Environmental Science and Pollution Research (2021) 28:39423–39431
https://doi.org/10.1007/s11356-021-13140-0

RESEARCH ARTICLE

Profiles and risk assessment of legacy and current use pesticides in urban rivers in Beijing, China

Yangping Zhang [1,2] · Haifeng Zhang [3] · Min Yang [2,3]

Received: 1 October 2020 / Accepted: 22 February 2021 / Published online: 23 March 2021

Abstract

Pesticides in the environment can pose serious risks to aquatic ecosystems. This study focused on the existence of 27 pesticides, including 13 pesticides regulated by the Stockholm Convention as persistent organic pollutants (POPs) and 14 commonly used pesticides in three urban rivers in Beijing that receive effluents from three municipal wastewater treatment plants (MWTPs). Among the 27 pesticides, 12 were detected at least once over a period of 4 seasons. Atrazine, aldrin and dieldrin were universally found in the three rivers, with the highest concentrations being 311, 163 and 23.3 ng/L, respectively. HCHs, DDTs, heptachlor and endosulfan, which are POPs, were detected at lower concentrations (ND–16.7 ng/L). Most of the insecticides and some of the herbicides in the rivers originated from MWTP effluents. The risk assessment results showed that aldrin posed medium risk ($0.1 \leq RQ < 1$) to fish, and atrazine exhibited medium risk to both fish and algae. Despite the implementation of the Stockholm Convention and the upgrades of MWTPs emitting ozone, high loads of aldrin, atrazine and dieldrin were discharged to the rivers. Efforts should be devoted to identifying POP pesticide sources and upgrading MWTPs with other technologies to ensure the ecological safety of rivers.

Keywords Pesticide · Urban river · Ecological risk · Municipal wastewater treatment plant · POPs

Introduction

Due to the intensive use of pesticides and the associated potential ecological risks in aquatic systems, pesticide pollution has attracted a great deal of attention worldwide (Heinz-R and Rita 2013; Iturburu et al. 2019; Zheng et al. 2016). China is one of the largest producers and consumers of pesticides in the world. Persistent pesticides, including hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT), have been found in water and soil at relatively high levels (Ma et al. 2020; Zhang et al. 2004). These compounds remain in the environment for several decades and can lead to bioaccumulation and biomagnification in aquatic organisms and in turn affect human health (Gaur et al. 2018; Rani et al. 2020). Until now, most previous studies have mainly focused on diffuse pesticide pollution in the agricultural sector (Arisekar et al. 2019; Donna et al. 2018; Tang et al. 2018). Recently, municipal wastewater treatment plants (MWTPs) have been recognized as an important source of diverse micropollutants, including pesticides (Bollmann et al. 2014; Florian et al. 2012; Heeb et al. 2012; Qi et al. 2015). Pesticides are widely applied in urban areas for household pest control and eventually flow into urban drainage systems (Jiujiang et al. 2013). Conventional MWTPs are not effective for removing micropollutants, including pesticides, and allow them to be discharged into receiving water bodies (Qi et al. 2015).

Beijing, a megacity in northern China, is known for its deficiency in fresh water sources, and MWTP effluents have become the major water source to supplement the surface water system (Heeb et al. 2012, Qi et al. 2015). Pesticides, including atrazine (Ge et al. 2010), heptachlor and dieldrin

Responsible Editor: Hongwen Sun

✉ Haifeng Zhang
hfzhang@rcees.ac.cn

✉ Min Yang
yangmin@rcees.ac.cn

[1] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Universty of Chinese Academy of Sciences, Beijing 100049, China

[2] Sino-Danish Center for Education and Research, University of Chinese Academy of Sciences, Beijing 100049, China

[3] Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

(Zhang et al. 2004), have been detected frequently in MWTP effluents in Beijing. Pesticides have also been detected frequently in downstream rivers (Heeb et al. 2012; Pernet-Coudrier et al. 2012; Qiao et al. 2011). Pesticide loads discharged from MWTPs to surrounding rivers has been estimated at 80–460 g/day (Qi et al. 2015). Continuous exposure to pesticides has caused concerns over damage to surface water ecological systems (Chen et al. 2018; Grung et al. 2015), particularly to aquatic organisms such as fish (Zheng et al. 2016) and invertebrates (Revankar and Shyama 2009).

