio in 83% of the samples was more than 1, indicating that DOC was the dominant form of organic carbon (Xia et al., 2011).

The estimated annual loads of DOC and POC were 1.7 Mt/yr and 1.3 Mt/yr, respectively, which compared well with the 2009 annual flux estimated by Wang et al. (2012) (see Table 1). The decrease in the POC load from 8.5 Mt/yr in 1958 to 1984 (Wang et al., 1989) to 2.3 Mt/yr in 1998 (Duan et al., 2008) to 1.3 Mt/yr in 2013 is striking and can be attributed to the damming of the Yangtze. Uncertainties of flux estimations may be large, as POC loads depend on the loads of suspended particles, which show seasonal variability and hence depend on the sampling frequency. The extremely high DOC load of 5.4 Mt/yr in 1998 to 1999 was caused by an unusually severe flood during this time.

3.2. Household chemicals and pharmaceuticals

The following household chemicals were targeted in the filtered samples: 2-Naphtalenesulfonic acid, benzotriazole, 4-/5-methyl-benzotriazole, acesulfam, caffeine, N,N-Diethyl-3-methylbenzamide (DEET) and sucralose. Only caffeine (15–157 ng/L), sucralose (120–430 ng/L), DEET (4–16 ng/L), benzotriazole (19–67 ng/L), 4-/5-methyl-benzotriazole (7–29 ng/L), and climbazole (3–4 ng/L) were detected in some of the samples (see Fig. 3 and Table S1). The sweetener sucralose occurred in the highest concentration (an average of 217 ng/L) out of all household chemicals screened in this study. The high sucralose concentrations come from the diet of the people in the south of China, who prefer sweetened food. The persistence of sucralose in wastewater treatment plants (WWTPs) and the aquatic environment (Mead et al., 2009; Torres et al., 2011) was another reason for the high sucralose in the river. The load of sucralose in the Yangtze River amounted to 169.1 t/yr, representing 85% of the sucralose consumption in China (200 t/yr).

3.2.1. Sucralose

The artificial sweetener sucralose has previously been used as an indicator of domestic wastewater loading to surface waters. Heeb et al. (2012) reported an average sucralose concentration of 2.6 µg/L in WWTP effluents in Beijing, China. Recently, Tollefsen et al. (2012) reviewed published studies for the presence, fate, and effects of sucralose in the aquatic environment and estimated an average concentration of sucralose in wastewater in the range of 0.4 to 11 µg/L (and up to 119 µg/L). Assuming that the sucralose level in the sewage effluents of southern China was in the range of around 10 µg/L, our determined total annual load of 170 t of sucralose in the Yangtze River would correspond to a wastewater discharge of about 47 Mio m^3/d (or 17 billion m^3/year) of wastewater into the Yangtze River. This signifies that during the dry season, up to 5% of the Yangtze water consists of sewage. Using the number for per-capita water consumption in southern China of 180 L per day in 2010 reported by the National Bureau of Statistics (NBSC, 2010), we estimate that the Yangtze transports the sewage of about 270 million people. This estimation could be improved if sewage effluent concentrations were known. However, even though the present assumption is very rough, it results in an estimate for the population that lies in the same order of magnitude as the estimated population in the catchment (approximately 400 million).

3.2.2. Caffeine

The concentration range of caffeine in the Yangtze was 15 to 157 ng/L (Fig. 3), which was higher than the Mississippi River (0–38 ng/L; Zhang et al., 2007) and lower than rivers downstream of Beijing (29–5000 ng/L; Heeb et al., 2012) and the rivers of the Pearl River Delta (15–865 ng/L, Yang et al., 2013). Caffeine is removed efficiently by WWTPs (more than 85%) and can be degraded in the natural environment (Buerge et al., 2003; Sui et al., 2010). Therefore, caffeine can be used as a molecular tracer for the efficiency of WWTPs (Buerge et al., 2003; Standley et al., 2000). Hence, higher loads of caffeine in the river may indicate higher wastewater input and/or lower wastewater treatment efficiency. During our 14-months of monitoring the Yangtze, the monthly load of caffeine was higher during the wet season (i.e., June and July; Fig. 4), indicating either that the capacity of WWTPs were exceeded due to precipitation or that the amount and type of caffeine-containing beverages consumed depended on the season (e.g., tea with varying caffeine levels).

3.2.3. Benzotriazole

Benzotriazole (BT) and 4-/5-methyl-benzotriazole (MBT) are “emerging contaminants” that are used as corrosion inhibitors in WWTPs’ effluent and receiving waters (Voutsa et al., 2006; Giger et al., 2006; Reemtsma et al., 2010). They can only be partly removed from wastewater during the treatment process (23%–85%) and have high stability in surface waters (Giger et al., 2006; Reemtsma et al., 2010; Kahle et al., 2009; Heeb et al., 2012). In this study, BT and MBT occurred in the Yangtze River in concentration ranges of 19 to 67 ng/L and 7 to 29 ng/L, respectively (Fig. 3). Temporally, the highest loads of BT and MBT were measured in August 2009 (7.2 t/month) and May 2010 (1.8 t/month) (Fig. S1). Usually, winter temperatures in southern China stay above zero degrees, resulting in a much smaller consumption of aircraft de-icing fluid and motor vehicle antifreeze, which both contain BT and MBT, as compared to northern China and Europe. Thus, BT and MBT in the Yangtze was possibly mainly influenced by wastewater input in the basin.

3.2.4. Pharmaceuticals

We also investigated the occurrence and loads of 43 pharmaceutical substances, including antibiotics, *β*-blockers, analgetics, lipid regulators, and antiepileptic drugs. Some commonly consumed antibiotics and analgesics in China, including sulfamethoxazole, sulfadiazine, sulfamethazine, erythromycin, 4-acetamidoantipyrin (the metabolite of metamizole), phenazone, and metronidazole, were detected in

most samples (Fig. 5). Fluconazole (dermatologicals), sulfamethazine, sulfamethoxazole, phenazone, 4-acetamidoantipyrin (metabolite of metamizole), and sulfadiazine were compounds with high detection frequency (more than 85%). Other pharmaceuticals, such as atonolol, metoprolol, and sotalol (*β*-blockers), bezafibrate (a lipid regulator), hydrochlorothiazid (a an diuretic), lidocaine (anesthetic), mefenamic acid (an anti-inflammatory), and sulfapyridine and trimetoprim (anti-infectives) were not detected or were below their limit of quantification (LOQ). As can be seen in Fig. 5, the concentrations of detected pharmaceuticals in most samples were below 50 ng/L except for the antibiotics metronidazole and erythromycin (and $-H_2O$). The concentrations of metronidazole ranged from 7 ng/L to 224 ng/L with the average value of 74 ng/L, and the concentrations of erythromycin (and $-H_2O$) ranged from 21 ng/L to 217 ng/L with an average value of 81 ng/L (Figure 5, Table S1).

Very few analyses of pharmaceuticals have been published for the Yangtze River to date. Yang et al. (2011) reported the detection of selected pharmaceuticals, and Yan et al. (2013) reported the occurrence and distribution of 20 antibiotics in the surface water of the Yangtze Estuary. Yang et al. (2011) found sulfamethoxazole, tamoxifen, and indomethacine with concentrations of more than 100 ng/L. The concentrations of sulfamethoxazole and carbamazepine detected in this study at Datong station were approximately 10 times lower than the concentrations further downstream in the estuary (Yang et al., 2011). Compared with Yang et al.'s results, the concentrations of sulfonamides (sulfadiazine, sulfamethoxazole, and sulfamethazine) in our study were 1 to 3 times lower. This supports the assumption of Yang et al. (2011) that WWTPs are the main sources of pharmaceuticals in the Yangtze River estuary. Hence, estimating the pollutant load is necessary for the assessment of the water quality in the estuary, which receives both the input from the river and the discharge from WWTPs along the coastal area.

