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RESEARCH ARTICLE

Depth profile of persistent and emerging organic pollutants upstream of the Three Gorges Dam gathered in 2012/2013

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Abstract Persistent and emerging organic pollutants were sampled in September 2012 and 2013 at a sampling site in front of the Three Gorges Dam near Maoping (China) in a water depth between 11 and 61 m to generate a depth profile of analytes. A novel compact water sampling system with self-packed glass cartridges was employed for the on-site enrichment of approximately 300 L of water per sample to enable the detection of low analytes levels in the picogram per liter-scale in the large water body. The overall performance of the sampling system was acceptable for the qualitative detection of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), perfluoroalkylic acids (PFAAs), pharmaceutical residues and polar pesticides. Strongly particle-associated analytes like PAHs and PCBs resided mainly in the glass wool filter of the sampling system, whereas all other compounds have mainly been enriched on the XAD-resin of the self-packed glass cartridges. The sampling results revealed qualitative information on the presence, depth distribution and origin of the investigated compounds. Although the depth profile of PAHs, PCBs, OCPs, and PFAAs appeared to be homogeneous, pharmaceuticals and polar pesticides were detected in distinct different patterns with water depth. Source analysis with diagnostic ratios for PAHs revealed their origin to be pyrogenic (burning of coal, wood and grass). In contrast, most PCBs and OCPs had to be regarded as legacy pollutants which have been released into the environment in former times and still remain present due to their persistence. The abundance of emerging organic pollutants could be confirmed, and their most abundant compounds could be identified as perfluorooctanoic acid, diclofenac and atrazine among investigated PFAAs, pharmaceuticals and polar pesticides, respectively.

Keywords Monitoring · Depth profile · Persistent organic compounds · Perfluoroalkylic acids · Pharmaceutical residues · Environmental fate

Introduction

The impoundment of the Yangtze River in the framework of the Three Gorges Project (TGP) in the People's Republic of China led to the creation of the Three Gorges Reservoir (TGR) with a length of 660 km (Bergmann et al. 2012). The construction of the world's largest hydroelectric power project with an installed capacity of 22,500 MW began in 1993 and was completed in 2009, whereas the normal impoundment level of

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175 m was reached in October 2010 for the first time (CNEMC 2011; Xu et al. 2013). In the same year, the TGR was able to store 26.43 billion m^3 of flood water (CNEMC 2011). Besides socioeconomic changes through human resettlement, the impoundment implied geological and environmental effects (Xu et al. 2013). Partly, the consequences of the TGP have been underestimated. Indicators for decreasing water quality are eutrophication and algal blooms which are a commonly observed phenomena at the bay of the reservoir (Bergmann et al. 2012; Floehr et al. 2013). The significant reduction of four major domestic fish species in the reservoir area between 2005 and 2010 and the decline in fish catches reported may also indicate ecotoxic consequences of the impoundment (Wang et al. 2014; Xu et al. 2011). Decreased river bank stability within the reservoir may lead to an increased burden of organic pollutants within the reservoir, originally associated to soil and sediment (Xu et al. 2013).

The water quality assessment criteria for surface water in China mainly cover bulk chemical parameters (Bao et al. 2012). Nevertheless, organic chemicals can have an additional influence on water quality. The group of substances which are referred to as persistent organic pollutants (POPs) is known to be resistant to chemical, biological, and photolytic degradation. Thus, they tend to bioaccumulation in the food chain. Besides, these substances are suspected to be carcinogenic, endocrine disrupting, and causing other dangers to human health. Beneath others, POPs listed by the Stockholm Convention are organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and perfluorooctane sulfonic acid and its salts (PFOS). OCPs were determined to be present in the Yangtze River at total concentrations between 0 and 47 ng L^{-1}, and they appeared to be equally distributed along the river with only a few exceptions (Floehr et al. 2013). Within the TGR, total OCP concentrations ranged from 4.29 to 19.6 ng L^{-1} in 2008 (Wang et al. 2009, 2013b). PCBs, which have former been used in power capacitors as dielectric fluid or paint additive, are still abundant in the environment. Being banned for production and use, one possible source may nowadays be the illegal disposal and leakage of PCB-containing waste (Xing et al. 2005). In water, PCB levels are usually expected to be lower than in soil and sediment due to their hydrophobicity and water solubility. Within the Yangtze River, PCBs were reported in total concentrations ranging from 0 to 44 ng L^{-1} (Floehr et al. 2013), whereas in the TGR, total concentrations in 2008 were as low as 0.01 to 0.09 ng L^{-1} (Wang et al. 2009, 2013b). PFOS has been listed by the Stockholm Convention for restriction since its fourth meeting in 2009: It was found to represent POP characteristics (persistence, bioaccumulation, and toxicity) and was therefore replaced where possible and restricted to certain acceptable purposes for which no adequate replacement is available yet (like photo-imaging, semiconductor coating and aviation hydraulic fluids to name only a few). Between 2004 and 2006, the annual production of PFOS in China increased in average by 130 % annually due to a transfer of PFOS industry from developed countries (Wang et al. 2010). For the category of perfluorinated compounds (PFCs), perfluorooctanoic acid (PFOA) and PFOS can be regarded as reference substances in terms of toxicology (Stahl et al. 2011). PFOA and PFOS concentration in the Yangtze River was found to vary between 0.2–298 and 0.01–144 ng L^{-1}, respectively (Floehr et al. 2013; Wang et al. 2010). Throughout the TGR, PFC concentrations show large variation which indicates pollution by point-sources and subsequent dilution which could be confirmed by a recent study (Xie et al. 2013).

Pharmaceuticals and personal care products (PPCPs) found as ubiquitous residues in the aquatic environment have drawn increasing attention over the last years (Campbell et al. 2006; Daughton 2004; Qi et al. 2014). The broad application of these chemicals in daily life and high prescription numbers of pharmaceuticals lead to a high burden of nonmetabolized PPCPs in wastewater treatment plants, where many of them show high persistence (Müller et al. 2011; Wode et al. 2012). Also in China, elevated residue levels of commonly used pharmaceuticals have been detected in surface wastewater treatment plants as well as in surface waters (Duan et al. 2013; Wolf et al. 2013; Yang et al. 2015; Zhou et al. 2014). Like POPs, some of these substances have a potential for bioaccumulation (Kannan et al. 2005). Besides, common applied antibiotics used in human therapy and intensive livestock farming can produce selection pressure possibly resulting in resistant bacteria which in turn may endanger human health (Zhang et al. 2009). The occurrence of PPCPs in the Yangtze River strongly depends on the single substances. Pharmaceuticals were detected between 2009 and 2010 near Datong (600 km from the East China Sea) at concentrations usually below 50 ng L^{-1}. Furthermore, other household chemicals were detected, especially the sweetener sucralose which occurred at an average concentration of 217 ng L^{-1} (Qi et al. 2014). The distribution pattern of PPCPs within the TGR is comparable to PFCs which are emitted by point sources. Thus, typically, the influents and effluents of wastewater treatment plants were targets of deeper investigation (Chang et al. 2010; Duan et al. 2013; Gao et al. 2012; Yan et al. 2014). Depending on the type and location of sampling as well as on stability of the single compounds, the detected concentrations vary over a large scale (approximately between lower micrograms per liter and lower nanograms per liter scale) (Chang et al. 2010; Qi et al. 2014; Wolf et al. 2013; Yan et al. 2014).