Organochlorine pesticides including HCHs and DDTs were widely applied in China until 1980s (Grung et al. 2015). These compounds were persistent in the environment and universally found in surface water and wastewater in Beijing (Zhang et al. 2004). According to a recent study, the concentrations of HCHs and DDTs decreased sharply from hundreds ng/L to dozens ng/L (Shao et al. 2016), perhaps due to the implementation of the Stockholm Convention (UNEP 2009). At the same time, to improve the water quality of receiving rivers, conventional MWTPs with activated sludge treatment have been upgraded with advanced treatment using ozone and other technologies since 2012 (Table 1). Therefore, it is necessary to investigate how pesticide regulation and MWTP upgradation affect pesticide contamination in Beijing urban rivers. The objectives of this study were (1) to investigate the existence of 27 pesticides, including 13 regulated pesticides as persistent organic pollutants (POPs)and 14 commonly used pesticides (Table S1), in the effluents from three MWTPs in Beijing and their corresponding receiving rivers and (2) to evaluate the ecological risk caused by the pesticides.

Chemicals and methods

Standard substances and reagents

A total of 27 kinds of pesticides, including 21 insecticides, 4 herbicides and 2 fungicides, were purchased from Beijing Manhage Biotechnology Co., Ltd. (Beijing, China). Three surrogates, including dichlorvos-d6, alpha-hexachlorocyclohexane-d6 (alpha-HCH-d6) and malathion-d6, were purchased from CDN Isotopes Inc. (Canada). Detailed information regarding the name and CAS of each compound is shown in Table S1. Methanol, dichloromethane and ethyl acetate from Fisher Scientific Co. (China) were HPLC grade. Ultrapure deionized water was prepared by a Milli-Q purification system (> 18.2 MΩ·cm).

Sample collection and pretreatment

Figure 1 illustrates the locations of the three MWTPs and the corresponding receiving rivers. Water samples were collected from five sampling sites, including two upstream sites, two downstream sites and one effluent site (Qiao et al. 2018). The distance between two neighbouring sites was approximately 200 m. Samples were collected in September and December 2018 and March and June 2019. Water samples were collected in 1-L glass bottles. Finally, a total of 60 water samples were collected in this study. To avoid pesticide degradation, samples were stored in the dark at 4 °C until extraction (Barion et al. 2018).

The samples were prepared according to a previous study (Shi et al. 2018). Water samples were first filtered through glass microfibre filters (GF/F, 0.7 μm, Whatman, UK). Then, surrogates were spiked into filtered water at a concentration of 50 ng/L. To improve the recovery rates, methanol was added to the water samples at a ratio of 1:100 before extraction. Water samples were extracted through solid phase extraction (SPE) using Sep-Pak C18 cartridges (6 cc/500 mg, Waters, USA). The cartridges were preconditioned sequentially with 5 mL of dichloromethane, ethyl acetate, a mixture of the two (1:1 of *v*/*v*) and 10 mL of methanol and ultrapure deionized water. Then, the water samples were passed through the cartridges at a flow rate of 10 mL/min controlled by a vacuum pump. After that, the cartridge was washed with 10 mL of ultrapure water. The target analytes were eluted with 5 mL of dichloromethane, ethyl acetate and a mixture of the two (1:1 of *v*/*v*) in succession. The elution was concentrated to approximately 200 μL with a gentle nitrogen flow. Finally, the analytes were reconstituted to 500 μL with dichloromethane and transferred into a 1.5-mL sample vial before analysis.

Instrumental analysis

The concentrations of the target contaminants were measured on a gas chromatograph mass spectrometer (GCMS-QP2010 Ultra, Shimadzu, Japan), which was equipped with a fused

Table 1 Description of MWTPs and the receiving rivers

MWTPs	Biological process	Upgradation technology	Ozone dosage (mg/L)/ time (min)	Capacity (10^4 m^3/day)	River length (km)
A	A^2O	UF + O_3	3.5–3.0/20	55	23.6
B	A^2O	UF + O_3	< 5.0/15	100	20.3
C	A^2O	UF + O_3	-	60	68.4

A^2O anaerobic-anoxic-aerobic, *MBR* membrane bioreactor, *UF* ultrafiltration, *O_3* ozone