Pharmaceuticals in the water samples displayed seasonal variations during the 14 months of our monitoring period (Fig. 6). The anti-infective sulfamethoxazole (SFMX) had higher concentrations and loads in July and September (the wet season) of 2009 than in any other months (Fig. 6). Higher concentrations and loads of pharmaceuticals were also reported by Radke et al. (2010) in a German river during precipitation events and by Tamtam et al. (2008). The authors attributed the concentration peaks during precipitation events to the accelerated displacement of wastewater from the sewer system and the WWTP into the river at the beginning of a rain event and the decreased removal

efficiency in the WWTP during periods of increased wastewater flow (Radke et al., 2010). This could explain the higher concentrations and loads of SFMX and sulfadiazine in the wet season in the Yangtze, although sampling with higher frequency would be necessary to study the dynamics and attenuation of the pharmaceuticals. In Yan's study (2013), higher concentrations of sulfonamides were found in January compared to other seasons in the Yangtze estuary. The authors attributed this feature to the low flow diluting the WWTPs inputs and the cold temperature inhibiting microbial degradation in January. In this study, some of the detected pharmaceuticals, including N4-acetylsulfamethoxazole (a metabolite of SFMX), diazepam, metronidazol, and diclofenac, showed higher concentrations in the winter. For example, diazepam was not detected in the summer, while its concentration was 63 ng/L in January 2010. In addition, sulfamethazine (SFMZ), 4-acetamidoantipyrine, and erythromycin (and $-H_2O$) showed higher concentrations and loads in the autumn and spring (Fig. 6).

3.3. PAHs in water and suspended particulate matter

PAHs are primarily produced by incomplete combustion of wood, petroleum, and coal and are emitted from coke ovens, automobile exhaust, or heat and power generation. Some PAH compounds have been found to be mutagenic and carcinogenic (Harvey, 1991; Nielsen, 1996). We detected a total of 16 PAHs ranging from 130 to 380 ng/L in water (mainly Nap, Ace, Fl, and Phe) and from 1830 to 9150 ng/g in SPM with the predominance of Fl, Ace, Fluo, and Pyr (Table 2, Fig. S2).

PAH concentrations have been previously reported in different sections of the Yangtze (Table 2), such as 240 to 620 ng/L in the Wuhan section in July 2005 (Feng et al., 2007a), an average of 5260 ng/L at Nanjing in January 2007 (Wu et al., 2009), and 10 to 3580 ng/L in the Jiangsu section (He et al., 2011). The level of dissolved PAHs from our study at Datong station (located right between the Wuhan and the Nanjing section) ranged 320 to 630 ng/L and was about one order of magnitude lower compared to the data from Nanjing from 2005 and 2007 (Table 2). The comparison among individual PAHs had similar results to the comparison among total PAHs. This may be explained by the three following factors. Firstly, the anthropogenic discharge of PAHs from big cities is generally larger than that from areas with a lower population density (Xu et al., 2006). The population density of Anhui province where the Datong station is located is only half of the populations of the Jiangsu and Hubei provinces (Table S2). Secondly, the percentage of households connected to WWTPs in Anhui province (91%) is

higher than in other provinces of the Yangtze Basin (Table S2). Lastly, resuspension of PAHs downstream of the Datong station might be influenced by the tide (Feng et al., 2007b) and could thus increase the PAH concentrations in the surface water.

The loads of both dissolved and particulate PAHs were higher in the wet season (9.3–12.0 and 9.2–12.9 t/month, respectively) than in the dry season (3.7–6.3 and 3.6–6.7 t/month, respectively) (Fig. 7). The flux of PAHs may have been increased due to higher atmospheric inputs from wet deposition and runoff in the wet season compared to the dry season, although the concentration levels were slightly decreased due to dilution in the wet season (Fig. 7). For some PAHs, such as phenathrene, which also has a biogenic source, the concentration was higher in the early wet season than the other seasons (Fig. 7) and could be also caused by runoff from soil. Due to the high flow rate, the annual flux of the total 16 PAHs at Datong station was some 370 tons. This corresponds to 30% of all PAHs emitted in Anhui province, or 4% of the whole Yangtze Basin (these data were compiled by Xu et al., 2006), if all emissions in 2010 were equal to the 2004 emissions.

3.4. Pesticides

A total of 51 compounds, including 2,4-D, atrazine, bentazon, diuron, metazochlor, terbutryn, and azoxystrobin, were quantified in the Yangtze water samples. Only eight were detected with an LOQ of 1 to 10 ng/L (Fig. 8). Our results were similar to the findings by Müller et al. (2008). The mean concentrations of pesticides in most of the samples analyzed in this study were below 30 ng/L except for atrazine-hydroxy (HA; a metabolite of atrazine) and carbendazim, with average concentrations of 45 ng/L and 43 ng/L, respectively. HA occurred in the samples with a maximum concentration of 284 ng/L in January 2010 and a minimum concentration close to the LOQ (2 ng/L). The concentrations were similar to those reported by Gfrerer et al. (2002), who detected atrazine (1.0-18.3 ng/L) without metabolites (the authors only analyzed atrazine-desethyl and atrazine-desisopropyl, not HA) in surface water from the Yangtze, peaking in May. As the main crop type in the Yangtze basin is rice (66% of all crops, Table S2), which is not tolerant to atrazine like corn, the levels of atrazine and its metabolites were generally much lower than those in other large rivers of the world (Clark et al., 1999; Liu et al., 2002).

The loads of most pesticides, such as atrazine, carbendazim, metolachlor, prometryn, and imidacloprid, were higher in summer (Fig. 9) as a result of higher application. The highest combined

monthly loads of carbedazim, atrazine, prometryn, metolachlor, and imidacloprid were 5730, 2420, 1710, 1770 and 1350 kg/month in August 2009, June 2010, July 2009, May 2010, and August 2009, respectively. In addition, the load of metolachlor was also high in October 2009 (1740 kg/month) when the water discharge was much lower than in summer. The load of atrazine and its metabolite HA also fluctuated in autumn and winter when the river water flow was the lowest of the studied period. This pattern suggests additional use of atrazine and metolochlor during the autumn and winter, which may be due to pesticide use for winter crops (wheat) and vegetables.

The occurrence of atrazine degradation products may be related to several factors, such as the season, the transformation products formed in the soil, or dilution by runoff. Obviously, HA was the predominant metabolite present at Datong station. Atrazine-desethyl (DEA) was detected in only 3 samples at levels between 4 to 12 ng/L, and atrazine-desisopropyl was detected in only one sample (see Table S1). DEA has been reported to be one of the most prevalent degradation products in bulk soil (Panshin et al., 2000), and its prevalence in rivers mainly happens shortly after the application of atrazine. This may explain the low detection frequency of DEA in this study. The prevalence of HA was also found in other watersheds like Missouri streams, although it is the least mobile degradation product (Lerch et al., 1995, 1998). The high winter concentration of HA in the Yangtze River was possibly caused by enhanced direct photolysis of atrazine due to lower water turbidity in the winter months (Fig. S3). This phenomenon was also observed by Steen et al. (2000) in the Scheldt estuary.