The presented study involves the application of a new methodical approach for the sensible detection and quantification of emerging organic pollutants in trace concentrations in the TGR. Large-scale water enrichment was combined with a suitable laboratory cleanup and measurement with gas chromatography or ultra-high-performance liquid chromatography system and mass detection. The intention behind the enrichment of a large water volume was the low analyte concentrations apparent in the TGR as mentioned above. We already demonstrated in our recent study that low concentrations of polycyclic aromatic hydrocarbons (PAHs) in the reservoir correspond to high total mass fluxes in the large water body (Deyerling et al. 2014). Qi et al. applied this principle (among other analytes) on PPCPs (Qi et al. 2014). We applied our method for determination of a depth profile at Maoping in front of the Three Gorges Dam (TGD) by sampling in three different water depths for investigating the homogeneity of the water body. In 2012, we determined PAHs, OCPs, and PCBs, and in 2013, we repeated the sampling in the same fashion for the analysis of selected active pharmaceutical compounds, polar pesticides, and PFCs.

Materials and methods

High volume water sampling

The sampling was divided in two independent campaigns that took place in September 2012 and 2013. Samples from 2012 were used for PAH and POP analysis (target list in supplementary Tables S1, S2, and S3), whereas samples taken in 2013 were investigated for emerging organic pollutants (target list in supplementary Tables S4 and S5) including PFAAs, selected pharmaceutical residues, and polar pesticides. During both campaigns, samples were taken at the same location which was in the middle of the Yangtze River near the small town Maoping slightly upstream of the TGD. The sampled water depths were comparable in both attempts (11, 31, and 61 m in 2012 and 11, 31, and 50 m in 2013) and covered the upper water layers of the Yangtze River that reaches, depending on the operation of the TGD, a maximum depth of 175 m. The sampling was carried out in a solid-phase extraction-like fashion with self-packed glass cartridges with a dimension of approximately 220×450 mm (length×diameter) packed with polymeric resin trapped within the cartridges by a glass frit at one side and tight packed glass wool at the other side (see Fig. 1). Pre-cleaned XAD-2 resin (styrene-divinylbenzene co-polymer) that reaches US EPA criteria (Supelpak-2, Sigma-Aldrich, Steinheim, Germany) was used as sorbent for POPs and PAHs. Emerging organic pollutants were enriched on a 50:50-mixture (m/m) of Amberlite XAD-16 (equals XAD-2 with higher surface area) and Amberlite XAD-7 (moderately polar acrylic resin, Sigma-Aldrich, Steinheim, Germany). The cartridge layout was adopted from the earlier sampling campaigns for polychlorinated dibenzodioxins and dibenzofurans and PCBs (Pandelova et al. 2009). Prior to application, the cartridges were extracted in a Soxhlet apparatus for 24 h under the same conditions used later for sample extraction (see "Extraction, cleanup, and analysis for PAHs, OCPs, and PCBs" and "Extraction, cleanup, and analysis for pharmaceuticals, polar pesticides, and PFAAs" section). In front of a sampling cartridge, a filter cartridge was mounted, tightly packed with glass wool in order to exclude large suspended particles from entering the sampling system. In 2012, only one sampling cartridge with XAD resin was used, and the resin was divided in the laboratory into a master and backup part. In contrast, an optimized design with separate master and backup cartridge was employed during sampling in 2013. For both sampling campaigns, blank cartridges were prepared which were subjected to the same conditions as the sampling cartridges but not exposed to water. The cartridge assembly was connected with a rubber tubing to a battery-driven peristaltic pump and an analog water meter. For sampling, the cartridges were placed within a protective cover made of stainless steel, submerged to the desired sampling depth and sampled with water by suction, thus avoiding sampling artifacts from the rubber tubing, the pump, and the water meter which were all located within the flow path after the cartridges. Water was sampled at a mean flow rate of 3 L min^{-1}, consequently reaching a sample size of approximately 300 to 400 L took between 13:30 and 14:15 hours. Until extraction, the samples were stored at 4 °C.

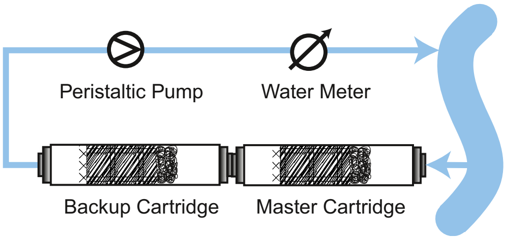

Fig. 1 Illustration of the sampling system layout

Extraction, cleanup, and analysis for PAHs, OCPs, and PCBs

Detailed description of cleanup and analysis can be reviewed from Deyerling et al. (2014) and Wang et al. (2009). In brief, the polymeric resin of each sampling cartridge was divided by half into a master and backup part using an additional spare glass cartridge. In addition, the filter cartridges packed with glass wool were extracted without further separation. Subsequently, every single sample was spiked with surrogate mixtures for PAH, OCP, and PCB analysis, containing all investigated analytes as mass labeled compounds. The cartridges were transferred into a Soxhlet apparatus and extracted for 24 h with 800 mL hexane/acetone 3:1 (*v*/*v*). The extracts were evaporated by rotary evaporation until a volume of about 200–300 mL was reached. Residual water was removed by passing the extracts through glass filters filled with dry sodium sulfate. To avoid any loss of analyte at this step, the round bottom flask containing the extract and the filter was rinsed with a small amount of extraction solvent three times. The dried extracts were evaporated again with a rotary evaporator to a volume of about 1 mL. Following up, the extracts were eluted from a column packed with heat-treated silica gel and alumina b with a mixture of *n*-hexane/dichloromethane 1:1 (*v*/*v*). Prior to a C-18 solid-phase extraction cleanup, the eluates were once again concentrated by rotary evaporation to a small residual volume, and the solvent was changed to acetonitrile. Subsequently, the samples were eluted from the acetonitrile pre-conditioned C-18 cartridges and evaporated to a small volume under a gentle stream of nitrogen at 40 °C. Finally, the samples were transferred to a GC vial, recovery standard was added and the sample was adjusted to a final volume of about 20 μL.

The instrumental measurement was carried out with gas chromatography (GC 5890 series II, Agilent Technologies, Palo Alto, USA) coupled to a high-resolution mass spectrometer Finnigan MAT 95S (Thermo Electron GmbH, Bremen, Germany). The analysis was carried out by splitless injection (cold injection system CIS4, Gerstel GmbH, Mülheim, Germany) of 1-μL sample volume on a Restek Stx-Cl Pesticides 2 column with a column length of 30 m, inner diameter of 0.25 mm, and 0.2-μm film thickness (Restek GmbH, Sulzbach, Germany).