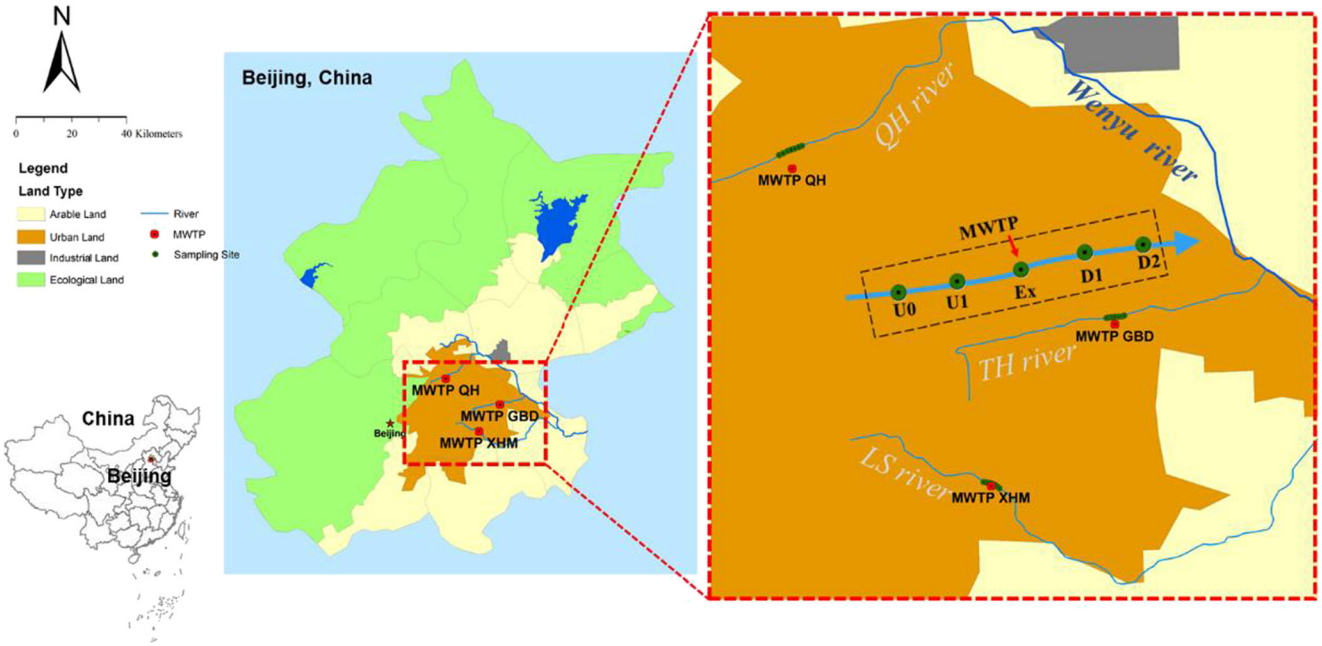

Fig. 1 Locations of the three MWTPs (red points) and the receiving rivers in Beijing

silica capillary column (Rtx-5MS, 30 m × 2.5 mm × 0.25 μm, Rextek, USA). The analytical procedure was the same as that used in a previous study (Yang et al. 2012). In brief, the sample (1 μL) was injected at 280 °C in spitless mode. Helium (> 99.999%, purity) was used as the carrier gas at a linear velocity of 36.3 cm/s. The oven temperature was kept at 60 °C for 1 min, then increased to 130 °C at 15 °C/min, then increased to 280 °C at 10 °C/min and kept for 5 min. The total run time was 26 min. We used the electron ionization (EI) mode at 70 eV in the mass spectrometer. The interface and ion source temperatures were both 200 °C.

Table 2 Comparison of pesticide concentrations detected in Beijing in different studies

	Concentration range (ng/L)		
	Previous studies	This study	References
Alpha-HCH	27.6–558	ND	(Zhang et al. 2004)
Beta-HCH	22.3–447	ND–16.7	
Gamma-HCH	11–50.2	ND	
Delta-HCH	ND–282	ND	
Heptachlor	ND–958	ND	
Aldrin	4.5–108	13.4–163	
Dieldrin	ND–36.6	1.1–23.3	
Endrin	ND–303	ND	
Alpha-endosulfan	ND–154	ND	
Beta-endosulfan	ND–446	ND	
4,4′-DDE	3.71–208	ND–3.5	
4,4′-DDT	14.9–415	ND–5.6	
2,4′-DDT	ND–1.4	ND–5.6	(Li et al. 2008b)
Atrazine	8–19	9.3–311	(Qi et al. 2015)
Dichlorvos		ND–5.5	-
Fenobucarb		ND–3.9	
Dicofol		ND–5.7	
Acetochlor		ND–76.9	
Chlorothalonil		ND–8.7	

