



Original Research Article

Unveiling the existence and ecological hazards of trace organic pollutants in wastewater treatment plant effluents across China

Jianchao Liu^{a,1}, Fang Yang^{b,1}, Yuanfei Cai^a, Guanghua Lu^{a,*}, Yiping Li^a, Ming Li^b, Linhua Fan^c, Li Gao^d^a Key Laboratory of Integrated Regulation and Resource Development of Shallow Lakes of Ministry of Education, College of Environment, Hohai University, Nanjing 210098, China^b College of Natural Resources and Environment, Northwest A&F University, Yangling 712100, China^c School of Engineering, RMIT University, Melbourne, VIC 3001, Australia^d Institute for Sustainable Industries and Liveable Cities, Victoria University, Melbourne, Victoria 8001, Australia

ARTICLE INFO

Keywords:

Wastewater treatment
Effluent
Trace organic pollutants
Ecological risk assessment

A B S T R A C T

The presence of trace organic pollutants in the effluent of wastewater treatment plants (WWTPs) poses considerable risks to aquatic organisms and human health. A large-scale survey of 302 trace organic pollutants in the effluent of 46 Chinese WWTPs was conducted to gain an improved understanding of their occurrence and ecological risks. The survey data showed that 216 compounds in 11 chemical classes had been detected in effluents. The sum concentrations of the trace contaminants in effluent ranged from 1,392 ng/L to 35,453 ng/L, with the maximum concentration of perfluoroalkyl substances (PFASs) recorded as the highest (30,573 ng/L), which was markedly less than the reported 185,000 ng/L for the 38 American WWTPs. The concentration of bisphenol analogs (BPs) was up to 4,422 ng/L, significantly higher than those reported in France, Germany, Japan, Korea, and the U.S. PFASs and BPs were the major pollutants, accounting for 59% of the total pollution. Additionally, a total of 119 contaminants were found to have ecological risks ($RQ > 0.01$). Among these, 23 contaminants ($RQ > 1.0$) warrant higher attention and should be prioritized for removal. This study lists valuable information for controlling contaminants with higher priority in WWTP effluent in China.

1. Introduction

Wastewater treatment plants (WWTPs) collect and purify domestic and industrial wastewater, which is a major engineering measure to prevent water pollution [1]. WWTPs are required to meet stringent discharge standards to keep the quality of surface water within a safe and acceptable range. These standards primarily control aerobic organics (such as Chemical Oxygen Demand and Biochemical Oxygen Demand) and nutrients (N and P) [2]. At the same time, heavy metals are also an important evaluation index, particularly for industrial wastewater [3]. However, until now, some trace organic pollutants have rarely been included in assessment and management, especially in some underdeveloped areas [4, 5]. It has been documented that the effluents of WWTPs are a significant source of these trace pollutants, leading to concerns about their ecological and environmental risks.

Trace organic pollutants generally refer to a large group of organic pollutants present in the aqueous environment at concentrations of ng/L

or $\mu\text{g/L}$ [6]. Trace pollutants pose a serious concern to both the environmental and ecological risks and human health since they may be long-lasting [7], bioaccumulative [8,9], and highly toxic [6]. Traditional persistent organic pollutants (POPs) like polycyclic aromatic hydrocarbons (PAHs), bisphenol analogs (BPs), polychlorinated biphenyls (PCBs), endocrine disrupting chemicals (EDCs), UV filters (UVs), and organochlorine pesticides (OPs) are among these trace pollutants, as well as the emerging organic pollutants of concern, including perfluoroalkyl substances (PFASs), antibiotics, plasticizers (PAEs), flame retardants (FRs), pharmaceutical products (PhAs), and others [8]. The above-mentioned groups of trace organic contaminants include thousands of compounds. In particular, EDCs, antibiotics, and PhAs have been proven to diffuse across the membrane in the process of WWTP. In addition, other pollutants with high hydrophobicity, polarity, and neutral charges could be adsorbed to the membrane polymer [10]. Trace organic pollutants generally have antibacterial properties and inhibit microbial degradation in the treatment process [11]. These organic pollutants are impossible to

* Corresponding author.

E-mail: ghlu@hhu.edu.cn (G. Lu).¹ Jianchao Liu and Fang Yang contributed equally to this work.

remove completely at WWTP owing to the above reasons and can further discharge effluent into natural aqueous.

As a result of recent developments in analytical technology, a significant amount of work has been done on monitoring and assessing the risks of trace organic pollutants in the effluent of WWTPs [1,12,13]. Most previous studies focused on assessing the risk of one type of trace organic pollution at only one location [13–16] gathered information on the make-up of 473 trace organic pollutants found in surface water, the ocean, and ground-water globally, highlighting 53 pollutants that require immediate global control. Zhou et al. [17] measured the concentrations and risks of 17 PFASs, 25 pharmaceutical and personal care products (PPCPs), and 8 heavy metals in the inlet and outlet water of six WWTPs in China and found that the risk of PPCPs was 1–2 orders higher than that of PFASs, except for heavy metals. However, results are barely transferrable to specific locations and aquatic bodies due to the study's global approach to world pollution situation analysis and the absence of systematic data within a region.

To date, there has not been a systematic survey to analyze major chemical classes at the level of hundreds of trace organic pollutants in the effluent of dozens of WWTPs in a single country. Some major knowledge gaps remain in the area including the relative levels of ecological risks of different chemical classes/compounds of the trace organic pollutants and the control strategies for the pollutants exhibiting higher risks. To address the knowledge gaps, it is ideal to conduct large-scale surveys of trace organic pollutants and their ecological risk levels in the effluent of many WWTPs for wide areas, particularly in regions where limited information has been obtained previously. This would allow the results to be obtained with consistent sampling and analytical methods. Such studies would be more helpful for water and environmental managers to gain an improved understanding of the occurrence and ecological risks of trace contaminants and develop effective measures to control the high-risk contaminants identified.

As such, this study aimed to determine the chemical classes and levels of the contaminants in the effluent of 46 WWTPs in China and investigate the impact of spatial differences on the survey results. The ecological risks of trace organic pollutants were quantified to compare the differences in ecological risks under different spatial conditions. The top contaminants that resulted in a high ecological risk were determined, which would significantly enrich the database for monitoring and developing control measures for the high-risk trace organic pollutants in China.

2. Materials and Methods

2.1. Chemicals and reagents

A total of 302 trace organic contaminants in 11 chemical classes including 30 antibiotics, 137 pesticides, 15 PFASs, 10 UVs, 14 pharmaceuticals, 14 PAEs, 9 BPs, 16 PAHs, 23 EDCs, 16 OPs, and 18 PCBs, were quantified for the effluents of 46 WWTPs in China. Standard pollutants were purchased from Jiangsu Aikon Co., Ltd. and Shanghai Anpel Co., Ltd. The purity of these contaminants was all higher than 97.0%. There were 216 trace organic contaminants that were detected in this study. The detailed full names and corresponding abbreviations, Chemical Abstracts Service, purity, provider, and detection rates of chemical compounds are summarized in the Appendix file.1. Stock solutions of the standards of the compounds were prepared separately with methanol. A mixed standard stock solution was configured for each chemical class, and the concentration of each contaminant was 1 mg/L.