3.5. Comparison of pollutant loads with other large rivers

As the discharge of the Yangtze (900 km^3/yr) is the third largest in the world after the Amazon (6930 km^3/yr) and Congo Rivers (1410 km^3/yr), the loads of micropollutants are large in spite of low concentration levels (Table S1). The total annual loads of organic micropollutants in the lower Yangtze at Datong amounted to approximately 890 t, consisting of 273 t household chemicals, 152 t pharmaceuticals and metabolites, 98 t pesticides and metabolites, and 370 t PAHs (see Appendix 1). It should be noted that attenuation processes, including volatilization, sorption, degradation, and transformation, could lead to the natural removal of organic pollutants in the river (Gioia et al., 2012). These attenuation processes could moderate the organic pollutants inputs from the Yangtze River to the East Sea.

About 60% of the load of household chemicals in the Yangtze consisted of the sweetener sucralose. The per-capita load of sucralose would be 0.77 g/year based on the assumed concentration in wastewater (10 µg/L) and wastewater discharge (47 Mio m^3/d) in the Yangtze Basin. This result was smaller compared to the United States, where sucralose is used more frequently and concentrations of sucralose in WWTP effluents can reach up to 27 µg/L (Oppenheimer et al., 2011) and 120 µg/L (Mead et al., 2009).

Antibiotics (110 t/yr) contributed 74% of the load of pharmaceuticals (152 t/yr) in the Yangtze. In comparison, antibiotics in the Haihe Basin downstream Beijing City (0.74 t/yr) contributed only 20% of the pharmaceuticals and metabolites loads (Heeb et al., 2012).

Carbendazim and atrazine, including its metabolites, accounted for 81% of the load of pesticides. As discussed above, due to the different crop patterns, the load of atrazine and its metabolites (43 t/yr) was considerably lower than in European and American rivers in the 1990s, when large amounts of herbicides were applied on field crops; e.g., the Mississippi River (640 t/yr, Clark et al., 1999), which has a water discharge rate that is similar to the Yangtze River.

4. Conclusions

Based on our 14-month survey, we present the first comprehensive assessment of concentrations and annual loads of a broad range of micropollutants in the Yangtze River. Most of the investigated compounds were below concentrations of 200 ng/L, mainly due to the enormous dilution by the large water discharge. However, the pollutant loads are large (Appendix 1), and they may have significant effects on the ecosystem of the receiving shelf area of the East China Sea. The loads of most pesticides, anti-infectives, and PAHs were higher in the wet than in the dry season. This was attributed to increased agricultural application of chemicals in the summer, elevated water discharge through the sewer systems and WWTPs 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 state-of-the-art analytical methods used in this study allowed for the quantification of 268 compounds. However, one has to keep in mind that many more are likely to be present in the river as thousands of organic chemicals are used in almost any application and product of the modern lifestyle. We found that the huge load of 8,200 t/day of organic carbon, when combined with the nutrient

discharge of 4,400 t/day of nitrogen and 290 t/day of phosphorus (Müller et al., 2012), significantly contributes to the eutrophication and algal blooms along the coast of the East China Sea.

The investigated cross-section at Datong proved to be an ideal study site to assess the integral discharge of pollutants from the 400 million inhabitants living in the Yangtze Basin. This is particularly due to the fact that river is not yet tidal at Datong and that the river water is well mixed because the last 50-km river section upstream Datong is barely populated and wastewater discharge to the river is therefore negligible. We hence suggest that the authorities consider this location in their planning to expand the Chinese river monitoring network with advanced chemical and physical analyses.

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Figure captions:

Figure 1. Map of the Yangtze River and its catchment. The middle right map shows the sampling location across the river near Datong, and the bottom map illustrates the three sampling sites across the river (Y1, Y2, Y3).

Figure 2. (**a**) Monthly river water discharge, precipitation in Anqing (60 km upstream of Datong), and load of suspended particulate matter (SPM); (**b**) Monthly dissolved organic carbon (DOC) and particulate organic carbon (POC) concentrations and fluxes at Datong station from May 2009 to June 2010.

Figure 3. Concentrations of anthropogenic substances in the Yangtze River at Datong station (only the results higher than LOQ are plotted). Boxes indicate the range between the 25th and 75th percentiles. The whiskers extend from the edge of the box to the minimum and maximum data values. The horizontal line and the square inside indicate the median value and the mean value, respectively. Additional data are provided in Table S1.

Figure 4. Seasonal trend of concentrations and cumulative discharge of selected household chemicals (t-cumul) and of water (Q-cumul) in the lower Yangtze River at Datong. For compounds with a detection frequency >50%, the LOQ-value was applied for results <LOQ, while for compounds with a detection frequency <50%, LOQ/2 was applied for results <LOQ. The inserted values (if results <LOQ) are depicted as filled circles. For samples where quantification was not feasible due to matrix interference, values were interpolated and are shown as marker asterisks. Additional data are provided in Appendix 1.

Figure 5. Concentrations of pharmaceuticals and other anthropogenic substances in the Yangtze River at Datong station (only the results higher than LOQ are plotted). The statistical definition of the boxes is described in the caption of Figure 3. The values at the bottom of the graph show the percentage of positive findings among all analyzed samples. Additional data are provided in Table S1.

Figure 6. Seasonal variation of concentrations and the cumulative discharge of selected pharmaceuticals (t-cumul) and of water (Q-cumul) in the lower Yangtze River at Datong. For

compounds with a detection frequency >50%, the LOQ-value was applied for results <LOQ, while for compounds with a detection frequency <50%, LOQ/2 was applied for results <LOQ. The inserted values (if results <LOQ) are depicted as filled circles. For samples where quantification was not feasible due to matrix interference, values were interpolated and are depicted as marker asterisks. Additional data are provided in Appendix 1.

Figure 7. Seasonal variation of concentrations and cumulative discharge of selected PAHs (t-cumul) and of water (Q-cumul) in the lower Yangtze River at Datong. Additional data are provided in Appendix 1.

Figure 8. Concentrations of pesticides and metabolites in the Yangtze River at Datong station (only results >LOQ are plotted). The statistical definition of the boxes is described in the caption of Figure 3. The values at the bottom of the graph show the percentage of positive findings among all analyzed samples. Additional data are provided in Table S1.

Figure 9. Seasonal variation of concentrations and cumulative discharge of selected pesticides (t-cumul) and of water (Q-cumul) in the lower Yangtze River at Datong. For compounds with a detection frequency >50%, the LOQ-value was applied for results <LOQ, while for compounds with a detection frequency <50%, LOQ/2 was applied for results <LOQ. The inserted values (if results <LOQ) are depicted as filled circles. For samples where quantification was not feasible due to matrix interference, values were interpolated and are depicted as marker asterisks. Additional data are provided in Appendix 1.

Figure 1: (color on the web, b/w in print)