Quality assurance and control (QA/QC)

Ultrapure deionized water was used as the blank sample to ensure no background contamination. Each batch, including 8~14 water samples and 2 blank samples, was extracted and analysed together. The recoveries of pesticides in ultrapure water were calculated by spiking accurate amounts of 27 standards at concentrations of 100 ng/L and 20 ng/L (n = 3). The mean recovery of each compound ranged from 72%~122% (RSD ≤ 12.2%). The limits of quantification (LOQs) were 1.0~5.0 ng/L at a signal-to-noise ratio (S/N) above 10. A sample concentration lower than the limit of detection (LOD) was regarded as not detected (ND). Dichlorvos-d6, alpha-HCH-d6 and malathion-d6 were used as surrogates to calibrate the standard curves.

Ecological risk assessment

The ecological risk was calculated for each pesticide in the three rivers using the risk quotient (RQ) method (Palma et al. 2014; Thomatou et al. 2013; Vryzas et al. 2011). The RQ for each compound was acquired by dividing the measured concentration (MEC) by the predicted no effect concentration (PNEC)

(Iturburu et al. 2019). PNEC (Table S2) was acquired by dividing the hazard concentration (HC5), which was derived from the species sensitivity distribution (SSD) model, with the affect factor (AF). Here, AF was set at 5 (Amiard and Amiard-Triquet 2015). In this study, the toxicity data for standard test species (fish and algae) were taken from the EPA ECOTOX database (https://cfpub.epa.gov/ecotox/), which provides basic SSD model construction data with a log-logistic fitting function. For the compounds whose NOEC values were not available, the lethal concentration (LC_{50}) or effect concentration (EC_{50}) were used (Vryzas et al. 2011). The NOEC or $L(E)C_{50}$ values met the screening criteria, including toxicity endpoints, laboratory freshwater environments and durations of more than 96 h (He et al. 2019). For test species less than 5 (Lewis and Thursby 2018), RQ was not calculated in this study. The restrictive RQ ranking was determined as follows: $0 \le RQ < 0.1$, low risk; $0.1 \le RQ < 1$, medium risk; and $RQ \ge 1$, high risk (Hernando et al. 2006; Tang et al. 2018).

$$\mathrm{PNEC} = \left(a - b \cdot \mathrm{Ln}\left(\frac{1}{Y_{5\%}} - 1\right)\right) / \mathrm{AF} \quad (1)$$

$$\mathrm{RQ} = \frac{\mathrm{MEC}}{\mathrm{PNEC}} \quad (2)$$

where a and b are two parameters of the log-logistic fitting function and $Y_{5\%}$ is the 5% cumulative frequency.

Results and discussion

Exposure

Detection frequency and concentrations of 27 target pesticides

A total of 27 pesticides were detected in this study, and the results showed that the concentrations of more than half of the contaminant were below LOD. It should be noted that 13 of them have been banned in China since 2009 (UNEP 2009).Twelve pesticides were found in the samples with concentrations of 1.0–311 ng/L and detection frequencies of 6.7–100%. Compared with previous studies, these pesticides were found in quite low concentrations (≤ 16.7 ng/L) and low frequencies (≤ 30%), except aldrin and dieldrin (Chen et al. 2008; Xue et al. 2005; Zhang et al. 2004). Although aldrin and dieldrin have been banned in China, both were universally detected in the samples at relatively high levels (13.4–163 ng/L and 1.14–23.3 ng/L, respectively) in Beijing's rivers (Table 2). These concentrations were comparable to the levels in Beijing reported in previous studies (4.5–118 ng/L and ND–36.6 ng/L, respectively) (Xue et al. 2006; Zhang et al. 2004). High concentrations of aldrin (357–683 ng/L) and dieldrin (258–196 ng/L) have also been found in the groundwater of the Yangtze River basin and Taihu Lake region (Pan et al. 2019; Wu et al. 2014). High concentrations of banned aldrin and dieldrin in water might have been attributed to historical applications (Xue et al. 2006). However, the presence of aldrin in the shallow sediment layer (0–10 cm) suggested that the possibility of illegal use (Wang et al. 2017). High concentrations of the two pesticides have also been detected in surface waters in India (Arisekar et al. 2019) and Vietnam (Nguyen et al. 2019) and in wastewater in Spain (Barco-Bonilla et al. 2013) and Greece (Katsoyiannis and Samara 2004), although they have been banned in the developed countries since the 1970s and 1980s. Thus, further exploration of potential pollution sources is required.

