

Screening of organic micropollutants in raw and drinking water in the Yangtze River Delta, China

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Research

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Abstract

Background The vast occurrence of organic micropollutants in surface waters has raised concerns about drinking water safety and public health. The Tai Hu Basin region in China, a typical developing and populous area, is facing the challenge of water pollution. To ensure drinking water safety, the knowledge on how treatment techniques and raw water quality affect the quality of finished water must be improved. The aim of the current study was to evaluate drinking water quality in relation to source water origin and treatment strategies. Five drinking water treatment plants (DWTPs), using three different source waters in the Tai Hu River Basin, (i) Yangtze River, (ii) Wetland River Network, and (iii) Lake Tai Hu, were studied by analyzing 291 micropollutants in raw and finished water.

Results Major differences in water characteristics were observed among the source waters. The dominating group of micropollutants in the River Network was pesticides, while Yangtze was mainly polluted by flame retardants. The total concentration of poly- and perfluoroalkyl substances (PFASs) in Tai Hu water was far higher than in others. In total, 51 compounds were detected in finished water, with an overall average total concentration of $730 \pm 160 \text{ ng L}^{-1}$. The removal efficiency of the detected compounds in the DWTPs averaged $24 \pm 149\%$, which highlights the major challenge for the DWTPs to remove emerging organic micropollutants through current treatment processes.

Conclusions Our study showed that if the source water contains high levels of PFASs and organophosphorus flame retardants, even advanced treatment procedures are inefficient in removing the micropollutants, and the finished water may contain cumulative levels in the mg L^{-1} range. On the other hand, if pesticides and pharmaceuticals dominate, high overall treatment efficiencies may be obtained if using advanced treatment techniques. DWTPs are advised to use advanced treatment techniques or alternative water sources to guarantee the safety of drinking water. As surface water systems are highly impacted by upstream activities, efforts should also be made in the comprehensive water sector for improved surface water quality.

Background

Access to clean drinking water is an indispensable resource for people's daily lives and one of the United Nations' sustainable development goals. The presence of organic micropollutants in raw and finished drinking water have raised concerns about drinking water safety and public health, and there is a need to protect source water from ongoing and future contamination [1–4]. China, the most populous country on the globe, is extremely scarce in terms of per capita water resources. Therefore, how to ensure the safety of drinking water for the citizens is a great challenge that needs to be faced.

The Chinese population is unevenly distributed, with the main population distributed in the southeastern coastal areas. The Yangtze River, China's most important drinking water supply, enters the East China Sea 6,300 kilometers downstream the primary catchment area in the west. The river delta is centered on the City of Shanghai and comprises in total three provinces (Jiangsu, Zhejiang and Anhui) and 26 cities,

which together constitutes an important population center and development area. The Yangtze River Delta occupies an important maritime transportation hub, with the Tai Hu River Basin covering most of the area. Therefore, agriculture, industry and trade activities are well developed in this region. Since Yangtze River Delta is one of the most urbanized areas in China, with a population of 36 billion, this part of China exemplifies an area with extraordinary high anthropogenic impact.

Abundant but complex, surface water is main water source of drinking water in Yangtze River Delta and Tai Hu River Basins. A number studies have reported on the presence of organic micropollutants in surface waters in this region, e.g. antibiotics [5], phthalate esters [6], organochlorine pesticides [7], flame retardants [8, 9] and poly- and perfluoroalkyl substances (PFASs) [10]. PFASs [11], flame retardants [12] and some drug metabolites [13] have also been detected in finished drinking water, posing a health risks for citizens in this region.

The diversity of human activities in the Yangtze and Tai Hu River Basins has led to a complex mixture of persistent organic pollutants in the water. Treatment of raw water at DWTPs can reduce levels and complexity of the water. The removal efficiency is, however, highly dependent on treatment strategies [14], and conventional treatment has shown largely inefficient [15]. Although previous studies revealed the presence of a number of compound groups (e.g. PFASs) and pollution categories (e.g. pesticides and flame retardants) in both raw and drinking water from this region of China, the relative impact of groups of pollutants has not been thoroughly investigated.

The aim of the current study was to evaluate drinking water quality in relation to source water origin and treatment strategies. Five drinking water treatment plants (DWTPs) in the Tai Hu River Basin, using three different water sources and various treatment strategies were studied. Almost 300 organic micropollutants were analysed in water samples before and after treatment. The micropollutants represented a broad variety of usage categories and compound groups, such as pharmaceuticals and personal care products (PCCPs), pesticides, poly- and perfluoroalkyl substances (PFASs), flame retardants, industrial chemicals, hormones, phthalates, and food additives. There was a large variability in pollutant levels and complexity in both raw and finished water, and conclusions could be drawn about the suitability of treatment options for different source water qualities.