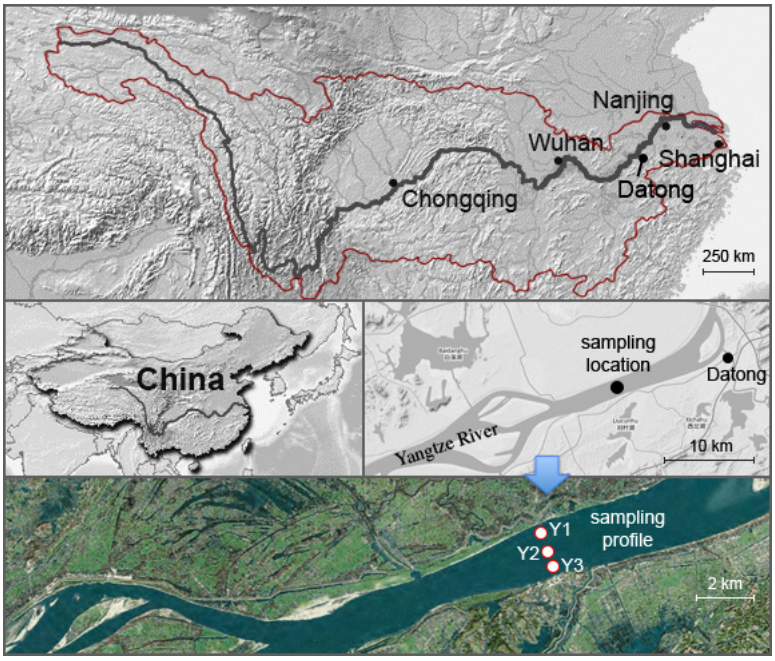
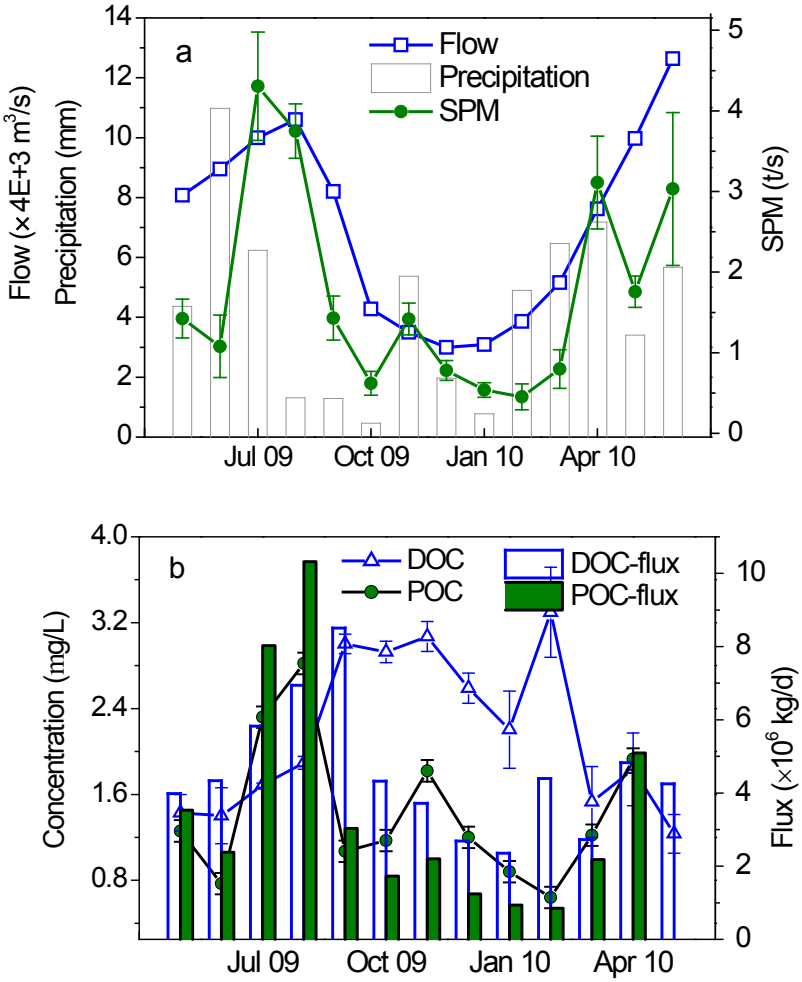


Figure 2: (color on the web, b/w in print)



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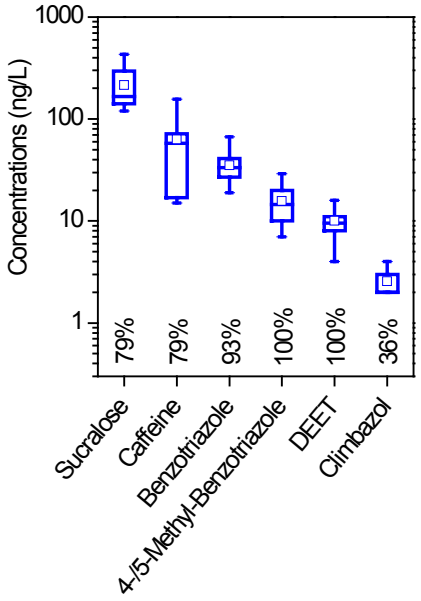

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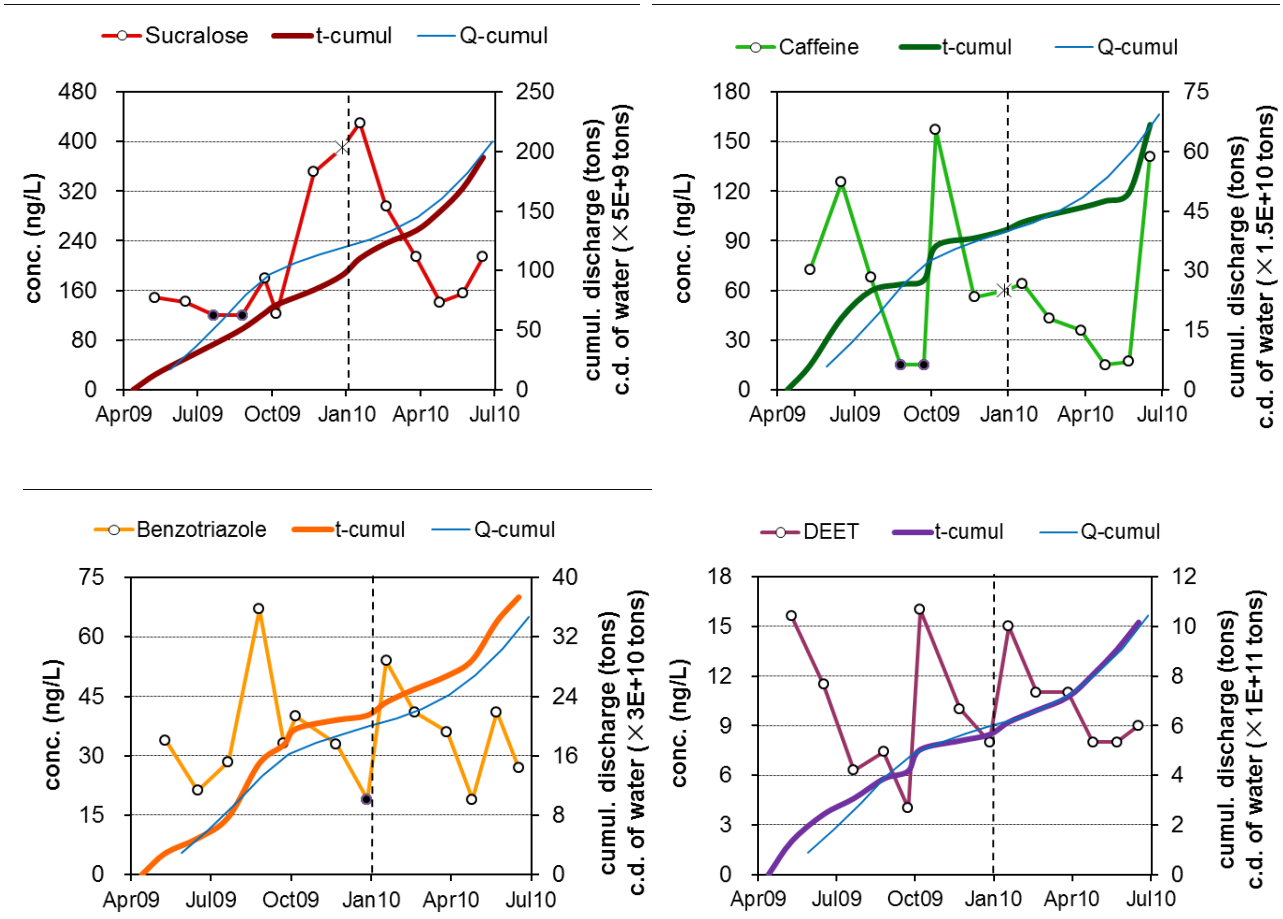