Pesticide concentrations found in this study were compared with other studies conducted in the same area (Florian et al. 2012; Zhang et al. 2004), as shown in Fig. 2. Insecticides, including heptachlor, HCHs, 4,4′-DDE, 4,4′-DDT and endosulfans, were detected at lower concentrations (ND–16.7 ng/L) in this study, while a 2003 study found concentrations as high as 958, 993, 208 and 446 ng/L, respectively (Zhang et al. 2004). The sharply decrease of HCHs and DDTs were consistent with a recent study conducted in Beijing (Shao et al. 2016). The decreases of DDTs (4′-DDE and 4,4′-DDT) and HCHs (alpha-HCH and gamma-HCH) might have been attributed to the Stockholm Convention implementation (UNEP 2009). DDTs and HCHs have been banned in China since 1983. Possible DDT and HCH sources may have been atmospheric deposition and contaminated soil in the study area (Man et al. 2011), as well as illegal use in China (Man et al. 2018). A number of studies from other regions of China continue to report significant levels of these compounds (Kan et al. 2020; Wang et al. 2014).

Most of the currently used pesticides were detected with low concentrations (≤ 8.7 ng/L) and low detection frequencies (≤ 50%). However, atrazine and acetochlor, the two widely used herbicides, exhibited high levels in the rivers (9.3–311 ng/L and ND–76.9 ng/L, respectively) (Fig. 2). Both herbicides are widely used for controlling grasses and broadleaf weeds in crops and grasslands. Atrazine and acetochlor were

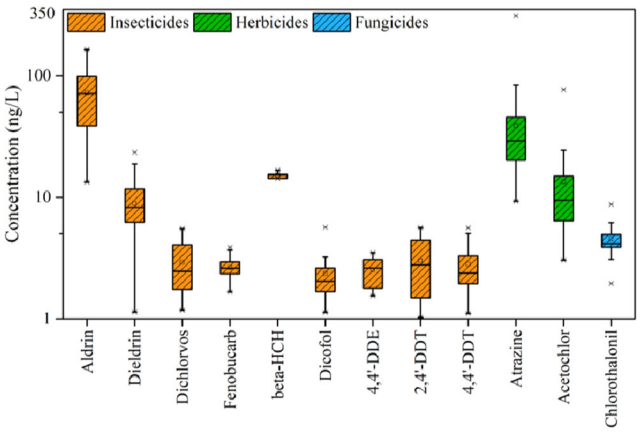

Fig. 2 Concentration ranges of 12 pesticides in all samples of the three Beijing rivers

reported to be the main pollutants in the surface water and wastewater in Beijing with ranges of 0.1–5.2 μg/L and 1.0–4.0 μg/L, respectively (Ge et al. 2010). Furthermore, in corn belts, the atrazine concentration could be as high as 95 μg/L (EPA USEPA 2017). The green space including small corn planting, golf courses, lawns and gardens (Metcalfe et al. 2016), which covers 47.4% urban area (Wu and Kim 2020), could be a substantial source of urban herbicide pollution in Beijing.

Exposure of pesticides in MWTP effluents and the corresponding rivers

The pesticide profiles in the MWTP effluents and the corresponding rivers in different seasons are shown in Fig. 3 and Fig. S1. It is clear that the MWTP effluents exhibited a pesticide profile similar to that of the corresponding rivers. In general, aldrin was the most abundant pesticide, followed by atrazine and dieldrin. In the summer, acetochlor was detected in the three rivers, while beta-HCH and 4,4′-DDT were detected in all of the TH river samples. It should be noted that the aldrin concentrations in the MWTP effluents were higher than those in the upstream rivers, suggesting that the source of aldrin in rivers was probably from MWTP inputs. In addition, the atrazine and acetochlor in the river samples usually exhibited higher concentrations than those in the effluent samples, suggesting that herbicides in rivers were mainly attributed to their application in urban landscapes.