2.2. Sampling

Water samples were collected from the final effluents of the WWTPs from June 1 to June 30, 2022, and the locations of 46 WWTPs are shown in Fig. S1. Each water sample was directly collected in a 1-L brown glass bottle (10 bottles) with screw caps with Teflon liners, and no air bubbles should be introduced during the sampling process. The water samples were filled to the mouth of the bottles, and upon tightening the caps, the

bottles were turned over for inspection. If any air bubbles were found, the samples were re-collected. To prevent organic pollutants from degrading due to high temperatures (above 30 °C) and strong light, water samples should be collected and stored for a short time. The sample storage bottles should be kept away from light as much as possible. In summer, ice should be used in the storage box to lower the temperature. The samples should be mixed from multiple points and processed in the laboratory within 24 h of storage.

2.3. Pre-treatment and analyses of samples

The extraction and determination of pesticides [18], PAHs [19], antibiotics and pharmaceuticals [20], PFASs [21], BPs [22], PAEs [23], UVs [23], EDCs [24], PCBs [25], and OPs [26] are modified based on corresponding references. Waters Oasis HLB (500 mg 6 cc) and Waters Oasis WAX (200 mg 6 cc) solid-phase extraction columns were used to enrich 1,000 mL of filtrate for the target contaminants. Briefly, HLB columns were used to collect pesticides and PAHs, antibiotics, pharmaceuticals, BPs, PAEs, UVs, EDCs, PCBs, and OPs by preconditioning with 5 mL of methanol (MeOH) and 5 mL of ultra-pure water. While WAX columns for collecting PFASs were first activated using methanol containing 0.10% ammonium hydroxide (NH₃·H₂O). The column tips were kept wet during the activation. After activation, the filtrate was passed through the HLB or WAX tandem columns at 3–5 mL/min. After enrichment, the column was blown dry using nitrogen gas to reduce moisture interference. Then, the eluates were collected in polypropylene (PP) tubes. In particular, WAX elution was performed with 10 mL MeOH containing 5.0% NH₃·H₂O, and HLB elution was used with 10 mL MeOH at 1 mL/min. The eluates were blown using nitrogen to near dryness, fixed to 1 mL with methanol (except PAHs, PCBs, DDTs), and hexane (for PAHs, PCBs, DDTs), filtered using 0.22 μm organic phase filter membranes, placed in 2 mL PP injection vials, and stored at –20 °C for measurement. The recovery of the extraction methods for the compounds of each chemical class was determined to validate the methods. The extraction recovery range of 40%–140% and each chemical class of pollutants under different concentrations are shown in Table S1.

The trace organic pollutants, such as pesticides, antibiotics, pharmaceuticals, PFASs, BPs, PAEs, UVs, EDCs, and OPs, were mainly determined by using HPLC-MS/MS (Waters ACQUITY UPLC Xevo TQ), and like PAHs, PCBs, and DDTs were measured by GC-MS/MS (Agilent GC-MS 7890B 5977). The main chromatographic and mass spectrometry parameters, including column, mobile phase, and ionization mode, were set differently for different chemical classes of pollutants and were given in Supporting Information.

2.4. Quality control

In this study, one process blank was run for each batch of 10 samples during sample pre-treatment. In addition, instrument blanks were prepared to monitor the residual effects or contamination of target compounds and to ensure the confidence of the analytical methods. One instrument blank was set for each batch of 10 samples during instrumental analysis. The concentration of the target compounds in the samples was quantified by standard methods. The standard curve was set in the concentration range of 0.1 ng/L–10 μg/L (the concentrations of the standards were 0.1 ng/L, 1 ng/L, 10 ng/L, 50 ng/L, 100 ng/L, 500 ng/L, 1,000 ng/L, and 10,000 ng/L, respectively). If the concentration of samples was beyond the standard curve, the samples should be re-diluted to ensure a concentration range of 0.1 ng/L–10 μg/L. The linearity and reproducibility of the standard curve for each contaminant were determined to meet the requirements ($R^2 \geq 0.99$) before each batch of samples was tested. The instrumental limit of quantification (LOQ) was defined as the concentration corresponding to a 10-fold signal-to-noise ratio (S/N) of the target compound at the lowest point of the constructed standard curve. The method detection limit (MDL) was 3 times the standard deviation of the process blank. For targets where the process blank was not detected, the MDL was calculated directly using its LOQ divided by the

corresponding enrichment factor. All values below the MDL were indicated by n.d. as non-detected in this study.

2.5. Ecological risk evaluation

The ecological risk quotients of each chemical class of pollutants or the various pollutants in the aquatic system were determined by using the risk entropy value method as reported in the literature in Eq. 1 [1,27]. The risk quotient (RQ) value represents the ratio of the actual measured concentration (MEC) of a single contaminant to the predicted no-effect concentration (PNEC) of that contaminant. The PNEC is calculated by taking the lowest toxicity data of at least three species [28,29], containing fish, algae, bacteria, invertebrate, or daphnia. The PNEC values used in this study were obtained mainly from the literature (see Appendix file. 2 for details of PNEC values for various contaminants). The values of $RQ \geq 1.0$, $0.1 < RQ < 1.0$, and $RQ \leq 0.1$ indicate the ecological risk levels of high, medium, and low risk, respectively.

$$RQ = \frac{MEC}{PNEC} \tag{1}$$

In this study, the ecological risk of a WWTP (RQ_{Total}) for each chemical class pollutant was determined as the sum of the RQ values of individual compounds detected in the WWTP, as shown in Eq. 2 [30].

$$RQ_{Total} = \sum_{i=1}^n RQ_i \tag{2}$$

3. Results

The spatial distribution of the concentration levels of 11 different chemical classes of trace organic pollutants at the 46 sampling locations is shown in Figs. 1a and b. Among all chemical classes under this study, the concentrations of UVs, PAHs, EDCs, and PCBs were in the range of n.d. to 200 ng/L. The concentrations of PFASs, BPs, and PAEs were higher than 200 ng/L. The highest concentrations of PFASs and BPs were more