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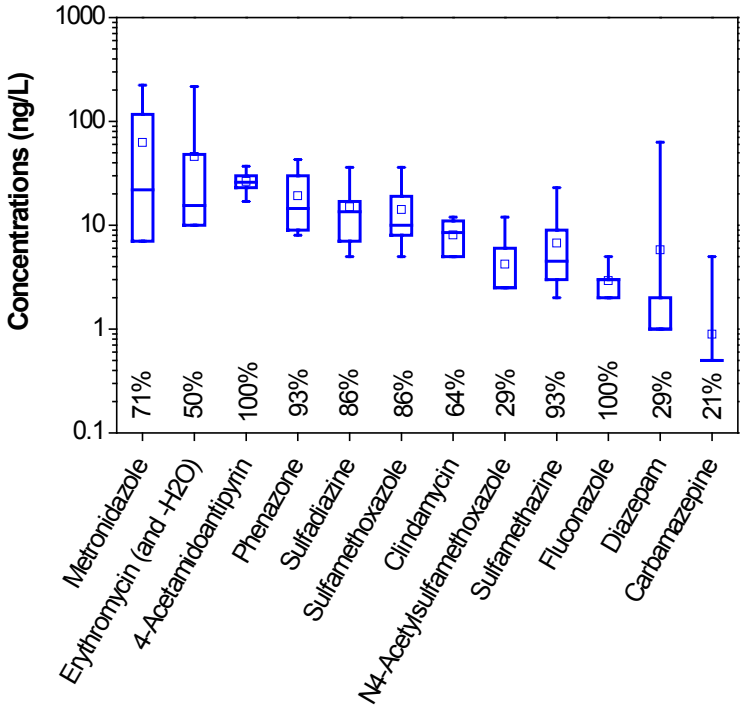

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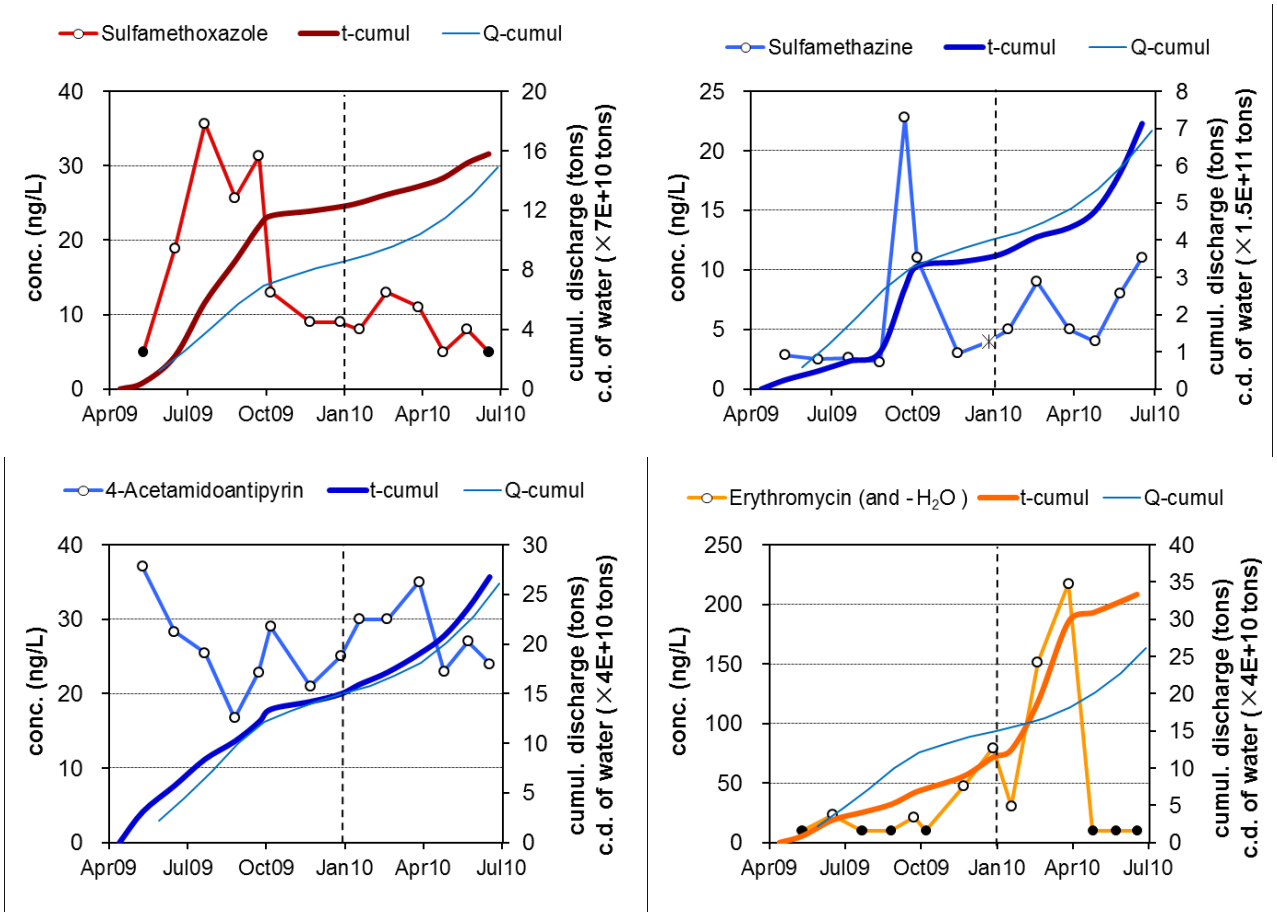

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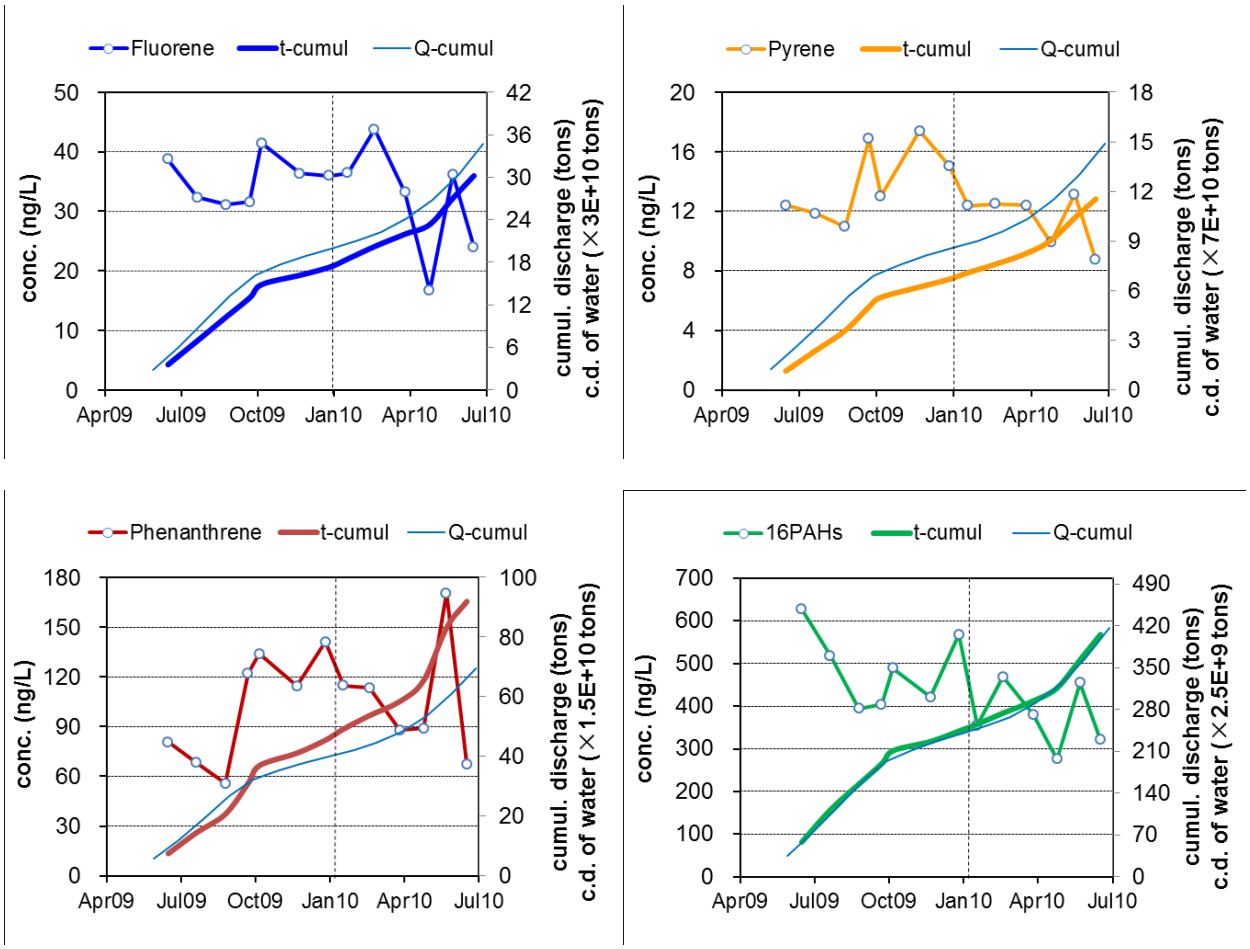