Extraction, cleanup, and analysis for pharmaceuticals, polar pesticides, and PFAAs

Cartridges packed with XAD-7/16 mixture for analysis of emerging organic pollutants were dried in a stream of nitrogen for 5 min and extracted with 800 mL acetone (Picograde, Promochem, LGC Standards GmbH, Wesel, Germany) in a Soxhlet apparatus for 24 h. Prior to extraction, each sample was spiked with two surrogate mixtures, one containing mass labeled pharmaceuticals and polar pesticides, one containing PFAAs. The first surrogate mixture contained sulfamethoxazole-D4, simazin-D5, atrazine-D5, and linuron-D6 purchased from Dr. Ehrenstorfer (LGC Standards GmbH, Augsburg, Germany), ibuprofen-D3 and carbamazepine-D10 from Sigma-Aldrich (Steinheim, Germany), and naproxen-D3 and diclofenac-D4 from Santa Cruz Biotechnology Inc. (Dallas, USA). The latter surrogate mixture was purchased from Wellington Laboratories (Guelph, Canada) and contained perfluoro-*n*-[1,2,3,4-$^{13}C_4$]butanoic acid, perfluoro-*n*-[1,2-$^{13}C_2$]hexanoic acid, perfluoro-*n*-[1,2,3,4-$^{13}C_4$]octanoic acid, perfluoro-*n*-[1,2,3,4,5-$^{13}C_5$]nonanoic acid, perfluoro-*n*-[1,2-$^{13}C_2$]decanoic acid, perfluoro-*n*-[1,2-$^{13}C_2$]undecanoic acid, perfluoro-*n*-[1,2-$^{13}C_2$]dodecanoic acid, sodium perfluoro-1-hexane[$^{18}O_2$]sulfonate and sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate. After extraction, the samples were evaporated on a rotary evaporator to a volume of about 200 mL. The extracts were dried by passing them through a filter filled with dry sodium sulfate (Promochem, LGC Standards GmbH, Wesel, Germany). The round bottom flask and the filter were rinsed three times with a small amount of acetone in order to transfer any remaining analytes. Then, the extracts were evaporated again to a remaining volume of about 1 mL for subsequent solid-phase extraction with a polar modified styrene divinylbenzene copolymer (Chromabond HR-X 500 mg PP-SPE-cartridge, Macherey-Nagel, Dueren, Germany). The cartridges were conditioned with 8 mL methanol/acetonitrile 1:1 (*v*/*v*) (UHPLC-grade, Promochem, LGC-Standards GmbH, Wesel, Germany) followed by 8 mL ultrapure water. The samples were transferred to the SPE cartridges by rinsing three times with a small amount of ultrapure water. Next, the cartridges were washed with 5 mL of ultrapure water and subsequently dried under gentle vacuum for about 40 min. The samples were eluted from the cartridges with two times 5 mL methanol/acetonitrile 1:1 (*v*/*v*) into pear-shaped flasks and evaporated to a residual volume of about 200 μL. For sample storage, the extracts were transferred with three times rinsing to polypropylene tubes, and a final sample volume of 200 μL was adjusted under a gentle stream of nitrogen and 40 °C.

The analysis was carried out by ultra-high-performance liquid chromatography (UHPLC, nanoAcquity, Waters, Milford, USA) in micro-scale coupled to a quadrupole time-of-flight mass spectrometer with collision cell (Q-TOF2, Waters-Micromass, Manchester, UK). The sample injection volume was 5 μL administered by an autosampler with sample compartment conditioned to 10 °C and a column oven heated to 30 °C. Samples were separated on a column with reversed-phase C-18 chemistry (HSS-T3, 150 mm×300 μm i.d., 1.8-μm particle size, Waters) by gradient elution with a binary pump at a flowrate of 4 $\mu L\ min^{-1}$ in a run-time of 35 min per injection. For positive ionization, 0.1 % formic acid in water and acetonitrile were used as solvents A and B, respectively. During work with negative ionization, a mixture of water/methanol 99.9:0.1 (*v*/*v*) served as solvent A and pure methanol as solvent B, both with 1 mM formic acid and 1 mM ammonium formate as organic modifiers. The binary gradient was the same for positive and negative ionization (see supplementary Table S6). The electrospray interface was operated with a desolvation gas flow of 200 $L\ h^{-1}$ of dry nitrogen heated to 120 °C and a cone gas flow of 50 $L\ h^{-1}$. The source block was heated to 100 °C and the capillary voltage optimized at 2.5 kV. Argon 5.0 was used as collision gas. The mass spectrometer was calibrated on a daily basis by continuous infusion of 0.1 % phosphoric acid in acetonitrile/ultrapure water 50:50 (*v*/*v*) with a syringe pump. Sample cone voltage and collision energy were acquired individually for each compound by directly infusing individual stock solutions with a syringe pump. Instrument calibration was achieved by dilutions of native target compounds with constant concentration of mass labeled compounds in 90:10 A/B for positive ionization, 70:30 A/B for negative ionizing pharmaceuticals, and 100:0 and 40:60 A/B for different chain lengths of PFAAs. For pharmaceuticals and polar pesticides a 10-point calibration was established from 0 to 450 pg μL^{-1}. For PFAA calibration, a 5-point calibration from 0 to 200 pg μL^{-1} was applied. Weighted linear regression (x^{-1}) was carried out with the software of the mass spectrometer (MassLynx 4.1, Waters, Milford, USA). The calibration standards were freshly prepared from stock solutions and measured in triplicate on a monthly basis and once just before each analysis.

Prior to measurement, sample aliquots solved in methanol/acetonitrile 1:1 (*v*/*v*) were evaporated to a small volume under a gentle stream of nitrogen and reconstituted in different fractions of mobile phase depending on the target of analysis.

Considerations regarding sampling and analysis

The analytical results were corrected for signal suppression due to matrix effects and extraction and cleanup recovery by isotope dilution analysis. In PAH and POP analysis, the addition of a recovery standard after cleanup and prior to the measurement allowed the calculation of cleanup recovery independent from matrix effects. In contrast, for emerging organic pollutant analysis on UHPLC-MS, cleanup recovery and signal suppression were judged as a combined value from the signal of the mass labeled internal standards. Subsequent to sample measurement, the concentration of analyte within the 200-μL sample extract could be calculated by the mass spectrometer data system on behalf of the instrument calibration. The separate analysis of master and backup parts allowed the judgment of analyte breakthrough. Nevertheless, for quantitative analysis, the concentrations found in master and backup samples from one water depth were added. According to the water volume determined with the water meter during sampling, an enrichment F_{EN} factor was determined for each sample according to the following equation:

$$F_{EN}[] = \frac{V_{sampled}\ [L]}{V_{extract}\ [\mu L] \cdot 10^{-6}} \tag{1}$$

where $V_{sampled}$ and $V_{extract}$ are the volumes of the water sample and of the final extract, respectively. Consequently, the concentration of a dissolved organic compound *i* in water $c_{i,w}$ was calculated by multiplication of the determined extract concentration $c_{i,extract}$ and the enrichment factor F_{EN}:

$$c_{i,w}\left[pg\ L^{-1}\right] = c_{i,extract}\left[pg\ \mu L^{-1}\right] \cdot F_{EN} \cdot 10^{6} \tag{2}$$

Blank values from XAD blank cartridges were calculated using the same equations and were subtracted from the reported values:

$$c_{i,w,blankcorr}\left[pg\ L^{-1}\right] = c_{i,w}\left[pg\ L^{-1}\right] - c_{i,blank}\left[pg\ L^{-1}\right] \tag{3}$$

where $c_{i,blank}$ is the theoretical blank concentration calculated from the blank cartridge referred to the sample volume. The limit of quantification (LOQ) was also calculated from the blank cartridges:

$$LOQ\ \left[pg\ L^{-1}\right] = 3 \cdot 0.25 \cdot c_{i,blank}\left[pg\ L^{-1}\right] \tag{4}$$