Methods And Materials

Reference standards and chemicals

In total 291 organic micropollutants were targeted including pharmaceuticals (n = 108), pesticides (n = 99), poly- and perfluoroalkyl substances (PFASs) (n = 18), flame retardants (n = 14), industrial chemicals (n = 14), hormones (n = 8), food additives (n = 6), phthalates (n = 5), personal care products (n = 4), surfactants (n = 4), fatty acids (n = 4), siloxanes (n = 2), stimulants (n = 2), isoflavones (n = 2), and contrast media (n = 1), (the informations are included in Supporting Information, Table A1). Additionally, 21 isotope labelled internal standards (ISs) were used (the informations are included in Supporting Information, Table A2). The pesticide standards (native and isotope-labelled) were purchased from

Teknolab Sorbent (Kungsbacka, Sweden) as accredited mixtures. Wellington Laboratories (Guelph, Canada) was the provider of the all PFAS standards. The remaining standards were bought from Sigma-Aldrich (Buchs, Switzerland) as solutions or crystalline of individual compounds, at analytical purity or higher, and were made into stock solutions in methanol or acetonitrile at a concentration of 1 mg mL^{-1} .

Ultrapure water (Milli-Q) for solid phase extraction (SPE) and mobile phases in the UPLC-system was generated in-house by a water purification system (Millipore; Bedford, USA). The buffers, acids and bases used for mobile phases were of LC-MS grade and purchased from Sigma Aldrich (Buchs, Switzerland). The methanol and acetonitrile (LC-MS grade) were from Merck (Darmstadt, Germany) and the ethanol (AnalaR quality) was purchased from VWR International (Fontenay-sous-Bois, France).

Sampling sites and sample collection

Raw water ($n = 1$) and finished water ($n = 1$, named 'Drinking water' in the figures) grab samples (4 L) were collected in September 2018 from five different drinking water treatment plants (DWTPs; N1(s), N2(s), N3-N5) located around Lake Tai Hu in the southeast of China and near the delta of the Yangtze River (Fig. 1). Additionally, two of the DWTPs were sampled a second time ($n = 2$, 4 L) three month later (December 2018; N1(w) and N2(w)). In the following, all N1 and N2 samples (September ($n = 1$) and December ($n = 2$); in total $n = 3 \times 2$ (raw and finished) $\times 2$ (sites) = 12 samples) are named as the Su Tai samples, and the N3, N4 and N5 samples are named the Wu Tai ($n = 1 \times 2 = 2$), the Yangtze ($n = 1 \times 2 = 2$) and RN ($n = 1 \times 2 = 2$) samples, respectively. The selected DWTPs provide drinking water to two cities in the Jiangsu province and one city in the Zhejiang province for in total about 8 million people. Detailed information on the five DWTPs including their source water and treatment strategies, are given in Table 1 and Fig. 1b. Note that the Yangtze DWTP receives its raw water from another DWTP, i.e. finished water, but transported approximately 36 km through a pipeline.

Figure 1 (a) Map showing the sampling locations at the Tai Hu Basin within the Yangtze River Delta (N1-N5). (b) DWTP treatment strategies and raw water sampling point. N1-N5: 5 different DWTP. PAC = powdered activated carbon, BACF = biological activated carbon filter, OZONE = ozone contactor, SED = flocculation/sedimentation, SAND = sand filter, COAG = aluminum coagulation, BP = biological pretreatment, FLO = flocculant, KMnO₄/Cl₂/Alum = chemical additive, SP = sampling point of raw water.

Table 1
Detailed information of the sampling locations

Sample name	Sampling site	Sampling Date	Source Water	Description of Raw Water
N1(s)	Su Tai	2018-09-30	Tai Hu	Water from Lake Tai Hu with pre-oxidation
N2(s)	Su Tai	2018-09-30	Tai Hu	Water from Lake Tai Hu
N3	Wu Tai	2018-09-30	Tai Hu	water from Lake Tai Hu with prechlorination
N4	Yangtze	2018-09-30	Yangtze River	Already treated at another DWTP, transported via pipeline (~ 36 km)
N5	RN	2018-09-30	river	river draining a wetland
N1(w)	Su Tai	2018-12-01	same as N1(s)	same as N1(s)
N2(w)	Su Tai	2018-12-01	same as N2(s)	same as N2(s)

The treatment processes at the five DWTPs and the sampling points for raw and finished water in the DWTPs are shown in Fig. 1b.

All samples were collected directly from tap in 4 L pre-cleaned glass containers. The pH was immediately adjusted to 3 using hydrochloric acid solution. The samples were transported to the laboratory at Tongji University, China, within 8 hours and stored at 4°C until sample preparation. One field blank sample was prepared using Milli-Q water in the same type of glass container.

Sample preparation

The water samples were filtered through 0.7 µm glass fiber filters (Grade GF/F circles 47 mm, Whatman, UK) including the field blank (Milli-Q water) control sample. Each sample was divided into four 1 L samples and extracted using solid phase extraction (SPE) cartridges in series: Oasis® HLB 6 cc Vac Cartridge (500 mg Sorbent per cartridge, Waters, USA) and Supelclean™ Coconut Charcoal SPE Tube (2 g, 6 mL, Sigma-Aldrich, USA). After loading and drying, the SPE cartridges were stored at -40°C. One randomly selected pair of SPE cartridges (out of the four pairs; consisting of one HLB and one Cocoa Charcoal cartridge), i.e. in total $18 \times 2 = 36$ cartridges plus the field blank, were shipped to the Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU, Uppsala, Sweden) and stored at 4°C until SPE elution. Before elution of the SPE cartridges, the 21 ISs were added (50 ng per IS) after dilution in Milli-Q water (approx. 40 mL).