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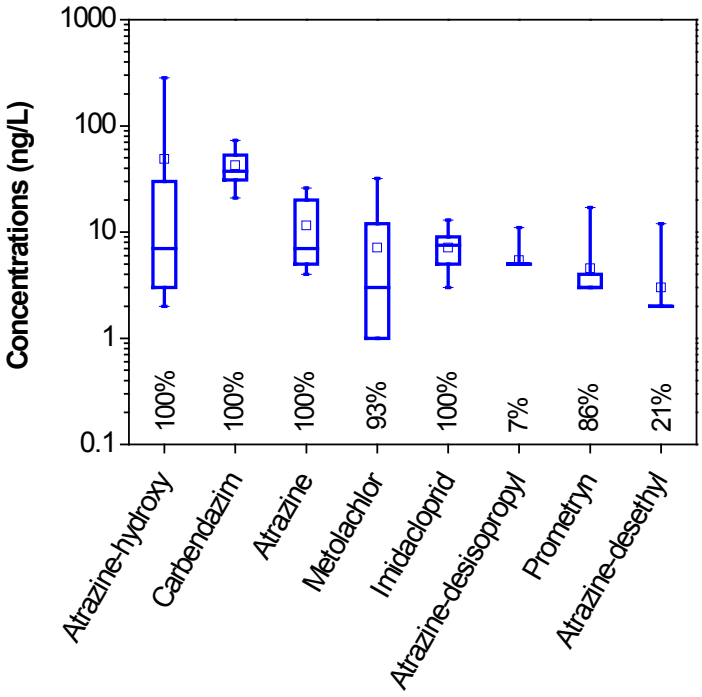

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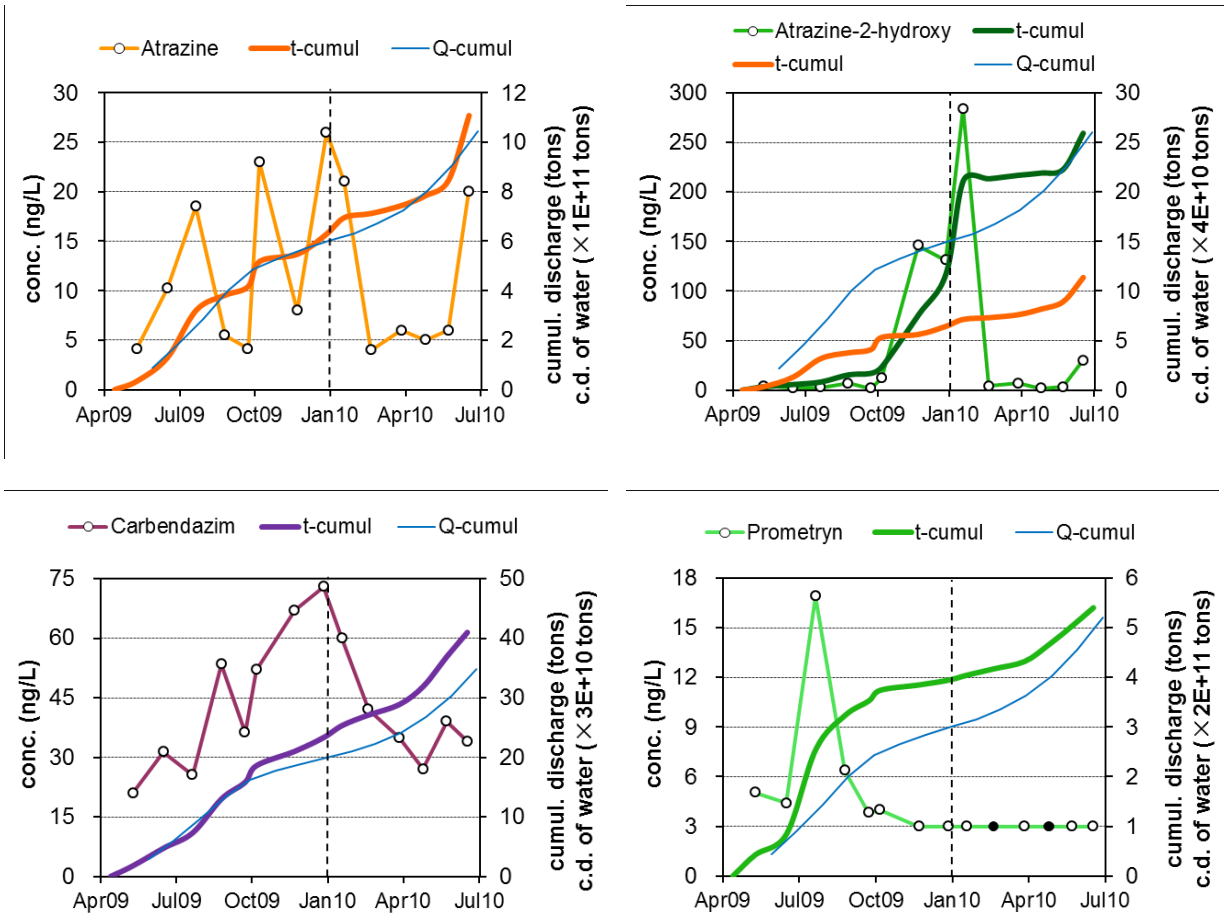

Table 1. Dissolved and particulate annual loads of organic carbon in the Yangtze River.