In the case of the LOQ value exceeding the detected concentrations, the compound was regarded as not detected (n.d.). In the case of analyte breakthrough detected by judging the values of master and backup samples separately, the results have to be regarded as semiquantitative. In this case, the determined concentrations may serve as minimum concentration boundary for the investigated compounds. Maximum concentration boundaries were estimated for the total concentration data of the single analyte groups from the partition between master and backup cartridge. This estimation was only possible if the abundance in the master sample was higher than in the backup sample. At first, an analyte dissipation factor F_{diss} was calculated:

$$F_{diss}[\%] = \frac{C_{total,backup}}{C_{total,master}} \cdot 100 \tag{5}$$

where $C_{total,backup}$ and $C_{total,master}$ are the blank corrected calculated water concentrations of an analyte group. The multiplication of F_{diss} with $C_{total,backup}$ revealed the theoretical concentration that would be expected in a third sampling cartridge. The maximum concentration boundary could then be estimated with the following equation:

$$C_{total,x} = \sum_{x=1}^{200} F_{diss}{}^{x-1} \cdot C_{total,master} \tag{6}$$

where $C_{total,x}$ corresponds to the total concentration in cartridge number *x* with setting the value for the master cartridge to 1. The sum of 200 theoretical sampling cartridges appeared to be sufficient to cover the observed concentration range.

Results and discussion

Sampling system

The performance of analyte enrichment was monitored by regarding the partition of the investigated compounds between glass wool filter, master, and backup cartridge with polymeric resin (XAD). Figure 2 shows the separation for the different groups of analytes in percent normalized to the total detected amount. Analyte partition varied obviously among the different analyte groups. PAHs and PCBs were mainly found within the glass wool filters. Nevertheless, there was a different behavior for OCPs, PFAAs, pharmaceuticals, and polar pesticides which mainly resided in the cartridges with XAD resin.

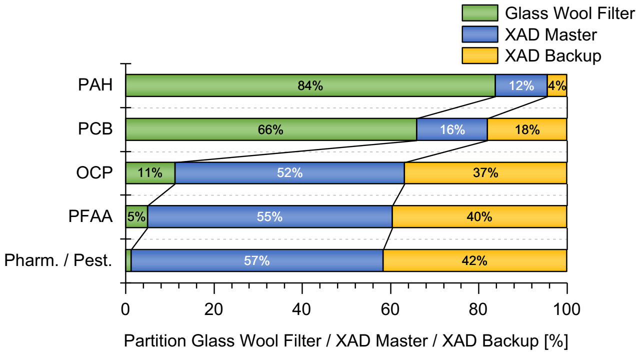

Fig. 2 Mean relative analyte partition in glass wool filter, XAD master, and XAD backup cartridge

All analytes were detected at a higher level within the master cartridges than in the backup cartridges. Unfortunately, the distribution between master and backup sample was near 50 % which indicated that the polymeric resin was not capable to retain the analytes sufficiently enough for quantitative enrichment. Thus, the results have to be regarded as semiquantitative as possibly some amounts of analytes escaped from the sampling system. As a compromise, we investigated the recorded depth profiles in a qualitative way. The results still offer the possibility to evaluate spatial analyte distribution and environmental fate within the TGR due to all samples having been taken reproducible in the same manner. Additionally, we were able to calculate absolute minimum and estimated maximum water concentrations based on our sampling results.

The observed partition of analytes might be explained by different reasons for each analyte group. In the case of PAHs and PCBs, their planar aromatic ring structure promotes strong interaction with organic carbon containing particles, black carbon, and soot (Ali et al. 2014). It is known that the partition coefficient for PAHs and PCBs between water and suspended particles depends on the organic carbon content of the particles (Seth et al. 1999). Studies also revealed a strong influence between the black carbon fraction of particles and sediment on the distribution of PAHs (Sánchez-García et al. 2010). Furthermore, analytes may have been enriched from water within the glass wool filters by already immobilized particles serving as sorption media. The sorption of the analytes onto glass wool as sorption media alone cannot explain the high fraction of compounds found within the filter. Particularly, PAHs and PCBs with mean octanol-water partition coefficient values of 5.30 and 6.81, respectively, are compounds with high hydrophobicity among the investigated compounds. It has to be remarked that the self-packed glass wool filter cartridges were intended to prevent the entrance of large particles into the XAD cartridges. The filter cartridges were not designed to exclude a certain particle size. Small suspended particles might still have passed the filters and entered the sampling cartridges. Consequently, the amount of analytes detected in the XAD cartridges cannot be strictly related to freely dissolved compounds but also to analytes sorbed to fine suspended particles.

For OCPs, PFAAs, pharmaceuticals, and polar pesticides, the observation was the opposite. They resided mainly within the polymeric resin. Particulate association is less common for these partly ionic substances, and our results indicate that most of these organic compounds are freely dissolved in water and thus available for the enrichment. As stated before, the employed polymeric resin was not capable of the quantitative enrichment of these compounds. The high sample volume of about 300 L water was for sure a key factor for analyte leakage from the master cartridge. The absorbent had not only to cope with the water volume itself but may have become saturated with other dissolved organic material like fulvic and humic acids. Additionally, inorganic salts are known to have influence on sorption capacity, too. Finally, the chosen sampling rate of 3 L h^{-1} might have been too high to allow complete equilibration between the liquid and solid phase.

PAH analysis

The analytes detected in highest total concentration were PAHs with a total minimum mean concentration of 15.7 ng L^{-1} and an estimated maximum mean concentration of 17.1 ng L^{-1} (sum of filter, master, and backup cartridge). The partition of PAHs into the cartridges with XAD resin and filter cartridges did not vary with water depth. The PAH fractions in dependence of water depth categorized by their ring number are illustrated in Fig. 3. Total minimum PAH concentration varied between 15.1 and 16.6 ng L^{-1} which equals 9.5 % deviation from the total minimum mean concentration and is in the range of the precision of the applied method. Thus, based on our results, it has to be assumed that the concentration and chemical composition of PAHs did not vary between the water layers. As already discussed, PAHs were mainly detected within the filter cartridges which supports the thesis of sorption onto suspended particles. An increasing concentration of PAHs with water depth could have been

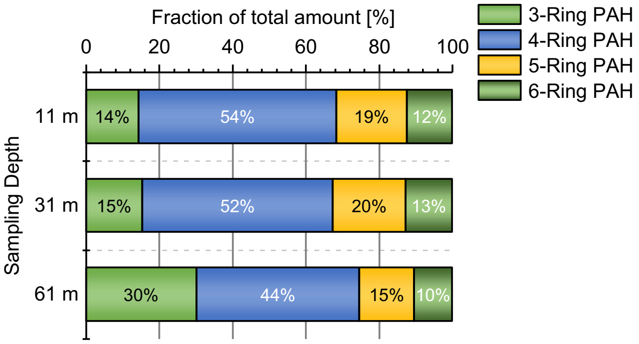

Fig. 3 Qualitative depth profile of PAHs detected in glass wool filter, master, and backup cartridge classified by PAH ring number (individual concentration data in Table S7)

explained with sedimentation taking place upstream of the TGD due to the reduction of flow velocity. In fact, we detected a slightly higher total concentration in 61 m than in 31-m depth but still lower than at 11 m. Consequently, the results do not clearly support our hypothesis. Four-ring PAHs were the most abundant species followed by three-, five-, and six-ring PAHs. Individual PAH concentrations ranged from nondetection to 2.5 pg L^{-1}, whereas fluoranthene was the most abundant compound. In our previous study, we investigated PAH mass fluxes within the TGR with the aid of virtual organisms and concluded that even low detected concentrations in this water body correspond to a high mass flux of PAHs in total (Deyerling et al. 2014) and consequently a high total input of these organic substances into the environment.