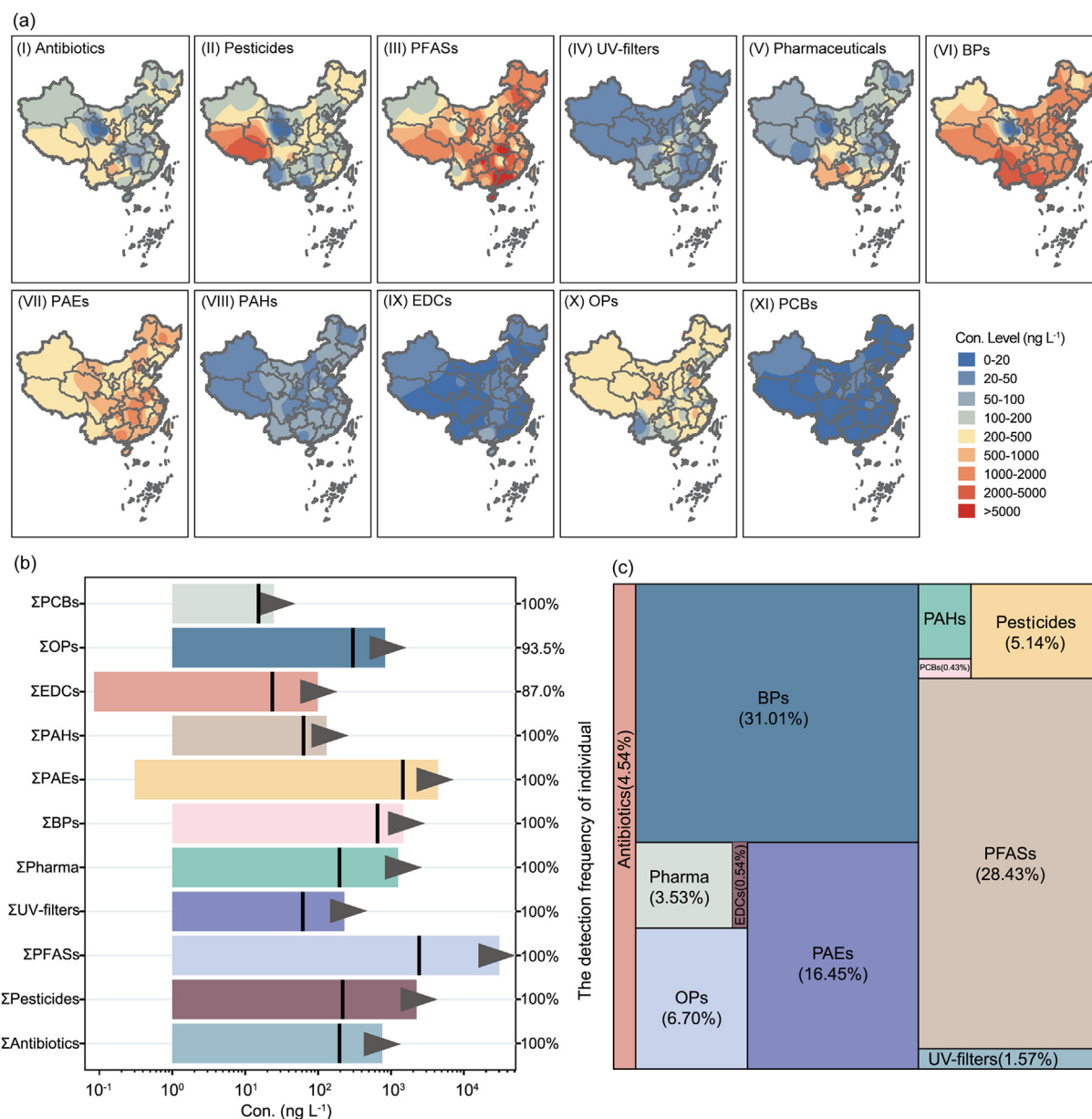


Fig. 1. The spatial distribution of concentrations range of target pollutants (a), detection rates (b), and concentration percentages (c) of 11 different chemical classes of trace organic pollutants in WWTP effluents. The vertical bar represents the average concentration of each chemical class, and the triangle points to the right axis, indicating the detection rate (b). WWTP, wastewater treatment plant.

than 5,000 ng/L. The detection rates of 11 different chemical classes of trace organic pollutants in 46 WWTPs are shown in Fig. 1b. These detection rates were observed to be 100% for all classes except for OPs (93.5%) and EDCs (87.0%). These results indicated the high occurrence of the 11 different chemical classes of trace organic pollutants in the effluents of all WWTPs under this study. Additionally, the pollution levels (based on the concentration percentage calculation) of these 11 chemical classes are shown in Fig. 1c. BP accounted for 31.01% with the highest pollution level, followed by PFASs (28.43%) and PAEs (16.45%). The total concentration of BPs, PFASs, and PAEs could be up to 75% in 11 chemical classes of pollution. In general, the results obtained in this study were consistent with several previous studies [13,28,31,32]. Notably, in the studied areas in China, the residue of trace organic pollutants in the effluent of domestic wastewater should gain more attention, especially for BPs, PFASs, and PAEs.

The concentration ranges and detection rates of various contaminants are shown in Fig. 2. For the chemical class of antibiotic pollutants, the detection rate of ofloxacin (OFX) was the highest (100%), and the detection rates for roxithromycin (ROX), erythromycin (ERY), and sulfamethoxazole (SMZ) were higher than 90%. The maximum detection concentration for ROX was 250 ng/L (Fig. 2a). The detection rates of three pesticides, difenoconazole (DFC), propiconazole (PPZ), and carbendazim (CBD), were 100%. In particular, the detection concentration of tebuconazole (TEB) could be as high as 1,500 ng/L (Fig. 2b). Five PFASs and five UVs were all detected at all WWTPs, including perfluorononanoic acid (PFNA), pentadecafluorooctanoic acid (PFOA), perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluorobutanesulfonic acid (PFBS), and octocrylene (OC), 2-ethylhexyl 4-methoxycinnamate (EHMC), 2-ethylhexyl salicylate (EHS), benzophenone-3, benzophenone, with the concentrations of PFBS and EHS being up to 1,000 ng/L and 100 ng/L, respectively (Fig. 2c and d). For the chemical class of common pharmaceuticals, caffeine (CFI) exhibited the highest detection rate and concentration of 97.8% and 124 ng/L, respectively (Fig. 2e). Detection rates of 100% were found for di-n-octyl phthalate (DNOP), dibutyl phthalate (DnBP), diisobutyl phthalate (DiBP), diethyl phthalate (DEP), and dimethyl phthalate (DMP), with a maximum average concentration of 1,000 ng/L (Fig. 2f). For the chemical classes of BP and PAH pollutants, bisphenol A (BPA), phenanthrene (PHE), and naphthalene (NAP) were detected at all WWTPs, among which the highest detection concentrations of BPA and PHE were 2,500 ng/L and 50 ng/L, respectively (Fig. 2g and h). The detection rates of EDC, OP, and PCB pollutants were less than 100%, with the highest concentration of 200 ng/L⁻¹ (Fig. 2i–k). The concentrations of PCBs ranged between 0.2 and 2 ng/L, which was markedly lower than that of other pollutants. These chemical classes of pollutants and contaminants detected in this study were comparable to the results of Stevens et al. [33]. They surveyed the digested sludge from 14 U.K. WWTPs and obtained contemporary data on the concentrations of certain classes of persistent organic compounds including PAHs, PCBs, pesticides, pharmaceuticals, PPCPs, and UV-filters. Our findings align with a report by Stevens et al. [33], suggesting that certain trace organic pollutants in the different chemical classes were frequently found in WWTP effluents around the world and should be targeted in monitoring and risk management.

4. Discussion

A total of 216 trace organic pollutants in 11 chemical classes were detected in the effluents of the 46 WWTPs. Among them, BPs, PFASs, and PAEs exhibited the highest concentration percentages, ranging from 500 to 1,500 ng/L. Conversely, the concentrations of PAHs, UVs, EDCs, and PCBs were lower, with the highest concentration mostly below 100 ng/L. It is worth noting that in our study, there were only three sample sites in the west of China, and all demonstrated the lowest concentrations of pollutants. Conversely, the concentrations of pollutants in other sample sites showed a significant trend; that is, the concentrations of the eastern sample sites were clearly higher than those of the western sample sites.