The two cartridges (HLB and Cocoa Charcoal) were eluted separately, first with 10 mL of a mixture of acetone and hexane ($V_{\text{acetone}}:V_{\text{hexane}}=1:1$) and then 10 mL of methanol [16] (Figure A1 in the Supporting Information). Each eluate was collected in a separate glass tube. The HLB and Cocoa Charcoal eluates were combined separately and evaporated under a gentle stream of nitrogen until approximately 4 mL. The HLB and Cocoa Charcoal eluates were then combined and reduced to below 0.5 mL and transferred to an LC-MS vial. After each transfer step, the previous container was washed twice with methanol, which was also transferred to the next vial. The final extract was evaporated to less than 500 μL in the vial and diluted to 1 mL with Milli-Q water (Figure A1 in the Supporting Information).

Instrumental analysis

The instrumental analysis was performed as described previously Tröger et al [14]. In brief, a time-of-flight mass spectrometer (ToF) (Xevo G2-S, Waters, Micromass; Manchester, UK) coupled to a ultra-performance liquid chromatography (UPLC) system (Acquity H-Class with FTN injector; Waters, Milford, MA, USA) equipped with either an Acquity UPLC HSS T3-C18 column (positive ionisation mode) or UPLC BEH-C18 column (negative mode) was used. The mobile phase was a gradient containing Milli-Q water and acetonitrile, and the injection volume was 10 μL . All data were collected in MS^{E} -mode, with a resolution of $\sim 30\,000$ at 556.28 m/z using leucine enkephalin for the lock spray and UNIFI v1.8.2 as the software for data collection and evaluation. Details of the targeted compounds and the analytical procedure (including IS used for each analyte) are given in Table A3 in the Supporting Information.

Quality assurance and method performance

Calibration curves were run for each target compound with a concentration range of 0.1–120 ng L^{-1} . The concentrations in the samples were mostly within this range, except a few data for tris(2-chloroethyl) phosphate (TCEP), triethyl phosphate (TEP), and butyl dihydrogen phosphate and a high fraction of the laurilsulfate data, which reached higher levels (Supporting Information, Table A4). Data reported outside the calibration curve are marked in the table and should be interpreted with care.

The lowest level detected in the calibration curve was used as the method detect limit (MDL; Table A3 in the Supporting Information). The results of the four duplicate samples (raw and drinking water for N1(w) and N2(w), respectively) were tested for similarity using Student's paired t-test and the data for compounds detected above the MDL. There was no significant difference between the duplicates at a p-level of < 0.05 for any of the duplicates. The average relative standard deviation of the concentration data for the duplicate samples ($n = 4$ and 68 detected compounds) were within the range 16–30%.

The apparent recovery of the ISs, calculated from the relative responses of each IS in all samples, was on average 39% ($\pm 20\%$) (Table A2 in the Supporting Information). The levels in the field blank were generally low (on average $< 1\%$ of levels in samples), except for six compounds (laurilsulfate, lidocaine, CDP, TPHP, TBEP, laureth-5), for which occasionally higher levels were detected (35–75%) (Supporting Information, Table A4). The sample concentrations were corrected by subtracting the blank levels.

Results And Discussion

Raw water quality

In total 68 (23%) of the 291 targeted compounds were detected above the MDL in at least one raw water sample, and the number of detected compounds per sampling site ranged from 49 to 64. The detected micropollutants represented a wide variety of compounds including pesticides (n = 27), pharmaceuticals (n = 15), PFASs (n = 10), organophosphorus flame retardants (n = 7), food additives (n = 2), industrial chemicals (n = 2), surfactants (n = 3), and a fatty acid (n = 1), stimulant (n = 1). The detected compounds and their concentrations at each sampling point are given in Table A4 in the Supporting Information.

The number of detected micropollutants on a category basis were rather similar between the five DWTPs (Fig. 2; raw water), indicating a rather even distribution of emission sources in the Tai Hu Lake and the Yangtze River Delta area, with the exception of pesticides, which showed a higher number of detected compounds at the river network (RN) site. Overall, pesticides was the most detected pollutant category with on average $35\% \pm 2\%$ of all compounds detected (including all samples and sampling sites; n = 18), followed by pharmaceuticals ($19\% \pm 2\%$), PFASs ($17\% \pm 2\%$), 'Others' ($16\% \pm 2\%$: food additives, industrial chemicals, surfactants, stimulant and fatty acid), and flame retardants ($13\% \pm 1\%$).

Figure 2 (a) Total number of compounds detected above MDL in the raw water at the different sites. (b) The fraction of the number of detected compounds (in relation to total) shown on a compound category basis for each site. Compounds detected above MDL and their concentrations are given in Table A4 in the Supporting Information.

The total concentrations of the micropollutants in the raw water (Fig. 3) showed that the wetland river network (RN) was the most polluted site ($4\,000\text{ ng L}^{-1}$), followed by the Tai Hu Lake ($1\,600\text{ ng L}^{-1}$ for Su Tai and Wu Tai, respectively; same source using water). As expected, Yangtze, with its raw water already treated through several steps at another DWTP (Fig. 1b), showed the lowest total level ($1\,000\text{ ng L}^{-1}$).

Overall, the most prevalent micropollutant was sucralose (food additive), which contributed to about one quarter of the total concentration in the water from Su Tai and Wu Tai (Fig. 3), and even more in the water from the Yangtze River (48%; Fig. 3). In contrast, sucralose made up only 5% of the total concentration in the river network (RN). Sucralose is frequently detected in rivers and lakes all over the world, with a reported concentration range of $0.08\text{--}1.0\text{ }\mu\text{g L}^{-1}$ in Europe and $200\text{--}400\text{ ng L}^{-1}$ in north China [17].