Polycyclic aromatic hydrocarbons are released into the environment mainly by partially incomplete natural and anthropogenic burning processes (EPA 2008). Common anthropogenic sources are coal burning energy plants, wood burning furnaces, or light duty and heavy duty diesel engines from cars, trucks, and ships. Nevertheless, natural emissions can occur among others by volcanic activity and forest fires. Due to the different conditions for these chemical reactions, the source of PAHs may be judged from the detected PAH composition (Tobiszewski and Namieśnik 2012; Yunker et al. 2002). We calculated common diagnostic PAH ratios from the PAH concentration values averaged over the water depth. Three commonly used diagnostic values discriminating between pyrogenic and petrogenic PAH origin were taken into account for our consideration:

- The fraction between the sum of two- and three-ring PAHs and the sum of four- and five-ring PAHs ($\sum$LMW/$\sum$HMW, >1: petrogenic; <1: pyrogenic; calculated: 0.25) (Tobiszewski and Namieśnik 2012)
- The fraction between anthracene and the sum of anthracene and phenanthrene (Ant/(Ant+Phe, <0.1: petrogenic; >0.1: pyrogenic; calculated: 0.16) (Tobiszewski and Namieśnik 2012)
- The fraction between fluoranthene and the sum of fluoranthene and pyrene (Flu/Flu+Pyr, <0.5: petrogenic; >0.5: pyrogenic; calculated: 0.51) (Yunker et al. 2002)

Overall, the diagnostic ratios indicate that the PAHs determined during our measurement campaign mainly had pyrogenic origin from grass, wood, and coal combustion (Tobiszewski and Namieśnik 2012; Yunker et al. 2002). Judging from our individual results per water depth, the decreasing proportion of five- and six-ring PAHs in the 61 m measurement does not influence the conclusions drawn based on the diagnostic ratios stated above. Nevertheless, the judgment of PAH origin from diagnostic ratios is discussed controversially. Once released into the environment, the ratios may not stay constant but be affected differently in matrices like air, soil, sediment, and water. In the latter case, photolysis and different partition coefficients between suspended particles and water (see also supplementary Table S1) may influence determined PAH ratios. At last, the applied sampling technique may alter PAH ratios by selective enrichment and sampling of an unknown amount and size of suspended particles.

PCB analysis

The polychlorinated biphenyls analyzed within this study account included the nonortho and mono-ortho congeners which are known for their dioxin-like activity. Additionally, six indicator PCBs with non-dioxin-like activity were chosen for determining a representative proportion of this group of analytes. PCBs were detected at the lowest concentrations of all investigated organic trace substances. Their total minimum concentration ranged between 8.4 and 11.4 pg L^{-1}, and total maximum concentration was estimated to 13.4 pg L^{-1} and thus was near the limit of quantification. The qualitative PCB depth profile is illustrated in Fig. 4. The indicator PCBs represented the largest fraction in all three investigated water depths followed by mono-ortho and nonortho PCBs. From the latter ones, PCB #77 was the only congener detected and the minimum concentration was below 0.1 pg L^{-1}. The most abundant congener was PCB #52 attributing 19.4 % of the total minimum mean PCB concentration. We did not observe a variation of PCB composition with water depth. The absolute concentration values indicated slightly increasing total PCB concentration with water depth, mainly caused by an increasing amount of indicator PCBs. The deviation from the mean minimum total PCB concentration of 9.6 pg L^{-1} was between 5.4 (31 m) and 18.4 % (61 m). Taking a method precision of about 10 % into account, we cannot determine for sure whether there was an increasing PCB concentration with water depth. Due to the major fraction of PCBs having been found in the glass wool filter (see "Sampling system" section), increasing PCB concentration with water depth might be

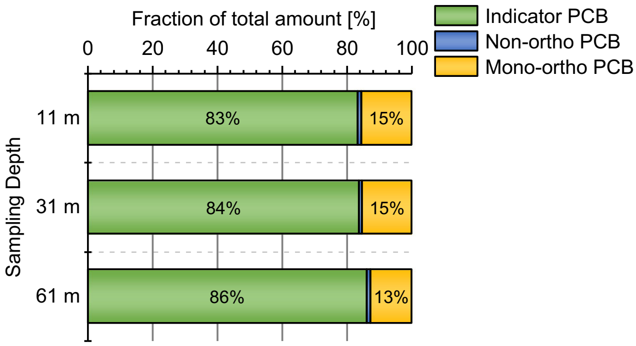

Fig. 4 Qualitative depth profile of PCBs detected in glass wool filter, master, and backup cartridge classified in indicator, nonortho, and mono-ortho PCBs (individual concentration data in Table S8)

explained again with PCBs sorbed onto settling suspended particles due to decreased flow velocity in front of the TGD. Nevertheless, the slight increase in PCB concentration could still be caused by insufficient method precision near the limit of detection.

The generally low PCB concentrations in the main stream of the Yangtze River could be expected. The results reflect the high dilution of these persistent organic compounds within the TGR as well as the ban of these compounds from production in China since 1974 (Xing et al. 2005). At least for the sampling site of this study, no PCB point-source was indicated by the results. During a previous study with virtual organisms as passive samplers covering the whole TGR, PCBs were detected in slightly higher amounts from 14.9 to 92.6 pg L^{-1} (Wang et al. 2009, 2013b). This discrepancy indicates a certain fluctuation of PCB concentration within the TGR. Nevertheless, the detected concentrations are low compared to the allowed 20 ng L^{-1} limit of the quality standards for surface water in China which is sometimes even exceeded at certain sampling sites in China, indicating point sources (Floehr et al. 2013). Within the TGR, PCBs have been reported to originate from floods, heavy rains, industrial wastewater, and domestic sewage (Yang et al. 2009). Higher PCB concentrations, however, could be observed in eastern China and the lower Yangtze Reaches (Xing et al. 2005; Zhang et al. 2011) where most of the PCB applications in industry have been located. With tri- and tetra-PCBs being the most abundant PCB congeners in our study, the results are in well accordance to the major produced and applied PCBs in China (Yang et al. 2009).