There are many factors contributing to this difference such as water resources, economic levels, living habits, treatment processes, and the emission standard of typical pollutants. Although this study lacked some relevant data to make the relevant analysis, its results were consistent with the spatial distribution of China's economic level, indicating that the economic level was an important factor influencing the concentrations of pollutants in the effluent.

In addition, although few studies have detected more than ten chemical classes of trace organic pollutants over a large area, the data for individual chemical classes of pollutants in individual regions showed significant distinctions from other countries (Fig. 3). For related references and detailed data, please refer to Table S23 and the appendix file. 3. The concentrations of antibiotic, pesticide, UV, pharmaceutical, PFAS, PAE, PAH, EDC, OP, and PCB pollutants detected in the effluents of other countries were significantly higher than those in this study. In addition, the concentration of trace organic pollutants also showed individual characteristics of different types of WWTPs. For example, in Spain, 14 WWTPs accepting industry wastewater showed PCB concentrations of 102,500 ng/L and 20,700 ng/L in the domestic wastewater, and 74,800 ng/L in the mixed wastewater, which exceeded the concentrations found in this study by three orders of magnitude. In contrast, the concentration of BPs in the effluent in this study was much higher than that reported in other regions such as France, Germany, Japan, Korea, and the U.S.. The distribution of pollutants in wastewater effluent varied between different countries. Thus, we hypothesized that the concentration of pollutants in the effluent of WWTPs in each country was related to consumption, economics, and living habits.

The number of chemical classes and pollutants measured has a great influence on the evaluation of effluent. In this study, 11 chemical classes containing 216 contaminants have been detected, with detection rates ranging from 2.17% to 100%. Unlike most studies, a significantly larger number of contaminants were measured for each of the major chemical classes of trace organic pollutants in the present work. In particular, 72 contaminants classified as pesticides have been detected in this study, making it the most prevalent chemical class detected. However, it is worth noting that the total concentration of pesticides was not the highest. In contrast, the number of contaminants (PFASs, BPs, and PAEs) detected was much lower than that of pesticides. Furthermore, the sum concentration of PAHs was less than the sum concentrations of PFASs, BPs, and PAEs, respectively. The results indicated that the order of magnitude of the sum concentration of each chemical class of pollutants remained consistent despite variations in the number of contaminants detected for each chemical class of pollutants. These results suggested that the total concentration of each class could reflect the actual pollution levels in each treatment plant and could be used for relative comparison among different classes of pollutants.

The ecological risk of trace organic pollutants depends on their concentrations and toxicity. The RQ_{Total} of each chemical class of pollutants in the 11 different chemical classes of pollutants was determined and is shown in Fig. 4. The descending order of RQ_{Total} can be seen as follows: PAEs, antibiotics, PAHs, pesticides, PFASs, and BPs. Among the 11 different chemical classes of pollutants, the concentrations of antibiotics and PAHs with high levels of ecological risk were at medium levels of concentration. This was mainly because the large number of antibiotic contaminants detected in this study led to a large cumulative value of ecological risk. Moreover, the high toxicity of PAHs also led to a high risk level. Additionally, despite the relatively low acute toxicity of PFASs, their high concentration still resulted in an elevated overall risk of various PFAS contaminants. RQ_{Total} of UVs and EDCs was less than 1.0, indicating a medium risk level, whereas OPs and PCBs showed an insignificant risk. These results underscore the importance of not only the concentrations of the pollutants but also their actual ecological risks when assessing the impact of the pollutants.

The spatial distribution of RQ_{Total} values for different classes of pollutants in the effluent varied across regions (Fig. 4). The eastern and southern regions had medium to high ecological risks ($RQ_{Total} > 0.1$)

from various classes of pollutants, except for antibiotics, PAEs, and PAHs. The western region, especially Xinjiang Province, had low to medium ecological risks ($RQ_{Total} < 0.1$) from most classes of pollutants. This trend

was similar to the spatial distribution of China's economic level, suggesting that economic development was a key factor influencing the pollutant levels and risks in wastewater effluents [34,35].

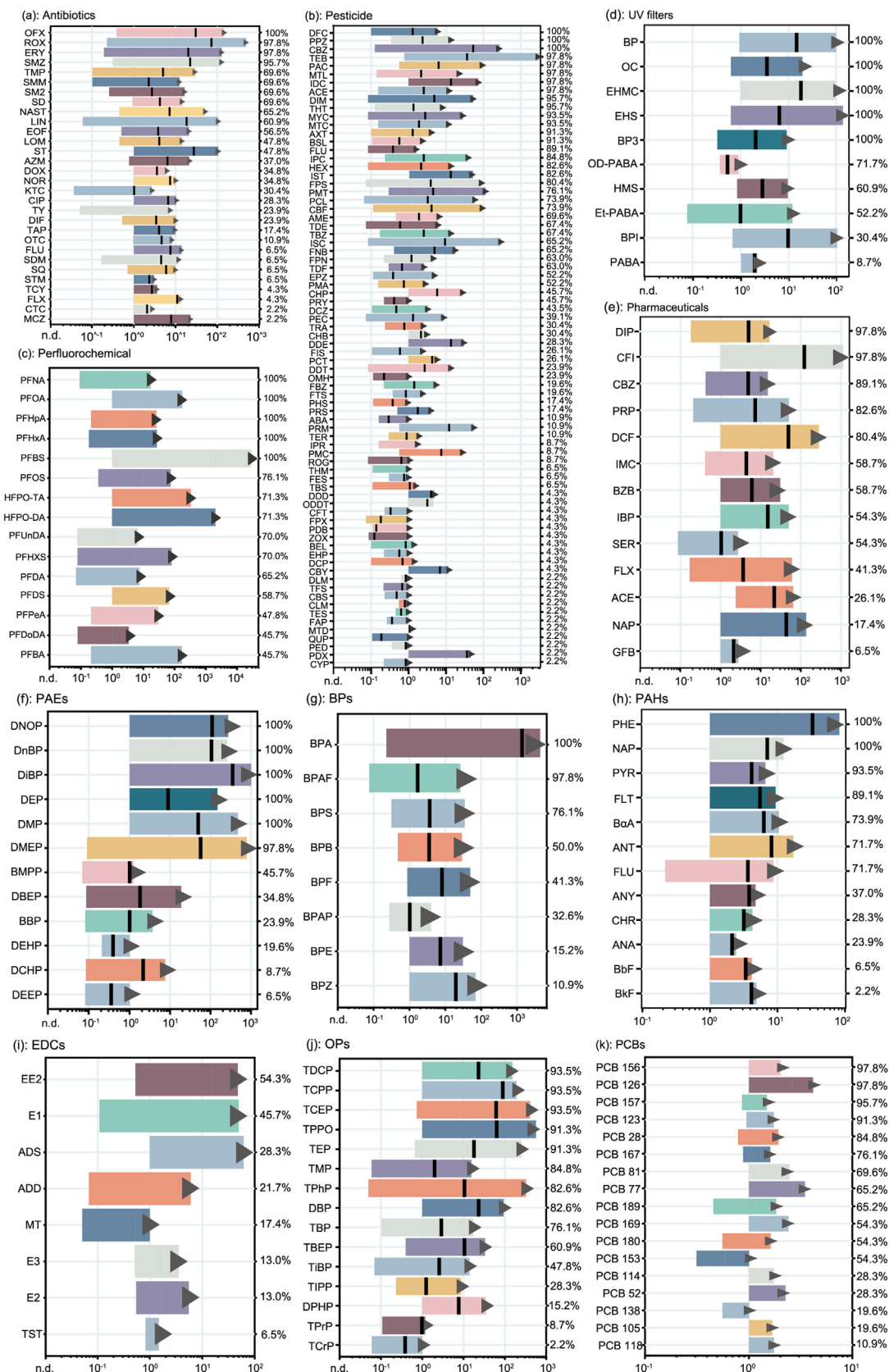


Fig. 2. The concentration ranges and corresponding detection rates of various contaminants in the effluents of the 46 WWTPs.