There were also clear differences in the composition of the three source waters: Yangtze, river network and Tai Hu (Su Tai/Wu Tai). In the river network (RN), the fraction made up by pesticides was 71% of the cumulative concentration, which was significantly higher than at the other three sites (8–23%; Fig. 3). The cumulative concentration was $2\,800\text{ ng L}^{-1}$, which is almost 10 times higher than the average concentrations at Tai Hu ($340 \pm 100\text{ ng L}^{-1}$) and 30 times higher than the Yangtze River raw water (97 ng L^{-1}). The reason for the high dominance of pesticides in the river network (RN) can be attributed to the land use in the river catchment, which has a high proportion of agricultural areas. Moreover,

although both Su Tai and Wu Tai are using Lake Tai Hu raw water, the Su Tai samples showed higher levels ($370 \pm 47 \text{ ng L}^{-1}$; 23% of total) than that at Wu Tai (130 ng L^{-1} ; 8%). The pesticides with the highest concentrations at RN were carbendazim, imidacloprid, bentazon and azoxystrobin, which were detected at levels in the range $420\text{--}670 \text{ ng L}^{-1}$. Overall (all sites), other common pesticides included bentazon ($85 \pm 47 \text{ ng L}^{-1}$), carbendazim ($60 \pm 40 \text{ ng L}^{-1}$), DEET ($38 \pm 32 \text{ ng L}^{-1}$) and atrazine ($32 \pm 11 \text{ ng L}^{-1}$) which showed high detection frequency in source waters. These concentrations are higher those reported from Europe, where e.g., DEET averaged 4.0 ng L^{-1} and atrazine averaged 2.2 ng L^{-1} in a study by Robles-Molina et al. (2014) [18].

Figure 3 Total concentrations of detected micropollutants and percentage composition of sucralose and main compound categories in raw and drinking (finished) water for each site, with the most northern on top (N4), then going south (N3, N1 + N2, and N5). Detected compounds above MDL and their concentrations are shown in Table A4 in the Supporting Information. PES = pesticide, PHAR = pharmaceutical, FLA = flame retardant, PFAS = poly- and perfluoroalkyl substances, OTH = Others (food additive, fatty acid, surfactant, industrial chemical), ALL = all detected compounds in each DWTP.

The number of detected PFASs differed between the sampling sites, with the lowest number at the Yangtze River site ($n = 7$; 14%), whereas for other raw waters, the number of detected PFASs ranged from 9 to 10 (18%-18%), indicating upstream point sources of PFASs. The average concentration of \sum PFASs in the Tai Hu raw water ($168 \pm 22 \text{ ng L}^{-1}$) was significantly higher (one-sided Student's t-test) than the level in the Yangtze River water (20 ng L^{-1}), and the water from the wetland river network (56 ng L^{-1}) ($p = 0.0001$). Perfluorohexane sulfonic acid (PFHxS) was dominant in the Tai Hu water (60% of the \sum PFASs), whereas perfluorooctanoic acid (PFOA) was dominant in the water from wetland river network (63%). On the other hand, PFHxS, PFOA and perfluorobutanoic acid (PFBA) were equally dominant in the Yangtze River water (22%, 23% and 27%, respectively). The PFAS concentrations were generally comparable to other river water concentrations in China [19] or in the river Rhine watershed in Europe [20], but lower than other parts of the world such as Sweden [21], or India [22].

Organophosphorus flame retardants was the major group of compounds in the Yangtze and Wu Tai water, with cumulative concentrations of 290 ng L^{-1} and 405 ng L^{-1} (28% and 26%), respectively. These levels are similar to that at Su Tai ($266 \pm 48 \text{ ng L}^{-1}$, but there the fraction of flame retardants was lower (16%). Previous research has also reported frequent detection of organophosphorus flame retardants, e.g., in Yangtze River water [23] and river water in Sweden [24]. Since the use of brominated flame retardants is decreasing because of environmental and human health risks, organophosphorus flame retardants has become widely produced and used since the 1970s [8]. Phosphorus flame retardants have been detected in abiotic compartments as well as in living organisms including humans [25, 26], indicating potential risk for environmental and human hazards.

The concentrations of the compound category 'Others', such as industrial chemicals (Table A4 in the Supporting Information), were in the range $250\text{--}400 \text{ ng L}^{-1}$. The most dominating compound was butyl

dihydrogen phosphate, a surface-active agent e.g., used as additive in lubricants and paints, with an overall (all sites) average concentration of $140 \pm 48 \text{ ng L}^{-1}$.

An overall observation was that there was a composition change from north to south, i.e. going from Yangtze (N4), to Wu Tai (N3) to Su Tai (N1 + N2) to RN (N5), with an increasing proportion of pesticides and a decreasing proportion of flame retardants in the samples. This tendency shows that local emission sources and land use play a large role for the overall pollution. It also suggests that the Yangtze River in the north and the river network in the south may influence different parts of Lake Tai Hu.