OCP analysis

Organochlorine pesticides were detected in total minimum concentrations ranging from 436.7 to 611.7 pg L^{-1} and were the most abundant persistent organic compounds investigated within the presented study. Estimated from the cartridge breakthrough, their maximum concentration was estimated to range from 695.5 to 1662.3 pg L^{-1}. The larger discrepancy between the minimum and maximum concentration of these analytes was caused by their higher abundance within the cartridges with polymeric resin. Consequently, the estimation of the maximum water concentration based on master and backup cartridge reveals larger impact. Additionally, this result implies less adsorption to glass wool or lower association with suspended particles (see "Sampling system" section). The qualitative OCP depth profile is presented in Fig. 5. The analyte groups hexachlorocyclohexanes (HCHs) and chlordane-related pesticides included additionally chlorinated benzenes and some legacy POPs, respectively (see S3). The proportion between HCHs, DDT-related and chlordane-related pesticides remained constant between the three investigated water depths. HCHs marked the highest OCP fraction followed by chlordane-related and DDT-related pesticides, respectively. We observed a decrease of 28.6 % in total OCP concentration from 11 to 61 m. In contrast to the results for PCBs, values for OCPs were clearly higher than the limit of detection; thus, the analysis can be regarded as more reliable. Consequently, judging from the presented results, the Yangtze River appeared to be a not completely mixed water body in terms of OCPs which might be due to the fact of a decreased flow velocity of the river due to the impoundment. This observation might differ with the flow velocity which is influenced by the operation status of the TGD (storage and release of flood water). Mean minimum concentrations of HCHs and chlorinated benzenes ranged from 3.1 pg L^{-1} for octachlorostyrene to 104 pg L^{-1} for hexachlorobenzene. The most abundant hexachlorocyclohexane was β-HCH with a minimum concentration of 76.9 pg L^{-1}. Among the group of DDT-related pesticides, minimum mean individual concentrations were in the range of 1.2 (2,4′-DDE) to 12.3 pg L^{-1} (4,4′-DDE). The lowest concentrations were detected for the group containing chlordane-related and other pesticides (see supplementary S3). Individual minimum concentrations were between nondetection to 1.0 pg L^{-1} except for endosulfan-I (1.1 pg L^{-1}) and endosulfan-sulfate (57.9 pg L^{-1}). The results for OCPs represent the lower end of reported concentrations for these compounds within the rivers of China (Bao et al. 2012; Floehr et al. 2013). The proportion between detected amounts of HCHs and DDTs is in well accordance with the fact that the used amount of HCHs in China was more than 12 times higher than the amount of DDTs (Bao et al. 2012). Regarding HCHs, technical HCH mixtures as well as lindane (γ-HCH) have been used in China. Therefore, relative abundances of α-HCH and γ-HCH may be used to judge whether the HCH burden originates from historical application of technical HCH mixtures or recently applied lindane. Within the presented study, the mean α-HCH/γ-HCH-ratio was 4.5 which is in the range of 3.7–11 indicating a historical HCH

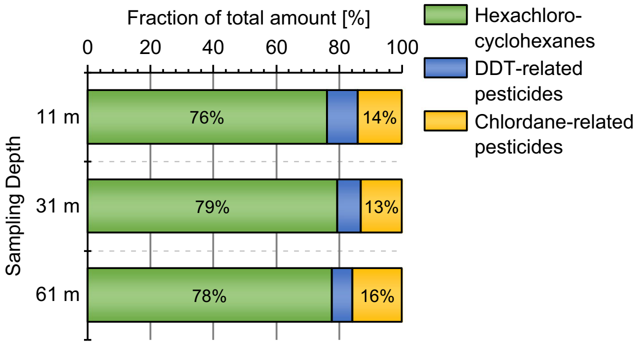

Fig. 5 Qualitative depth profile of OCPs detected in glass wool filter, master, and backup cartridge categorized in hexachlorocyclohexanes (including chlorinated benzenes, see S3), DDT-related and chlordane-related pesticides (including some others, see S3 and S9 for individual concentrations)

burden at Maoping (Bao et al. 2012). The origin of DDTs may be discriminated from technical DDT usage in antifouling paints of boats and DDT usage as pesticide (dicofol) by the ratio of 2,4′-DDT/4,4′-DDT. Values close to 0.2 suggest technical DDT usage, whereas values around 7 are an indicator for recently applied dicofol (Bao et al. 2012). In our investigation, this ratio was calculated to 0.3 indicating the usage of DDT in antifouling paint. The Three Gorges Project increased shipping activities on the Yangtze River easing navigation of ships with deeper draft to transport cargo from Shanghai up to Chongqing (Hobbs 2008). Thus, results reasonably indicate DDT emission into the TGR by increased shipping traffic.

Another diagnostic ratio to judge the origin of the DDT-legacy is 4,4′-DDT/(4,4′-DDE + 4,4′-DDD). Values smaller than 1 indicate historic input, whereas values above 1 indicate recent input (Bao et al. 2012). The mean concentration values from the presented sampling campaign result in a value of 0.6; consequently, the DDTs detected in the TGR might originate from historic DDT applications. Concluding the results from both diagnostic ratios, the DDT load detected in the TGR could be determined as technical DDT which is abundant due to both, historic use and application in antifouling paint of ships. Concentrations of chlordane-related pesticides below 1 pg L^{-1} might be related to the elimination of these substances caused by stopping the release of these substances into the environment. Endosulfan I, endosulfan II, and their main metabolite endosulfan sulfate, however, were detected in higher concentrations than the other substances of that OCP group. Technical formulations of this insecticide have been widely used around the globe since the 1950s (Weber et al. 2010). With beginning in year 2000, more and more countries banned the insecticide from their markets and the Stockholm Convention amended endosulfan isomers since 2011 for elimination in annex A. Nevertheless, endosulfan is still in use for agriculture in China up until now. Between 2000 and 2004, approximately 3000 t of this insecticide was used per year for pest control on cotton, tea, tobacco, wheat, apples, and pears (Jia et al. 2011). Endosulfan is known to be acutely neurotoxic for insects and mammals. Furthermore, endocrine disrupting activity has been confirmed for this compound in several in vitro studies (Jia et al. 2011; Weber et al. 2010). The insecticide shows typical POP properties like persistence and bioaccumulation in the environment. It can undergo atmospheric long range transport and thus reach remote areas in which the insecticide has never been applied before (Weber et al. 2010). With this background information, the main source of endosulfan in the TGR may be the application in domestic agriculture. Endosulfan may enter the reservoir by washing-out from agricultural areas as well as by wet deposition from the air. Due to its persistence in the environment, further application of endosulfan in China should be critically considered in order to limit further domestic accumulation of this toxic compound.

Levels of perfluoroalkylic acids

Another group of organic substances, of which two have been added in the Annex B for restriction by the Stockholm Convention since 2009, are perfluoroalkylic acids (UNEP 2009). The results of our PFC analysis in the TGR are presented in Fig. 5. Unfortunately, the sample amount for 11-m water depth was insufficient. Consequently, the results for PFCs are only based on the measurement in 31 and 50-m water depth. The qualitative PFC depth profile in Fig. 6 shows that the proportion between the single PFCs did not vary characteristically between the investigated water depths. The PFCs mainly resided in the polymeric resin. We did not observe elevated PFC levels in the glass wool filter which could be explained either by adsorption onto glass wool or by adsorption onto suspended particles. The latter finding is consistent with investigations on the sorption behavior of PFOA, PFOS, and other PFCs on suspended particles which revealed in general low affinity of these compounds toward suspended particles (Ahrens et al. 2011). Total minimum PFC concentration was 1045 pg L^{-1} in 31 m and 1276 pg L^{-1} in 50 m water depth which equals a variation of 9.9 % of the minimum total mean concentration (1161 pg L^{-1}). The estimated maximum determined PFC concentration was 2100 pg L^{-1} in 31 m and 2833 pg L^{-1} in 50-m water depth. Again higher abundance of the analytes in the polymeric resin caused higher discrepancy between the determined minimum and maximum concentration according to the cartridge breakthrough.