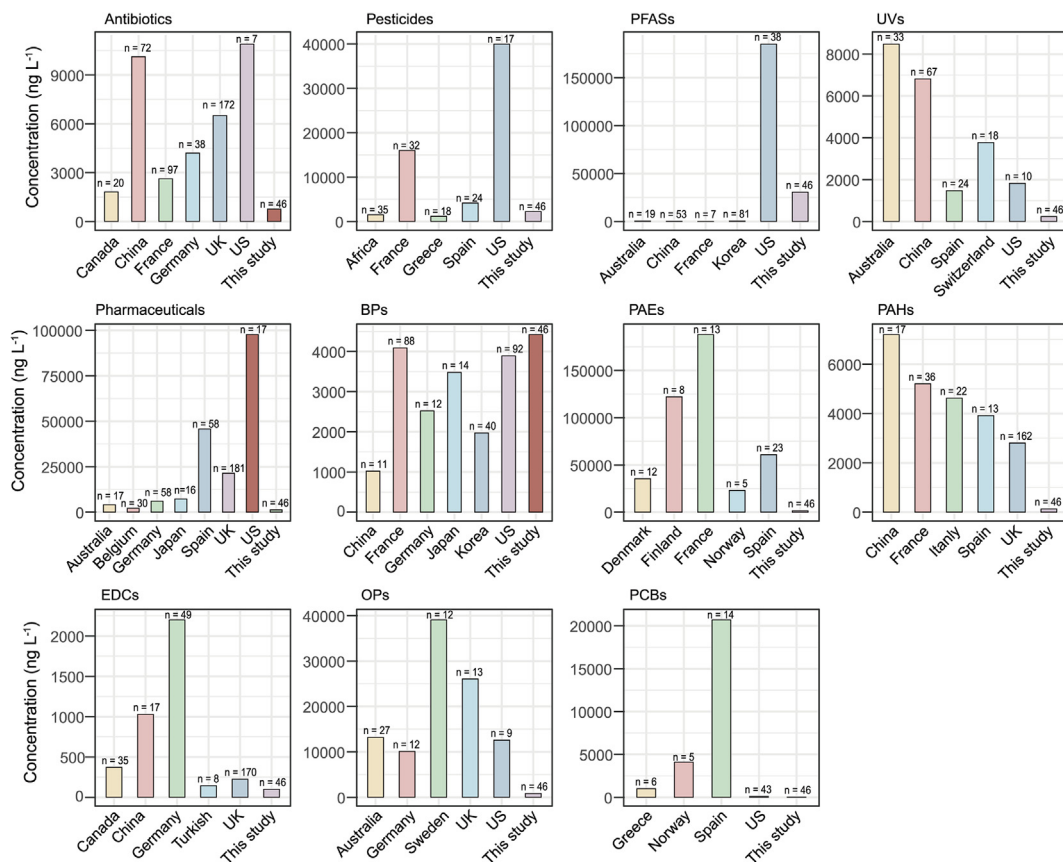


Fig. 3. Comparison of the concentrations of 11 different chemical classes of pollutants detected in the effluent in other countries with this study.

This research was aimed at identifying the contaminants that pose the highest ecological and environmental risk in WWTP effluent in China. The RQ values of various contaminants were calculated and ranked, as shown in Fig. 5. The RQ of each contaminant calculated by literature data

might introduce some errors in this study, which, however, did not alter the overall trend. Hence, RQ would also reflect the observable difference in ecology and environmental risks for each contaminant. The RQ value of PFBS was the highest, exceeding 30 and indicating a serious ecological

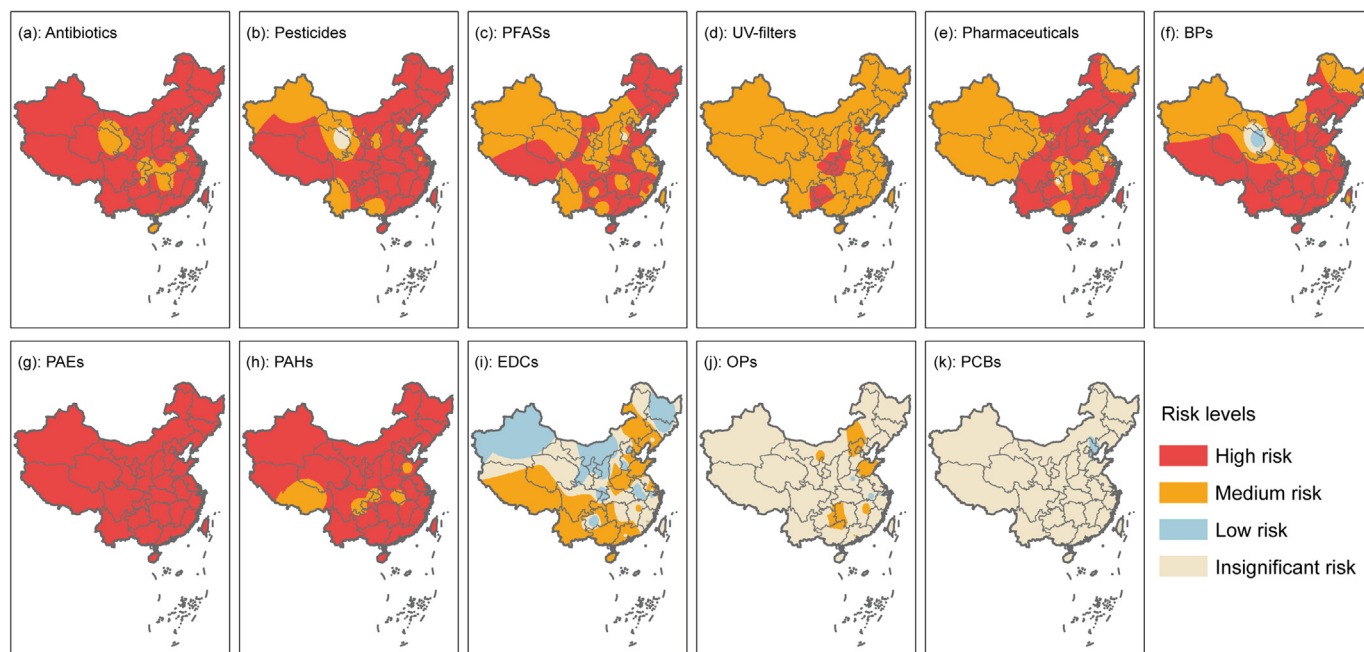


Fig. 4. Spatial distribution of ecological risk levels of 11 different chemical classes of pollutants in effluents of 46 WWTPs in China.