Sampling site	Distance to estuary	Time	Water discharge	DOC	POC	DOC load	POC load	Reference
	km		$\times 10^3$ m^3/s	mg/L	mg/L	kt/yr	kt/yr	
Datong Station	525	1958-1984		3.4		2980	8500	Wang et al., 1989
Inner estuary		Jan.-Jul. 1986	28			1800	4500-6000	Cauwet et al., 1993
Nantong	188	1997 (bimonthly)	25-31	1.26		900	2200	Wu et al., 2007
Datong Station	525	1998-1999 (bimonthly)	10-75	2.6-6.1	0.4-3.0	5405	2279	Duan et al., 2008
Datong Station	525	2009 (monthly)	12-40	1.6-2.7	0.6-3.6	1580	1520	Wang et al., 2012
Datong Station	525	2009-2010 (monthly)	12-51	0.9-3.1	0.6-2.8	1660	1270	this study

Table 2. Concentrations of PAHs in water (ng/L) and SPM (ng/g) of the Yangtze River.

location	sampling medium	sampling time	Concentrations (ng/L, ng/g)	Reference
Wuhan reach	water	Jul. 2005	874 (median)	Feng et al. 2007a
Datong Station	water	2009-2010	130-380	**this study**
Nanjing reach	water + SPM	Jan. 2007	5260 (average)	Wu et al. 2009
Jiangsu reach	water	Sep. 2004;Jan. 2005	10-3580	He et al. 2011
River	SPM	Nov. 2006	<700-48580	Beat et al. 2008
Wuhan reach	sediments	Jul. 2005	30-4000	Feng et al. 2007a
Wuhan reach	sediments	Dec. 2005	70-1210	Feng et al. 2007a
Wuhan reach	SPM	Jul. 2005	4290-5000	Feng et al. 2007a
Wuhan reach	SPM	Dec. 2005	950-15350	Feng et al. 2007a
Datong Station	SPM	May 2009-Jun. 2010	1830-9150	**this study**
Estuary	sediment core	Sep. 1996	80-11740	Liu et al. 2000
Estuary	sediment core	Jul. 1998	10-2370	Xu et al. 2001
Estuary	sediments	Apr. 2004	850-620	Hui et al. 2009

[a] Surface water samples without filtration were extracted for PAHs using liquid–liquid extraction.

Appendix 1. Annual loads of micropollutants determined in the lower Yangtze River at Datong (from July 2009 to June 2010). For compounds with detection frequency >50%, the LOQ-value was applied for the calculation of loads, while for compounds with detection frequency <50%, LOQ/2 was applied. For samples where quantification was not feasible due to matrix interference, values were interpolated and used for load calculation.

Pharmaceuticals	**annual load (t/yr)**	**PAHs**	**annual load (t/yr)**
Sulfamethoxazole	13.6	Nap	168.8
N4-Acetylsulfamethoxazole	3.2	Acy	4.3
Clindamycin	6.6	Ace	10.3
Sulfadiazine	12.5	Fl	27.5
Sulfamethazine	6.6	Phe	84.5
Erythromycin (and -H_2O)	30.3	Ant	7.1
4-Acetamidoantipyrine	22.0	Fluo	14.2
Phenazone	13.2	Pyrene	10.6
Fluconazole	2.3	BaA	4.7
Diazepam	3.1	Chry	7.7
Metronidazole	37.5	BbF	3.8
Carbamazepine	0.7	BkF	2.2
		BaP	4.2
		Ind	4.9
		DBA	1.9
		BghiP	5.5
Total	**151.7**		**368.9**

Household chemicals	**annual load (t/yr)**	**Pesticides**	**annual load (t/yr)**
Caffeine	48.7	Carbendazim	36.2
Sucralose	169.1	Atrazine	10.0
Benzotriazole	32.5	Prometryn	4.6
4-/5-Methyl-Benzotriazole	12.4	Metolachlor	7.0
DEET	7.7	Atrazine-hydroxy	25.4
Climbazole	1.8	Atrazine-desethyl	2.6
		Atrazine-desisopropyl	4.8
		Imidacloprid	6.9
Total	**272.7**		**97.5**

Appendix A. Supplementary data

This appendix includes four figures and two tables showing additional parameters determined for the Yangtze River at the Datong Station during the 14-month study period; i.e., the seasonal loads of individual household chemicals (Fig. S1), seasonal concentrations of dissolved and particulate polycyclic aromatic hydrocarbons (PAHs) (Fig. S2), fluxes of dissolved and particulate PAHs (Fig. S3), dissolved oxygen and suspended sediment (Fig. S4), and concentrations and detected frequency of individual micropollutants (Table S1). Statistical data on population, wastewater discharge and treatment, and crops patterns in the Yangtze basin are provided in Table S2. This supplementary data can be found online at http://dx.doi.org/10.1016/j.scitotenv.xxxx.yy.zzz.

Supplementary data

Table S1. Detected frequency and concentrations of pesticides, pharmaceuticals and their metabolites, and household and industrial chemicals in the Yangtze River at Datong Station (May 2009 to June 2010).

	LOQ [1)]	Recovery [2)]	Frequency of detection	Concentration [3)]			
				min	max	mean	median
Pesticides and metabolites	[ng/L]	[%]	[%]	[ng/L]			
Atrazine*	4	87	100	4	26	12	7
*Atrazine-hydroxy**	*2*	*87*	*100*	*2*	*284*	*45*	*5*
*Atrazine-desethyl**	*4*	*100*	*21*	*4*	*12*	*7*	*4*
*Atrazine-desisopropyl**	*10*	*98*	*7*	*11*	*11*	*11*	*11*
Carbendazim*	10	109	100	21	73	43	38
Imidacloprid	3	71	100	3	13	7	7
Metolachlor*	1	98	93	1	32	8	4
Prometryn	3	81	86	3	17	5	3
Household and industrial chemicals							
4-/5-Methyl-Benzotriazole	5	93	100	7	29	16	15
Benzotriazole*	19	86	93	19	67	37	34
Caffeine*	15	86	79	15	157	72	64
Climbazol	3	87	36	3	4	4	4
Diethyltoluamide (DEET)*	4	102	100	4	16	10	10
Sucralose*	120	119	79	123	430	217	179
Pharmaceuticals and metabolites							
4-Acetamidoantipyrin	*10*	*87*	*100*	*17*	*37*	*26*	*26*
Carbamazepine*	1	95	21	1	5	2	1
Clindamycin	5	88	64	5	12	10	11
Diazepam*	2	102	29	2	63	18	3
Erythromycin (and -H_2O)*	10	92	50	21	217	81	48
Fluconazole*	2	102	100	2	5	3	3
Metronidazole	7	65	71	7	224	74	35
Phenazone*	8	95	93	9	43	20	17
Sulfadiazine*	5	101	86	6	36	16	14
Sulfamethoxazole*	5	96	86	5	36	16	12
*N4-Acetylsulfamethoxazole**	*5*	*116*	*29*	*6*	*12*	*9*	*8*
Sulfamethazine*	2	96	93	2	23	7	5

* structurally identical isotope labeled internal standard used for quantification; for all other compounds the isotope labeled standards with the nearest retention time was used

[1)] limit of quantification was determined from the analyte concentration producing at least a signal-to-noise ratio of 10:1 in the matrix sample

[2)] recoveries were calculated from Yangtze river samples (N=3) spiked with analytes concentration of 200 ng/L considering the analyte background of the unspiked sample

[3)] only detections > LOQ are considered for the calculation of min, max, mean, and median

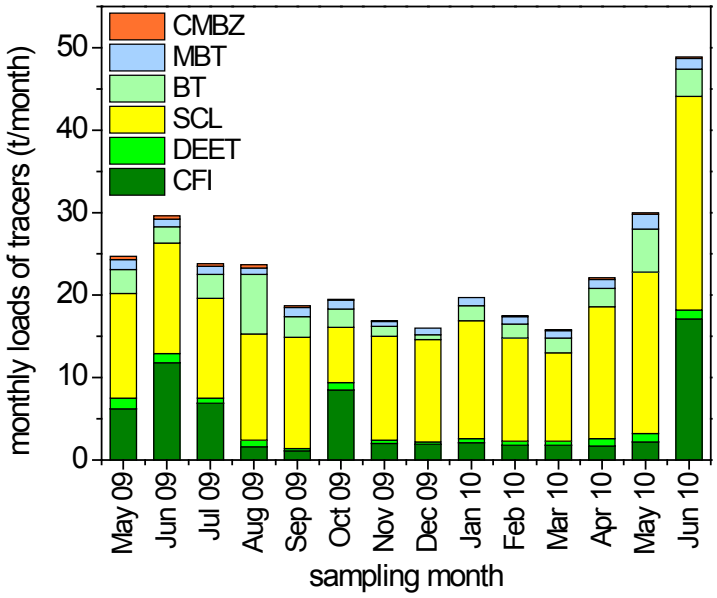

Figure S1. Seasonal loads of caffeine (CFI), sucralose (SCL), benzotriazole (BT), 4-/5-methyl-benzotriazole (MBT), climbazol (CMBZ), and DEET in the Yangtze River at Datong.