Drinking water quality

The number of micropollutants detected above MDL decreased with on average 22% through the drinking water treatment process (Fig. 2a). In total, 51 compounds were detected in at least one sample including pesticides ($n = 17$), pharmaceuticals ($n = 9$), PFASs ($n = 10$), organophosphorus flame retardants ($n = 7$), food additives ($n = 2$), industrial chemicals ($n = 2$), surfactants ($n = 3$), and a fatty acid ($n = 1$). Similar to the raw water, the pesticide group was the most prevalent pollution category with on average 13 compounds per sample, followed by PFASs ($n = 10$), flame retardants ($n = 7$), pharmaceuticals ($n = 6$), and food additives ($n = 1$).

The total concentrations of the micropollutants mostly decreased but also increased through the drinking water treatment process (Fig. 3, bar charts). The overall ($n = 9$) average total concentration was $730 \pm 160 \text{ ng L}^{-1}$, and the concentration range was $720\text{--}2700 \text{ ng L}^{-1}$. As in the raw water, sucralose dominated the concentration in every sample with a top concentration of 1900 ng L^{-1} (N1(s); 71% of total) and an overall average concentration of $630 \pm 520 \text{ ng L}^{-1}$, which corresponds to a proportion of 30% or more in most of the samples. The average concentration is far higher than levels found in drinking water from northern China ($110\text{--}160 \text{ ng L}^{-1}$) [27], and also higher than waste water treatment plant (WWTP) influents in some American cities ($78\text{--}120 \text{ ng L}^{-1}$) [28].

The cumulative concentrations of other detected micropollutants (without sucralose) were in the range of $540\text{--}1100 \text{ ng L}^{-1}$ including all sites. The lowest value was 550 ng L^{-1} (RN), which is approximately 10 times higher than the micropollutant concentration in drinking water from northern Europe (Sweden) [15], where a similar set of compounds were targeted (134 compounds and an overlap of 43% with the current study). Because of the relatively high removal rates of pesticides and pharmaceuticals, the PFASs, flame retardants and the category 'Others' were the dominant micropollutants in the drinking water (Fig. 3).

The concentration of \sum PFASs ranged from 110 to 200 ng L^{-1} at N1-N3 (Tai Hu Basin water; Su Tai/Wu Tai), and was 27 ng L^{-1} in the sample from N4 (Yangtze River water). The PFHxS was the dominant PFAS in Tai Hu ($60\text{--}120 \text{ ng L}^{-1}$, N1-N3), while PFBA was the highest PFAS in Yangtze River (11 ng L^{-1}) and PFOA was the highest in RN water (RN, 54 ng L^{-1}). The PFAS concentrations in drinking water were generally higher than those in drinking water from USA, Brazil, Spain, and France [29–31].

It is clear that flame retardants was the main micropollutant category in drinking water from the Yangtze River (370 ng L^{-1} ; 42% of total) and generally contributed to more than 20% of the total concentration of all compounds in the drinking water at all sites, except for N1(s). Overall (all sites), the compounds with the highest concentrations were TEP (average 120 ng L^{-1}) and TCEP (average 96 ng L^{-1}). These two organophosphorus flame retardants are at almost the same level as in drinking water in the Netherlands ($48\text{--}100 \text{ ng L}^{-1}$) [13]. Another compound with high concentration was butyl dihydrogen phosphate (average 130 ng L^{-1}), an industrial chemical, rarely (if ever) reported as present in drinking water before. The occurrence of micropollutants in drinking water is dependent on the quality of water source (Fig. 3) as well as on the treatment efficiency at the DWTP. In the next section, the impact of the treatment process is examined.

Removal efficiency

The removal efficiencies for all compounds at all DWTPs are given in Table A5 in the Supporting Information and are illustrated in Fig. 4a, b. The overall average removal efficiency of all compounds averaged $24 \pm 149\%$ (N1-N5, $n = 9$, including the two extra samples and the duplicates at N1 + N2). The pesticides averaged $65 \pm 50\%$ and the pharmaceuticals $74 \pm 49\%$, while the removal of other compound categories were significantly lower ($p < 10^{-8}$, two-sided Student's t-test), with average efficiencies of $3 \pm 99\%$ for 'Others' (food additives, surfactant, industrial chemicals, fatty acid), $-1 \pm 13\%$ for flame retardants, and $-140 \pm 329\%$ for PFASs. Thus, the flame retardants showed negative treatment efficiencies, which means they boosted through the treatment process. Similarly, the removal of PFASs was often inefficient or even negative at the investigated DWTPs. Previous studies have shown that conventional treatment techniques are inefficient in removing PFASs [32]. Negative removal efficiency may be explained by time-dependent concentrations and the lag time between sampling raw and finished water, degradation of PFAS precursors to persistent PFASs [33] and desorption/breakthrough of PFASs from granular activated carbon (GAC) or other filter types within the DWTP [34].

There were no significant differences in the removal efficiencies of all detected compounds among the five DWTP ($p > 0.06$, two-sided Student's t-test), although the DWTPs used different treatment strategies (Fig. 1b and 4a). It should be noted that three of the DWTPs use ozonation, i.e. advanced treatment technology; yet removal efficiencies are moderate to low. This demonstrates the major challenge in removing organic micropollutants through modern drinking water treatment technologies.