risk (Fig. 5a). According to previous studies, $RQ > 1.0$ means that contaminants pose a serious ecological and environmental risk [16]. It was found that a total of 23 contaminants had high ecological risks (Fig. 5a), including 7 pesticides [Fipronil sulfide (FPS), Ametryn (AME), Metolachlor (MTC), Tebuconazole (TEB), Imidacloprid (IDC), Triazophos (TRA), Isocarbofos (ISC)], 6 antibiotics and pharmaceuticals [OFX, ROX, Enrofloxacin (EOF), Bezafibrate (BZB), diclofenac (DCF), CFI], 3 PAHs [PHE, Acenaphthylene (ANY), Benzo(k)Fluoranthene (BkF)], 2 PFASs

[PFBS, Perfluoro(2-methyl-3-oxahexanoic) acid (HFPO-DA)], 2 PAEs (DMP, DNOP), 2 UVs (EHS, EHMC), and 1 BP (BPA). These 23 contaminants require more attention and should be removed with higher priority [17]. Fig. 5b shows 46 contaminants posing medium risks ($1.0 > RQ > 0.1$), including 20 pesticides, 12 antibiotics and pharmaceuticals, 3 PAHs, 3 PAEs, 3 PFASs, 1 UV, 2 OPs, 1 EDC, and 1 BP. Efficient technologies are needed to enhance their removal and reduce their concentrations in effluent water.

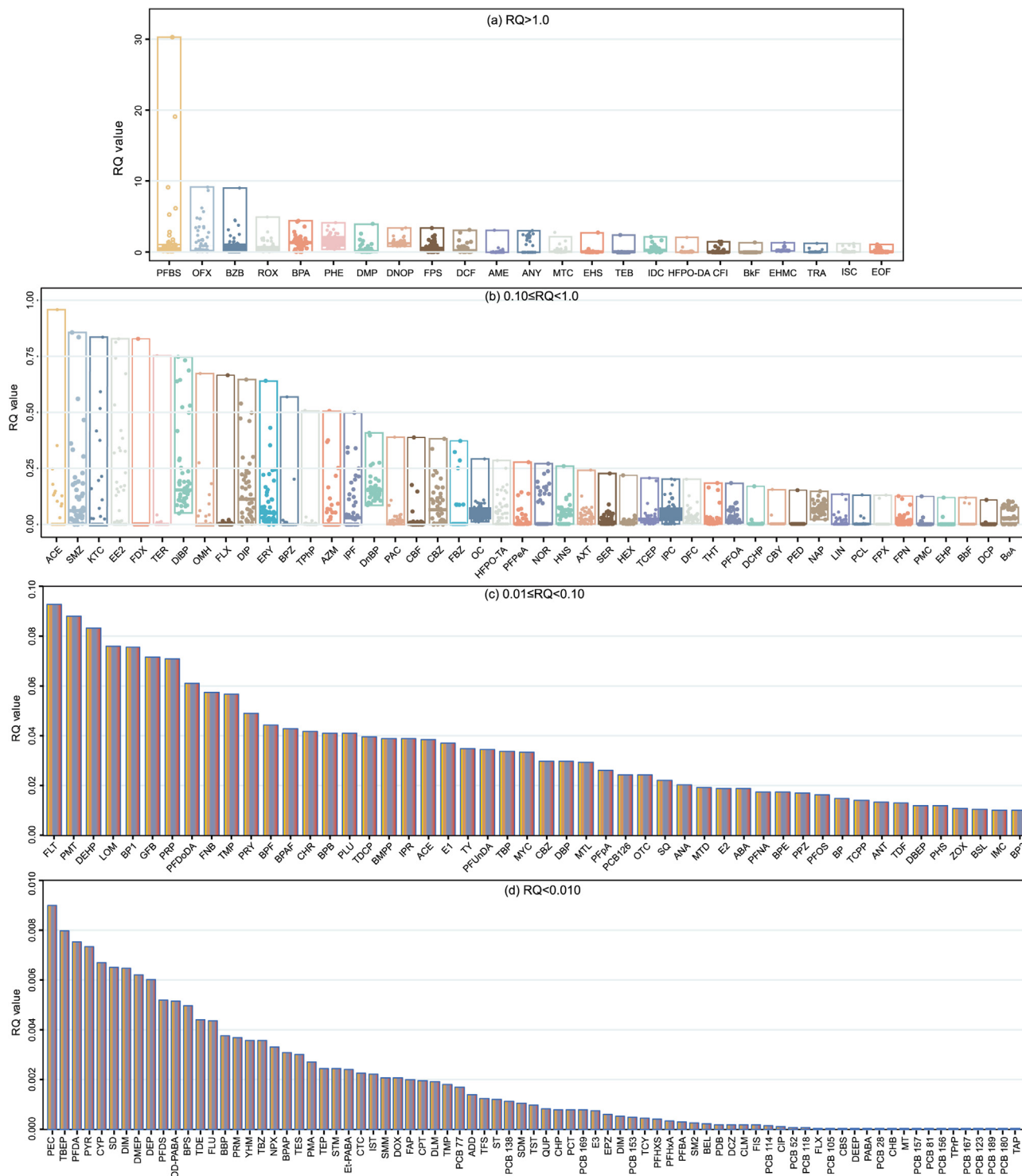


Fig. 5. Distribution of ecological and environmental risks (risk quotient values) caused by various contaminants in the effluent of this study.

Additionally, 50 contaminants had RQ values between 0.01 and 0.1, indicating a low risk level (Fig. 5c). Of the 216 pollutants detected in this study, 97 contaminants had RQ values below 0.01, indicating an insignificant risk level (Fig. 5d). It was observed that 27 pesticides and 16 antibiotics posed high and medium ecological risks. This may be because pesticides originate from pesticide residues on vegetables and fruits, and antibiotics are commonly used pharmaceuticals in daily life [36]. The detection rates and concentrations of pesticides and antibiotic pollutants were higher than those of other pollutants. Moreover, the concentrations of pesticides and antibiotics were mostly around 100 ng/L, and nearly half of the contaminants posing a medium to high risk were pesticide and antibiotic compounds. These results suggest that to minimize the ecological risks of certain contaminants, as identified above, we need to prevent various forms of pesticide and antibiotic pollutants from entering WWTPs [16].

PAHs, PFASs, PAEs, UVs, and BPs pose high risks, mainly originating from air, clothes, cooking utensils, toys, drinks, cosmetics, and other PPCPs. Therefore, besides pesticides and antibiotics, trace organic pollutants, such as PAHs (PHE, ANY, BkF), PAEs (DMP, DNOP), PFASs (PFBS, HFPO-DA), UVs (EHS, EHMC), and BP (BPA), should be properly managed by monitoring, input control, and removal. These trace organic pollutants in the effluent of WWTPs would ultimately enter rivers and lakes, albeit with some potential for dilution and natural degradation in aqueous environments. However, the increase in the variety of pollutants can aggravate the toxicity of fish, microalgae, plankton, and microorganisms, leading to the destruction of aquatic ecosystems. Thus, it is more effective to calculate the RQ for one pollutant or the RQ_{Total} for pollutants of one chemical class when evaluating the risk induced by one pollutant or pollutants of one chemical class. Meanwhile, these values could also draw researchers' or regulators' attention to certain pollutants that warrant closer scrutiny. In general, mitigating the ecological risks of pollutants in municipal WWTP effluent necessitates a dual approach. First, there should be a focus on improving the removal efficiency of pollutants through the adoption of promising technologies. Simultaneously, it is crucial to enforce relevant laws and regulations to restrict the use of certain chemical compounds in various sectors. For instance, stricter standards for pesticide residues on fruits and vegetables may be implemented to ensure human and environmental health. Moreover, we should apply advanced treatment technologies such as biological or natural removal techniques, to further remove the trace organic pollutants from the effluents.