The results indicate that PFOA was the dominant PFC representing more than 80 % of the total PFC concentration. Moreover, the main increase in total PFC concentration with water depth had to be attributed to PFOA. According to our results, PFAAs with either shorter or longer carbon chain than PFOA or PFOS accounted for only 7.9 % to the mean total PFAA abundance. Nevertheless, these compounds have been detected free of doubt; consequently, they have to be released into the environment albeit in a lower amount. We found lower concentrations of PFOS than PFOA which is partly in accordance and partly in contrast to reported values (Bao et al.

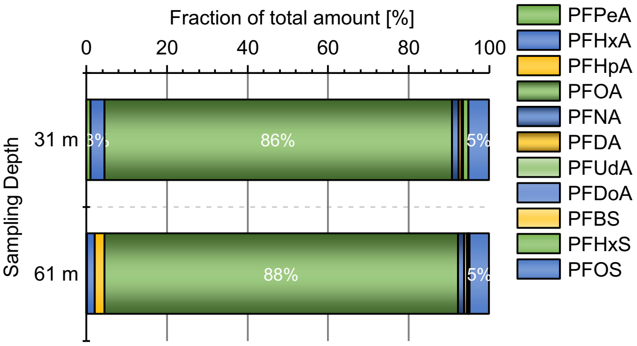

Fig. 6 Qualitative depth profile of PFAAs detected in glass wool filter, master, and backup cartridge; only data for 31- and 50-m water depth was available (see S10 for individual concentrations)

2012; Wang et al. 2013a). PFCs originate with high likelihood from point sources like PFC manufacturing industry or industrial processes involving PFC application. Therefore, different PFOS/PFOA ratios might be associated with differing point sources. Wang et al. found in 2010 considerable amounts of PFCs in a tributary of the Yangtze River (Hanjiang River) at Wuhan, downstream of PFC employing industrial sites (Wang et al. 2013a). Xie et al. correlated spatial distribution of PFOS emission with industrial branches and determined for the TGR (Hubei and Chongqing province) elevated emission density and intensity compared to the rest of China. Whereas PFOS in Hubei province could be mainly attributed to metal plating and PFOS manufacturing, the production of aquatic firefighting foams seems to be the driving factor for PFOS release in Chongqing Province (Xie et al. 2013). The toxicity of PFOS was found to be higher than of PFOA (Yang et al. 2014). Yang et al. derived concentration criteria for PFOA and PFOS upon the exposure of common Chinese aquatic animals in a controlled environment. They determined acute toxic effects (CMC, criterion maximum concentration, US Environmental Protection Agency) for PFOS and PFOA above 3.78 and 45.54 mg L^{-1} and chronic effects (CCC, criterion continuous concentration, US EPA) above 0.25 and 3.52 mg L^{-1} (Yang et al. 2014). These values are obviously higher than commonly reported values within the TGR even at sites with elevated PFC concentrations (Floehr et al. 2013; Wang et al. 2013a, 2010). Yang et al. remarked, however, that the criterion concentrations significantly depend on species selection and the chosen toxicity endpoints. The selected local aquatic species might show lower sensitivity toward PFOS and PFOA than aquatic animals from a different origin. Qi et al. monitored toxicity of PFOS toward a broader selection of species, including aquatic plants and more sensitive toxicity endpoints like mRNA expression. They reported predicted no-effect concentrations (PNECs) between 0.61 and 6.66 μg L^{-1} using four different approaches (Qi et al. 2011). The absolute PFC concentration reported in our study was far below the range of toxicological effect values. This might be due to the fact that the analytes have not been enriched quantitatively from the water which was indicated by the breakthrough of analytes from the master to the backup sampling cartridge. Besides, the high dilution of organic trace compounds in the TGR contributes in many cases to lowering the concentration of organic pollutants. Attention should be paid toward point sources of PFCs which have already caused total PFC concentrations in surface water in China near the PNECs reported by Qi et al. (Qi et al. 2011; Wang et al. 2013a).

Analysis of pharmaceuticals and polar herbicides

The presented investigation included the analysis of selected pharmaceutical active compounds. Additionally, due to mass spectrometry easily allowing multi-residue analysis, the analysis of the polar herbicides atrazine, simazin, and linuron was amended. The resulting qualitative depth profile of this group of compounds is presented in Fig. 7. The depth distribution was clearly dominated by the amounts found for the polar herbicide atrazine which caused in mean 86.3 % of the total analyte abundance detected for this analytical group. The absolute analyte abundance of all three herbicides indicated a decreasing amount with water depth. For atrazine, this finding was indicated by a reduction of 73.1 % from 11- to 50-m water depth. For simazine and linuron, this reduction was only slightly observable. We experienced problems in the quantification of linuron and ibuprofen due to coelution of matrix compounds with the corresponding internal standard linuron-D6 and ibuprofen-D3. Consequently, we could not determine linuron in 50-m depth and ibuprofen in 11- and 50-m depth. In the case of the pharmaceutical active compounds, the results were less homogenous. For diclofenac and naproxen, the absolute abundance peaked at 31-m water depth and was comparable for 11 and 50 m. For carbamazepine and sulfamethoxazole, the results did not indicate a characteristic change with water depth. The depth distribution of pharmaceutical residues and polar herbicides was less homogeneous than the distribution of all other investigated organic substances. This might be due to the fact that this depth profile draws the concentration of individual analytes compared to mean values of congener groups illustrated in the other depth profiles. Moreover, the heterogeneity of this group of analytes in terms of molecular structure and chemical properties is higher compared to PAHs, PCBs, OCPs, and PFAAs. The polarity of the pharmaceuticals and pesticides is comparably high among all analytes; thus, their water solubility is high and the tendency for association with suspended particles can be regarded as low. Consequently, the inhomogeneous depth profile might result from the Yangtze River being not completely mixed at the sampling site in front of the TGD due to decreased flow velocity. The decreasing load of atrazine with water depth opposes the theory of sedimentation with

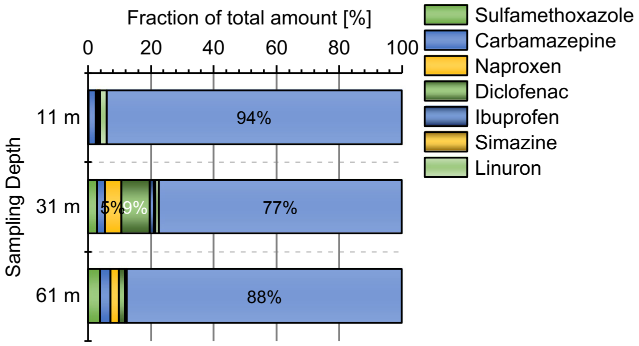

Fig. 7 Qualitative depth profile of selected pharmaceutical active compounds and polar pesticides/herbicides detected in glass wool filter, master, and backup cartridge (individual concentrations in S11)

suspended particles. In this case, higher concentrations of the herbicide might indicate the input of this water soluble herbicide by washing out of agricultural areas.