Figure 4 Treatment efficiency for (a) each compound category for DTWPs with similar treatment strategy and (b) DWTPs with similar treatment strategy per compound category. PES = pesticide, PHAR = pharmaceutical, FLA = flame retardant, PFAS = poly- and perfluoroalkyl substances, OTH = Others (food additive, fatty acid, surfactant, industrial chemical), ALL = all detected compounds in each DWTP.

The removal efficiencies among different treatment strategies are shown in Fig. 4b. N1, N2 and N5 have ozone treatment and biological activated carbon filter (BACF) in contrast to N3 and N4. Additionally, N5 has an extra biological pretreatment step as compared to N1-N4. The removal efficiencies of the

pesticides and the pharmaceuticals at N3 + N4 are significantly lower than at N1 + N2 and N5 ($p < 0.05$, two-sided Student's t-test), which shows that the conventional treatment (sedimentation, filtration and disinfection) cannot remove pesticides and pharmaceuticals in water effectively. On the other hand, N1 + N2 and N5 with their more advanced treatment process (including ozonation) are successful with these two substance groups. This is also illustrated for N5 in Fig. 3, with a 5-fold drop in total concentration from raw to drinking water (from 3990 to 720 ng L^{-1} , going from 76% 'pesticides + pharmaceuticals' of total to 17%). The removal efficiency of flame retardants in N5 was also rather efficient, with significantly higher efficiency than N1 + N2 and N3 + N4 ($p < 0.02$, two-sided Student's t-test). This suggests that the biological treatment have the ability to remove flame retardants in water.

The removal efficiency of PFASs was often unchanged or even negative at the investigated DWTPs. Previous studies have shown that conventional treatment techniques are not efficient in removing PFASs [32]. Negative removal efficiency can be explained by time-varying concentrations and the sample were only taken from one point and time, degradation of PFAS precursors to persistent PFASs [33] and desorption of PFASs from granular activated carbon (GAC) or other filter types within the WWTP [34].

Potential human health risks

Sucralose, an artificial sweetener, discovered in 1976, is widely used in food industry, because of its perfect sweetness and stability. Sucralose has been shown to be resistant to metabolism and is a persistent, ubiquitously occurring pollutant in aquatic environments [35]. It is commonly detected in wastewater, surface water, groundwater [36, 37] and even in drinking water [38]. The concentration ranged from hundreds ng L^{-1} to $\mu\text{g L}^{-1}$ levels. Sucralose has been tested for toxicity, and there are some reports on that exposure may led to negative effects e.g., on locomotion and physiological behavior of crustaceans [39]. However, there is a lack of studies focusing on chronical and low-dose effects of sucralose [40, 41]. Rahn et al. [42] found that sucralose can degrade and produce amounts of chloropropanols (3-monochloropropanediol and 1,2- and 1,3-dichloropropanols) under thermal decomposition. These metabolites are known as a potentially toxic class of compounds that may cause cancer. Another study indicated that ingestion of sucralose can affect the glucose metabolism of obese people who rarely use non-nutritive sweeteners [43]. More studies on sucralose are needed, and it is important to consider the potential toxicity of its metabolites, which e.g., are formed during cooking under high temperature, which is a common practice in China.

Conclusions

Our study showed that the finished (drinking) water quality is dependent both on source water quality and treatment strategies. If the source water contains high levels of PFASs, flame retardants and other pollutants (e.g. sucralose and butyl dihydrogen phosphate), even advanced treatment procedures, including e.g. ozonation, are inefficient and the finished water may contain cumulative micropollutant levels in the mg L^{-1} range. On the other hand, if the dominating pollution categories are pesticides and pharmaceuticals, high overall treatment efficiencies can be obtained if using advanced treatment steps,

while DWTPs using conventional treatment are largely not successful in removing the micropollutants. DWTPs have the tremendously challenging task of purifying reused water, i.e. water that was contaminated by many upstream pollution sources such as WWTP and industrial effluents. For improved overall drinking water quality, it is imperative that water quality comes into focus in the water sector as a whole. DWTPs should pay attention to the characteristic of their source water and make efforts to use efficient treatment processes, enhancing the quality of finished water. In our study, organic micropollutants were found in drinking water at cumulative levels from 0.7 mg L^{-1} up to 2.7 mg L^{-1} , clearly demonstrating the challenge with organic micropollutants in the water from source to tap. Thus, advanced drinking water treatment techniques or alternative drinking water source areas are needed to guarantee safety of drinking water.

List Of Abbreviations

Drinking water treatment plant (DWTP)

Waste water treatment plant (WWTP)

Ultra-performance liquid chromatography (UPLC)

Time-of-flight mass spectrometer (ToF MS)

Method detect limit (MDL)

Solid phase extraction (SPE)

Phthalate esters (PAEs)

Organochlorine pesticides (OCPs)

Poly- and perfluoroalkyl substances (PFASs)

Tris(2-chloroethyl) phosphate (TCEP)

Triethyl phosphate (TEP)

Perfluorohexane sulfonic acid (PFHxS)

Perfluorooctanoic acid (PFOA)

Perfluorobutanoic acid (PFBA)

Biological activated carbon filter (BACF)

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable.

Availability of data and material

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

HR was the major contributor in experiments, data analysis and manuscript writing. HR and DY designed the study. RT helped with the instrumental analysis, micropollutant quantification, and quality assurance / quality control of data. KW and LA contributed to data evaluation and manuscript writing. KW and DY contributed to improvements of the manuscript. All authors read and approved the final manuscript.