5. Conclusions

The large survey of this study revealed that hundreds of trace organic pollutants were present in the effluents of the WWTPs in China and posed serious ecological risks. These pollutants include 27 pesticides, 16 antibiotics, and 26 PPCPs that have high or medium risk levels. The monitored trace organic compounds belonged to 11 different classes of pollutants, which would provide more comprehensive information about their occurrence and ecological risks than most previous studies focusing on only one or very limited classes. The survey showed that in effluent water, 23 contaminants with RQ > 1.0 had caused serious ecological risk, including 7 pesticides (FPS, AME, MTC, TEB, IDC, TRA, ISC), 6 antibiotics and pharmaceuticals (OFX, ROX, EOF, BZB, DCF, CFI), 3 PAHs (PHE, ANY, BkF), 2 PFASs (PFBS, HFPO-DA), 2 PAEs (DMP, DNOP), 2 UV-filters (EHS, EHMC), and 1 BP (BPA). These 23 contaminants require more attention and should be controlled or removed with higher priority. Additionally, 46 contaminants with RQ values falling between 1.0 and 0.1 have posed medium risks, including 20 pesticides, 12 antibiotics and pharmaceuticals, 3 PAHs, 3 PAEs, 3 PFASs, 2 UVs, 2 OPs, 1 EDC, and 1 BP. This underscores the need for researchers to develop technologies that improve the removal efficiency and minimize the associated risks. Therefore, this study provides valuable information for controlling certain contaminants with higher priority and lists the organic trace pollutants that need

more efficient removal technologies to reduce the concentration in WWTP effluent and eliminate ecological risks.

Author contributions

J.C.L. and Y.F.C.: writing—original draft, methodology, investigation. F.Y. and G.H.L.: writing—review & editing, data curation. Y.P.L. and M.L.: investigation, software. J.C. L., L.H.F. and L.G.: conceptualization, writing—review & editing, supervision.

Declaration of competing interests

The authors declare that they have no conflict of interest.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (Grant 52179063 and 42177353), the Natural Science Foundation of Jiangsu Province (BK20221505), and the key program of National Natural Science Foundation of China (Grant 52039003).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eehl.2023.09.006>.

References

- [1] R. Zhang, S. Zhao, X. Liu, M.W. Thomes, C.W. Bong, D.N.D. Samaraweera, T. Priyadarshana, G. Zhong, J. Li, G. Zhang, Fates of benzotriazoles, benzothiazoles, and *p*-phenylenediamines in wastewater treatment plants in Malaysia and Sri Lanka, *Environ. Sci. Technol. Water* 3 (2023) 1630–1640.
- [2] T.-M.-T. Le, T.-N.-S. Truong, P.-D. Nguyen, Q.-D.-T. Le, Q.-V. Tran, T.-T. Le, Q.-H. Nguyen, T.-C. Kieu-Le, E. Strady, Evaluation of microplastic removal efficiency of wastewater-treatment plants in a developing country, Vietnam. *Environ. Technol. Innov.* 29 (2023) 102994.
- [3] X. Cheng, C. Wei, X. Ke, J. Pan, G. Wei, Y. Chen, C. Wei, F. Li, S. Preis, Nationwide review of heavy metals in municipal sludge wastewater treatment plants in China: sources, composition, accumulation and risk assessment, *J. Hazard Mater.* 437 (2022) 129267.
- [4] F. Xue, B. Tang, L. Bin, J. Ye, S. Huang, F. Fu, P. Li, J. Cui, Residual micro organic pollutants and their biotoxicity of the effluent from the typical textile wastewater treatment plants at Pearl River Delta, *Sci. Total Environ.* 657 (2019) 696–703.
- [5] A. Yadav, A. Raj, D. Purchase, L.F.R. Ferreira, G.D. Saratale, R.N. Bharagava, Phytotoxicity, cytotoxicity and genotoxicity evaluation of organic and inorganic pollutants rich tannery wastewater from a Common Effluent Treatment Plant (CETP) in Unnao district, India using *Vigna radiata* and *Allium cepa*, *Chemosphere* 224 (2019) 324–332.
- [6] A.M. Gorito, A.R. Ribeiro, C.M.R. Almeida, A.M.T. Silva, A review on the application of constructed wetlands for the removal of priority substances and contaminants of emerging concern listed in recently launched EU legislation, *Environ. Pollut.* 227 (2017) 428–443.
- [7] S. Adithya, R.S. Jayaraman, A. Krishnan, R. Malolan, K.P. Gopinath, J. Arun, W. Kim, M. Govarthanan, A critical review on the formation, fate and degradation of the persistent organic pollutant hexachlorocyclohexane in water systems and waste streams, *Chemosphere* 271 (2021) 129866.
- [8] G. Choo, W. Wang, H.-S. Cho, K. Kim, K. Park, J.-E. Oh, Legacy and emerging persistent organic pollutants in the freshwater system: relative distribution, contamination trends, and bioaccumulation, *Environ. Int.* 135 (2020) 105377.
- [9] A. Ranjbar Jafarabadi, A. Riyahi Bakhtiari, M. Aliabadian, H. Laetitia, A. Shadmehri Toosi, C.K. Yap, First report of bioaccumulation and bioconcentration of aliphatic hydrocarbons (AHs) and persistent organic pollutants (PAHs, PCBs and PCNs) and their effects on alcyonacea and scleractinian corals and their endosymbiotic algae from the Persian Gulf, Iran: inter and intra-species differences, *Sci. Total Environ.* 627 (2018) 141–157.
- [10] L. Liu, X. Lin, W. Li, X. Liu, F. Fan, Y. Yang, Y. Mei, Thin film composite reverse osmosis membranes with metal-organic coordination complexes stabilized CNTs interlayer for enhanced removal of trace organic contaminants, *J. Membr. Sci.* 687 (2023) 122012.
- [11] H. Guo, Y. Deng, Z. Tao, Z. Yao, J. Wang, C. Lin, T. Zhang, B. Zhu, C.Y. Tang, Does hydrophilic polydopamine coating enhance membrane rejection of hydrophobic endocrine-disrupting compounds? *Environ. Sci. Technol. Lett.* 3 (9) (2016) 332–338.
- [12] A. Sunyer-Caldú, B. Benedetti, C. Valhondo, L. Martínez-Landa, J. Carrera, M. Di Carro, E. Magi, M.S. Diaz-Cruz, Using integrative samplers to estimate the removal of pharmaceuticals and personal care products in a WWTP and by soil aquifer treatment enhanced with a reactive barrier, *Sci. Total Environ.* 867 (2023) 161466.