The minimum mean concentration of atrazine was determined to 2509 pg L^{-1}. In comparison, the minimum individual concentrations of the other herbicides ranged from 9.4 to 107 pg L^{-1}. Regarding pharmaceutical active compounds, the anticonvulsant and mood-stabilizer carbamazepine and the nonsteroidal anti-inflammatory drug diclofenac were abundant in higher minimum mean concentrations of 71.6 and 74.0 pg L^{-1}. The maximum concentrations estimated from the partition in master and backup cartridge for this group of analytes ranged from 4.6 to 10.3 ng L^{-1}.

The release of pesticides into the Yangtze River and the TGR can be mainly attributed to agricultural applications. Thus, the input mainly occurs diffuse rather than from point sources (Heeb et al. 2012). Regarding atrazine, seasonal fluctuations in concentration could be observed downstream of Beijing originating from agricultural areas. A distinct peak in atrazine level was observed in July 2009, whereas the levels in winter were near the LOQ which is an expected pattern for agricultural appliance of the pesticide (Heeb et al. 2012). Our sampling campaign near the TGD in a more rural area of Hubei Province took place in September 2013 after the period Heeb et al. observed the peak level of atrazine. The absolute concentrations for atrazine presented in our study are slightly lower than the concentrations reported near Beijing from Heeb et al. (range 10–100 ng L^{-1}) which might be caused by the high dilution in the TGR or by analyte loss of the sampling technique (see "Sampling system" section). The toxicological threats to the environment from the investigated herbicides can be estimated as lower than the threat originating from the total load of household chemicals and pharmaceuticals (Fig. 7). These micropollutants represent a higher fraction than pesticides originating from agriculture (Heeb et al. 2012). Nevertheless, both pose a threat to groundwater resources as they survive classic wastewater treatment techniques like coagulation and flocculation by 50–70 % and thus end up in surface water (Liu and Wong 2013). According to Liu and Wong, especially the extended use of antibiotics in China may affect public health in the future. After a rapid increase of pharmaceutical production in recent years, China has become the largest producer of active pharmaceutical compounds in the world with a production of more than 2.5 million t per year (Liu and Wong 2013). High prescription numbers of antibiotics in cases where they might not be mandatory as well as the broad application of antibiotics in livestock farms may increase the selective pressure on bacteria to promote antibiotic resistance genes which have already been reported in the aquatic environment in China (Liu and Wong 2013; Zhang et al. 2009). Indeed, we also investigated sulfamethoxazole, one commonly administered sulfonamide antibiotic in veterinary medicine worldwide. Although sulfamethoxazole only caused a small fraction of the total pharmaceutical amount detected in the present study, antibiotics were reported in concentrations of the micrograms per liter scale in influents and effluents of wastewater treatment plants (Liu and Wong 2013). High dilution and fast metabolism of these compounds in the environment may explain the lower concentrations observed in surface water. All other pharmaceutical active compounds observed in this study have already been reported either in surface waters or in the influent/effluent of wastewater treatment plants in China (Bu et al. 2013; Heeb et al. 2012; Liu and Wong 2013; Qi et al. 2014). Values for carbamazepine and diclofenac which were determined in this study with higher mean abundance have been reported in surface water in China with concentration ranges from nondetection to 675 and nondetection to 843 ng L^{-1}, respectively (Bu et al. 2013). Data on toxicity and chronic exposure to pharmaceutical active compounds are limited up until now. Bu et al. established the calculation of PNECs in water based on the scarce analytical data available on pharmaceuticals and personal care products (PPCPs) in China (Bu et al. 2013). They estimated PNECs for diclofenac, ibuprofen, naproxen, and sulfamethoxazole to 50, 1,000, 10,000, and 590 ng L^{-1}, respectively. Only highest reported values for PPCPs in surface water in China actually exceed these boundaries. Bu et al. judged the risk for many PPCPs (including naproxen) regularly investigated in China as insignificant or low risk based on a risk quotient of measured environmental concentrations and PNECs. According to the maximum water concentrations, diclofenac posed a moderate to high risk. Nevertheless, further investigation is needed for a more sophisticated risk assessment of PPCPs involving the identification of priority compounds, further method development, and exposure models analog to the ones described for PFAAs (Bu et al. 2013). Bioassays may help in addition to chemical analysis for the identification of priority analytes and further exploration of PPCPs which are not targeted up until now. Tang et al. combined cell-based bioassays with chemical analysis and investigated treated water samples in Australia. They generated artificial mixtures of the detected wide range of micropollutants and concluded that the majority of specific receptor-mediated effects could be attributed to known chemicals. In contrast, only less than 1 % of cytotoxicity and oxidative stress response could be explained by the 269 quantified micropollutants (Tang et al. 2014; Tang et al. 2013). These results give an outlook in terms of upcoming analytical challenges and in evaluation of mixture toxicity which is neglected by regulatory limits for single compounds.

Conclusion

We developed and applied a novel sampling system for the enrichment of high volumes of water on compact shaped glass cartridges suitable for water bodies with low charge of analyte. The system performance proved to be satisfactory for the detection of PAHs, PCBs, OCPs, PFAAs, polar pharmaceutical residues, and polar pesticides at the same time. The differentiated analytical approach of the active sampler allowed us to recognize analyte breakthrough. Consequently, the results were used to determine minimum water concentrations and to estimate maximum water concentrations mathematically.

PAHs were identified as most abundant organic analytes. There was no clear dependence of PAH abundance on water depth found. Based on the determination of PAH diagnostic ratio, their origin was assigned to be pyrogenic from burning of coal, wood, or grass. In contrast, PCB levels resided at the low end of concentration near the LOD of our method. Therefore, hints for characteristic depth distribution were weak. Source analysis revealed that the detected PCB pattern matches legacy PCB production and usage in China. Within the group of OCPs, we observed a slight decrease in abundance with water depth which was above method precision and clearly above LOQ levels. We attributed this observation to the mixing state of the investigated water body. Historic sources have been suggested for some HCH and DDT contamination within the Yangtze River as well as intense shipping traffic and the involved antifouling paint. PFAAs which are considered as emerging organic pollutants could be detected with PFOA being the most dominant representative. We discussed the possible environmental threats originating from these compounds and concluded that industrial point sources are the main type of entrance of these substances into the environment in China. At the same time, PFAA levels at Maoping indicated that there was no PFAA source in direct surroundings of the sampling site. Our investigation on pharmaceutical residues in the Yangtze River revealed low absolute concentrations of the individual compounds which still corresponds to high mass fluxes due to the large water body. The depth distribution was diverse, and the results did not indicate characteristic trends. We highlighted environmental threats based on the emission of nonmetabolized antibiotics as well as the lack of information regarding environmental toxicity of many of the detected pharmaceutical active compounds. Polar pesticides were determined at higher relative concentration within this group of analytes, and agriculture was traded as diffuse input source into surface water.

All in all, we could demonstrate the abundance of a diverse mixture of organic compounds at the investigated sampling site in the Yangtze River. These compounds are partly toxic, persistent, and bioaccumulating or impose unwanted metabolic activity in the environment. Furthermore, it is not clear up until now how these complex mixtures of chemicals affect environmental and human health. Promising approaches like bioassays for cytotoxicity and oxidative stress may help to get an understanding of mixture effects. Nevertheless, further research has to incorporate both, chemical analysis and biological testing in order to draw a whole picture of organic environmental pollutants.

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