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Figures



Figure 1

(a) Map showing the sampling locations at the Tai Hu Basin within the Yangtze River Delta (N1-N5). (b) DWTP treatment strategies and raw water sampling point. N1-N5: 5 different DWTP. PAC = powdered activated carbon, BACF = biological activated carbon filter, OZONE = ozone contactor, SED = flocculation/sedimentation, SAND = sand filter, COAG = aluminum coagulation, BP = biological pretreatment, FLO = flocculant, KMnO₄/Cl₂/Alum = chemical additive, SP = sampling point of raw water. Note: The designations employed and the presentation of the material on this map do not imply the

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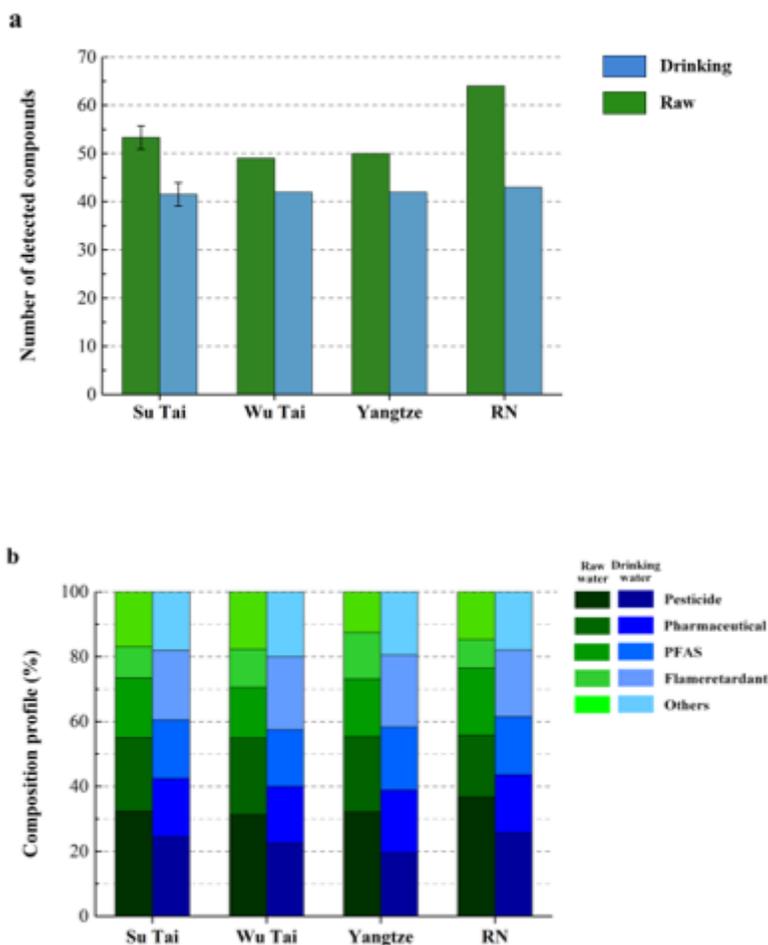


Figure 2

(a) Total number of compounds detected above MDL in the raw water at the different sites. (b) The fraction of the number of detected compounds (in relation to total) shown on a compound category basis for each site. Compounds detected above MDL and their concentrations are given in Table A4 in the Supporting Information.