- [13] S. Wang, J. Qian, B. Zhang, L. Chen, S. Wei, B. Pan, Unveiling the occurrence and potential ecological risks of organophosphate esters in municipal wastewater treatment plants across China, *Environ. Sci. Technol.* 57 (5) (2023) 1907–1918.
- [14] M.G. Doyle, M.T. Odenkirk, A.K. Stewart, J.P. Nelson, E.S. Baker, F. De La Cruz, Assessing the fate of dissolved organic compounds in landfill leachate and wastewater treatment systems, *Environ. Sci. Technol. Water* 2 (12) (2022) 2502–2509.
- [15] Y. Sun, S. Bai, X. Wang, N. Ren, S. You, Prospective life cycle assessment for the electrochemical oxidation wastewater treatment process: from laboratory to industrial scale, *Environ. Sci. Technol.* 57 (3) (2023) 1456–1466.
- [16] Y. Yang, X. Zhang, J. Jiang, Which micropollutants in water environments deserve more attention globally? *Environ. Sci. Technol.* (1) (2022) 56.
- [17] Y. Zhou, J. Meng, M. Zhang, S. Chen, B. He, H. Zhao, Q. Li, S. Zhang, T. Wang, Which type of pollutants need to be controlled with priority in wastewater treatment plants: traditional or emerging pollutants? *Environ. Int.* 131 (2019) 104982.
- [18] L. Wei, N. Zhu, X. Liu, H. Zheng, K. Xiao, Q. Huang, H. Liu, M. Cai, Application of Hi-throat/Hi-volume SPE technique in assessing organophosphorus pesticides and their degradation products in surface water from Tai Lake, east China, *J. Environ. Manag.* 305 (2022) 114346.
- [19] C. Rizzi, S. Villa, A.V. Waichman, G.S. de Souza Nunes, R. de Oliveira, M. Vighi, A. Rico, Occurrence, sources, and ecological risks of polycyclic aromatic hydrocarbons (PAHs) in the Amazon river, *Chemosphere* 336 (2023) 139285.
- [20] S. Emami, A.Y. Taha, Effects of carotenoid pigmentation in salmon on antibiotic extraction recovery, matrix effects and accuracy of quantification by ultrahigh performance liquid chromatography coupled to tandem mass spectrometry, *J. Chromatogr. B* 1216 (2023) 123585.
- [21] H. Hu, M. Liu, L. Shen, L. Zhang, H. Zhu, Q. Wu, Simultaneous determination of multiple perfluoroalkyl and polyfluoroalkyl substances in aquatic products by ultra-performance liquid chromatography-tandem mass spectrometry with automated solid-phase extraction, *J. Chromatogr. B* 1224 (2023) 123736.
- [22] X. Gao, J. Li, Y. Xu, Q. Zhou, M. Ma, Z. Wang, Passive sampling hydrophilic and hydrophobic bisphenol analogues using hydrophilic-lipophilic balance sorbent-embedded cellulose acetate membrane in surface waters, *Sci. Total Environ.* 839 (2022) 156239.
- [23] M.-L. Chen, J.-S. Chen, C.-L. Tang, I.F. Mao, The internal exposure of Taiwanese to phthalate—an evidence of intensive use of plastic materials, *Environ. Int.* 34 (1) (2008) 79–85.
- [24] Y. Li, M.A. Taggart, C. McKenzie, Z. Zhang, Y. Lu, S. Pap, S.W. Gibb, A SPE-HPLC-MS/MS method for the simultaneous determination of prioritised pharmaceuticals and EDCs with high environmental risk potential in freshwater, *J. Environ. Sci.* 100 (2021) 18–27.
- [25] M.J. Rocha, A.B. Ribeiro, D. Campos, E. Rocha, Temporal-spatial survey of PAHs and PCBs in the Atlantic Iberian northwest coastline, and evaluation of their sources and risks for both humans and aquatic organisms, *Chemosphere* 279 (2021) 130506.
- [26] N.I.P. Valente, S. Tarelho, A.L. Castro, A. Silvestre, H.M. Teixeira, Analysis of organophosphorus pesticides in whole blood by GC-MS- μ ECD with forensic purposes, *J. Forensic Legal Medicine* 33 (2015) 28–34.
- [27] A. Ofrydopoulou, C. Nannou, E. Evgenidou, A. Christodoulou, D. Lambropoulou, Assessment of a wide array of organic micropollutants of emerging concern in wastewater treatment plants in Greece: occurrence, removals, mass loading and potential risks, *Sci. Total Environ.* 802 (2022) 149860.
- [28] W. Chen, F. Yang, E. Hu, C. Yang, C. Sun, M. Li, Occurrence, fate and risk assessment of per- and polyfluoroalkyl substances in wastewater treatment plants in Shaanxi, China, *Environ. Pollut.* 314 (2022) 120226.
- [29] A. Mostafa, H. Shaaban, A. Alqarni, R. Al-Ansari, A. Alrashidi, F. Al-Sultan, M. Alsulaiman, F. Alsaif, O. Aga, Multi-class determination of pharmaceuticals as emerging contaminants in wastewater from Eastern Province, Saudi Arabia using eco-friendly SPE-UHPLC-MS/MS: occurrence, removal and environmental risk assessment, *Microchem. J.* 187 (2023) 108453.
- [30] R. Guedes-Alonso, S. Montesdeoca-Esponda, J.A. Herrera-Melián, R. Rodríguez-Rodríguez, Z. Ojeda-González, V. Landívar-Andrade, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, Pharmaceutical and personal care product residues in a macrophyte pond-constructed wetland treating wastewater from a university campus: presence, removal and ecological risk assessment, *Sci. Total Environ.* 703 (2020) 135596.
- [31] V. Nikolopoulou, A.S. Ajibola, R. Aalizadeh, N.S. Thomaidis, Wide-scope target and suspect screening of emerging contaminants in sewage sludge from Nigerian WWTPs by UPLC-qToF-MS, *Sci. Total Environ.* 857 (2023) 159529.
- [32] Y. Pan, M. Shen, B. Du, D. Luo, H. Chen, C. Zhu, L. Zeng, Occurrence and nationwide distribution of multiple novel bisphenol S analogues in municipal sewage sludge across China, *Environ. Sci. Technol. Lett.* 8 (9) (2021) 766–772.
- [33] J.L. Stevens, G.L. Northcott, G.A. Stern, G.T. Tomy, K.C. Jones, PAHs, PCBs, PCNs, organochlorine pesticides, synthetic musks, and polychlorinated n-alkanes in U.K. Sewage sludge: survey results and implications, *Environ. Sci. Technol.* 37 (3) (2003) 462–467.
- [34] J. Kou, X. Li, M. Zhang, L. Wang, L. Hu, X. Liu, S. Mei, G. Xu, Accumulative levels, temporal and spatial distribution of common chemical pollutants in the blood of Chinese adults, *Environ. Pollut.* 311 (2022) 119980.
- [35] M.H.Y. Lau, K.M.Y. Leung, S.W.Y. Wong, H. Wang, Z.-G. Yan, Environmental policy, legislation and management of persistent organic pollutants (POPs) in China, *Environ. Pollut.* 165 (2012) 182–192.
- [36] L.B. Weger, J. Leitão, M.G. Lawrence, Expected impacts on greenhouse gas and air pollutant emissions due to a possible transition towards a hydrogen economy in German road transport, *Int. J. Hydrogen Energy* 46 (7) (2021) 5875–5890.