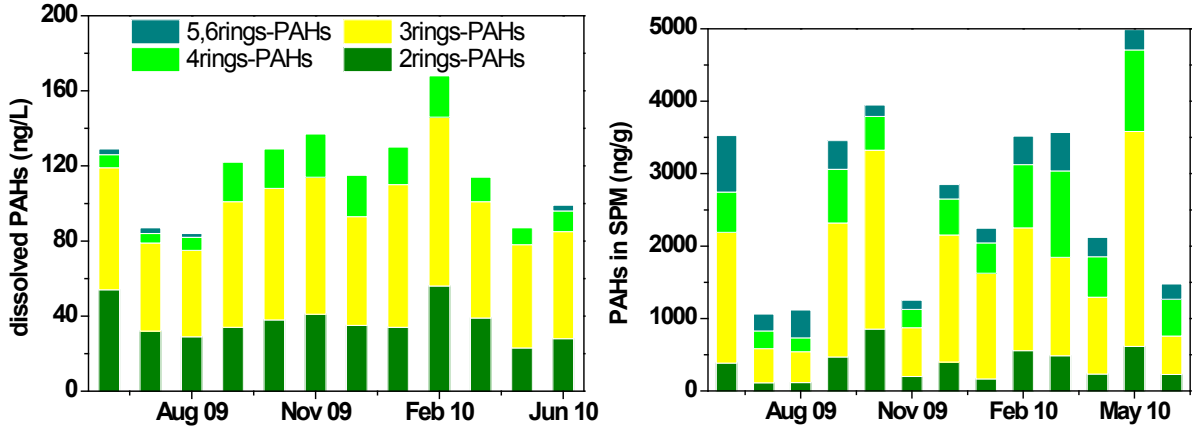

Figure S2. Concentrations of dissolved and particulate polycyclic aromatic hydrocarbons (PAHs) of different aromatic rings.

Table S2. Population, wastewater discharge and treatment, and crop patterns in the Yangtze Basin

Main Provinces in the Yangtze Basin	population				wastewater discharge and treatment			predominant crops (percentage %)
	Total [x10^6]	urban (% of total)	rural (% of total)	population density (km^{-2})	municipal wastewater [m^3/year]	treatment percentage (%)	predominant treatment technology in WWTPs	
Sichuan (Chongqing)	111	4.6%	22.4%	197	2.55E+09	70	oxidation ditch (24.5%), CASS(19.3%), A/A/O(14.6%), BAF(8.9%), activated sludge(7.3%), constructed wetland(6.8%)	*rice (46.9%), corn(20.5%), tuber (17.2%), wheat(11.0%)*
Hunan	63	2.8%	12.4%	296	1.64E+09	36	oxidation ditch(44.6%), A/A/O(15.8%), SBR(11.9%), activated sludge(6.9%)	rice (88.8%), corn(5.5%)
Hubei	57	3.6%	10.3%	309	1.76E+09	74	oxidation ditch(39.3%), A/A/O(25%), A/O(9.5%), activated sludge(9.5%)	rice(68.9%), wheat(14.4%), corn(10.6%)
Jiangxi	40	2.0%	7.8%	241	8.81E+08	69	oxidation ditch(>80%)	rice(95.2%)
Jiangsu	32	2.6%	5.0%	296	-	-	-	rice(55.8%), wheat(31.1%), corn(6.7%)
Guizhou	26	1.3%	5.0%	147	4.67E+08	66	oxidation ditch(25.8%), activated sludge(16.1%), SBR(16.1%), A/O(16.1%)	rice(38.8%), corn(34.7%), potato(17.9%)
Anhui	24	1.3%	4.5%	168	1.14E+09	91	oxidation ditch(72%), A/A/O(10.3%)	rice(45.8%), wheat(38.3%), corn(9.9%)
Yunnan	13	0.6%	2.6%	34	6.11E+08	85	SBR(35.5%), oxidation ditch(29.0%), A/A/O(16.1%)	rice(40.3%), corn(34.4%), potato(10.9%)
Shanghai	13	2.2%	1.0%	1604	1.89E+09	91	A/O(28.2%), oxidation ditch(25.6), A/A/O(23.1%)	rice(74%), wheat(18.2%)
Total	**412**	**22%**	**78%**					

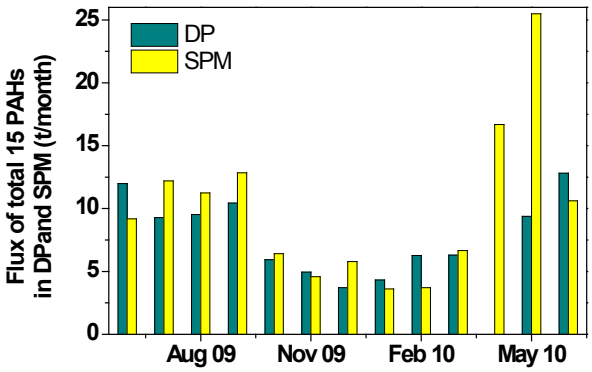

Figure S3. Flux of dissolved and particulate polycyclic aromatic hydrocarbons (PAHs) in the Yangtze River at Datong.

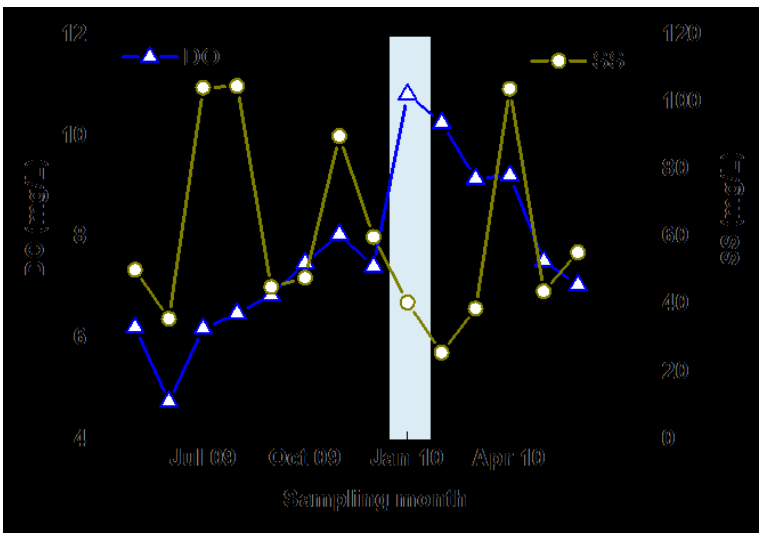

Figure S4. Dissolved oxygen (DO) and suspended sediment (SS) levels in the Yangtze River at Datong Station (May 2009 to June 2010).