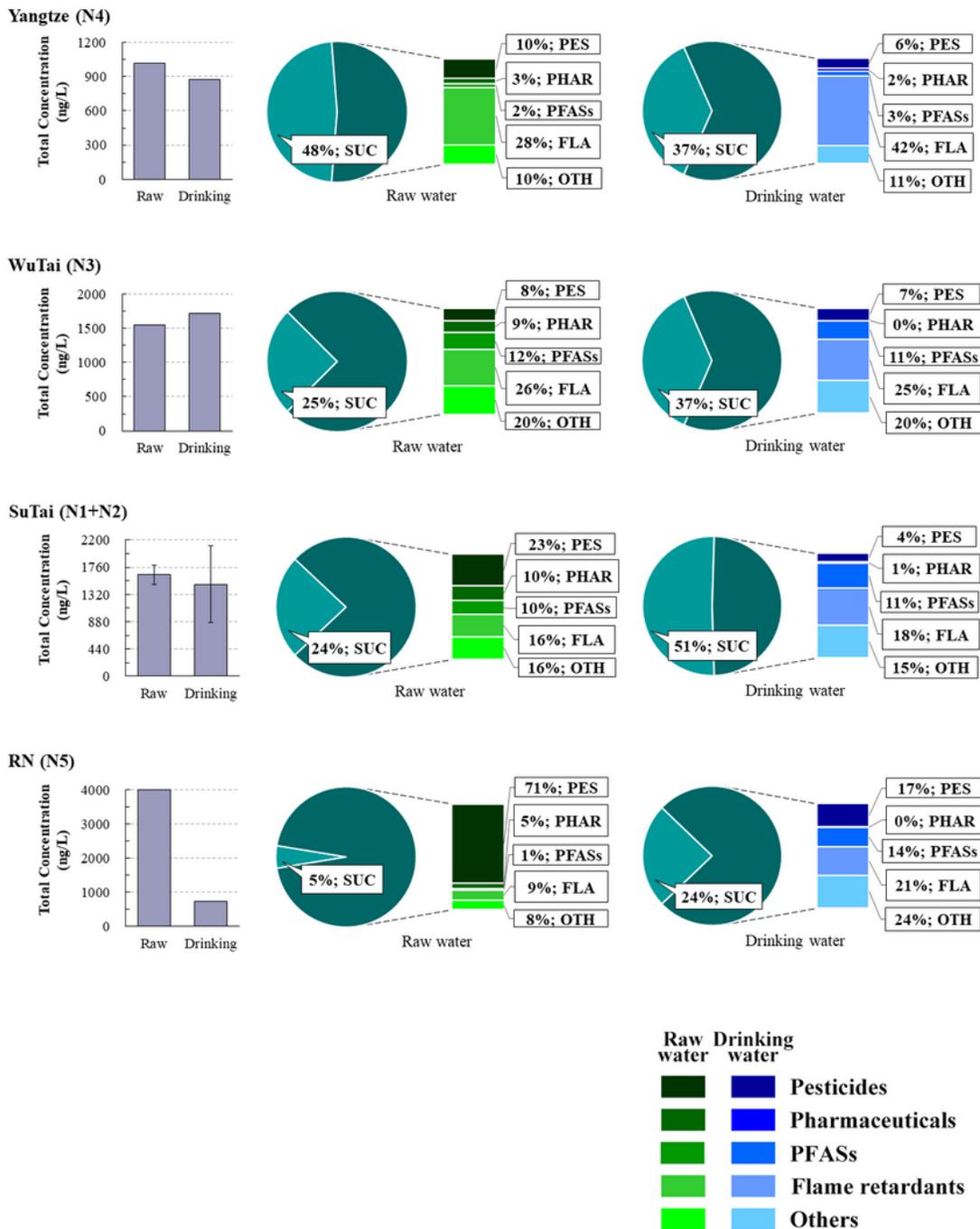


Figure 3

Total concentrations of detected micropollutants and percentage composition of sucralose and main compound categories in raw and drinking (finished) water for each site, with the most northern on top (N4), then going south (N3, N1+N2, and N5). Detected compounds above MDL and their concentrations are shown in Table A4 in the Supporting Information. PES = pesticide, PHAR = pharmaceutical, FLA =

flame retardant, PFAS = poly- and perfluoroalkyl substances, OTH = Others (food additive, fatty acid, surfactant, industrial chemical), ALL = all detected compounds in each DWTP.

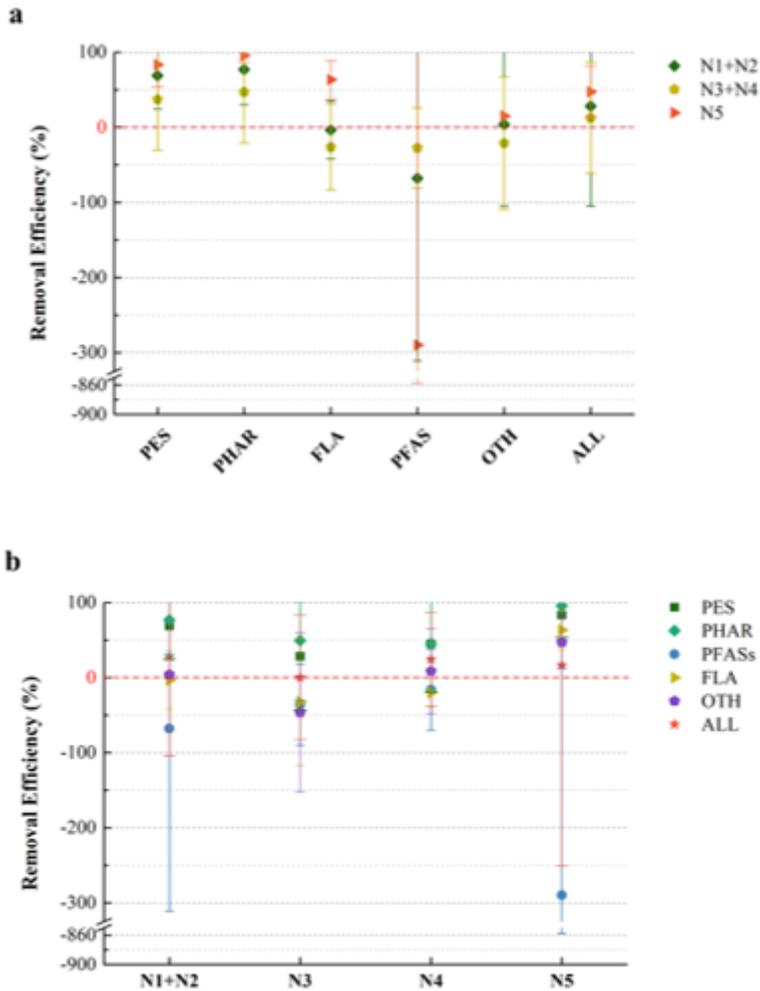


Figure 4

Treatment efficiency for (a) each compound category for DTWPs with similar treatment strategy and (b) DWTPs with similar treatment strategy per compound category. PES = pesticide, PHAR = pharmaceutical, FLA = flame retardant, PFAS = poly- and perfluoroalkyl substances, OTH = Others (food additive, fatty acid, surfactant, industrial chemical), ALL = all detected compounds in each DWTP.

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