There were higher total pesticide concentrations (97.4 ng/L, 380 ng/L and 105 ng/L for rivers QH, TH and LS, respectively) in summer. In general, more pesticides were applied in summer, and there is 80% precipitation in Beijing during this season (Heeb et al. 2012). Therefore, the high pesticide usage and rain events might have been the main reasons for the relatively high pesticide concentrations in the summer (Glinski et al. 2018). Among the three rivers, the TH river generally had the highest total concentrations (55.2–380 ng/L). The TH river receives effluent from the GBD MWTP, which has the largest wastewater treatment capacity in Beijing (1,000,000 m^3/day). The predominant TH river contaminants were atrazine (9.3–311 ng/L), aldrin (14.9–163 ng/L) and acetochlor (5.1–34.6 ng/L), with the greatest concentrations of herbicides atrazine and acetochlor occurring in the summer (Fig. 3). The total average pesticide concentration detected in the TH river in 2003 was 1.76 times higher than that in this study (Zhang et al. 2004), which might have been associated with MWTP regulation and upgrades. In addition, the occurrence of beta-HCH in the TH river, particularly in summer, might have been associated with release from contaminated soil and rive sediments. There was a pesticide plant in the TH river basin that produced HCHs and DDTs until 1983. Although the factory was decommissioned, HCHs and DDTs were found in contaminated soil in the ranges of 13.2–149 mg/kg and 3.0–67.4 mg/kg, respectively (Yang et al. 2009). Thus, these pesticides might have been released from the contaminated soil and sediments during rainy seasons.

Beijing MWTP pesticide discharge loads

Figure 4 shows the pesticide discharge loads from the three MWTPs during the four seasons. In general, high loads of aldrin, atrazine and dieldrin were discharged from the three MWTPs in different seasons. The GBD MWTP had the greatest load due to its high wastewater treatment capacity. According to previous studies, DDTs, HCHs, heptachlor, endosulfan, aldrin and dieldrin were the most dominant pesticides in Beijing MWTP effluents and sludge (Li et al. 2008a; Liu et al. 2013; Zhang et al. 2004). As shown in Table 2, these pesticide concentrations have significantly decreased, and some pesticides, such as heptachlor and endosulfan, could not be detected. Part of the reason for the decreased pesticide occurrence was attributed to their regulation under the Stockholm Convention. Another reason might have been associated with the three MWTP upgrades to ozone use. MWTP ozonation could significantly reduce micropollutant effluent loads because ozone and its self-decomposing hydroxyl radicals (OH) react quickly with electron-rich compounds such as amines, aromatics and alkanes (Bourgin et al. 2018). Ozonation has been demonstrated to substantially reduce certain pesticides in wastewater, including dichlorvos (100%) (Cruz-Alcalde et al. 2018) and HCHs (≥ 80%) (Derco et al. 2015). However, many pesticides cannot be removed by ozonation. For instance, 8% atrazine and less than 30% alachlor were removed from real wastewater treatment effluent when applying 0.5 g O_3/g DOC (Liu et al. 2019), and less than 23% aldrin and dieldrin were removed from natural water using 3 mg O_3/L (Ormad et al. 2010). This could explain why the concentrations of atrazine, aldrin and dieldrin were still quite high despite the MWTP upgrades. Thus, ozone alone does not sufficiently reduce MWTP pesticide loads.

Ecological risk assessment

The RQ for each pesticide in the 3 rivers supplemented with the corresponding MWTP effluents were derived based on the measured concentrations of each compound and the derived PNEC values (Table S2). Interestingly, as depicted in Fig. 5, a majority of the pesticides exhibited low risks to fish and algae in the receiving bodies. The RQ values of many legacy pesticides were below 0.1, which was a marked decrease from the study conducted before the Stockholm Convention implementation (Zhang et al. 2004). However, aldrin, which is known to affect river fish gene expression (Jhamtani et al. 2018) and has been banned in China since 2002, posed a medium risk to fish. Atrazine, ubiquitously found in this study, posed a

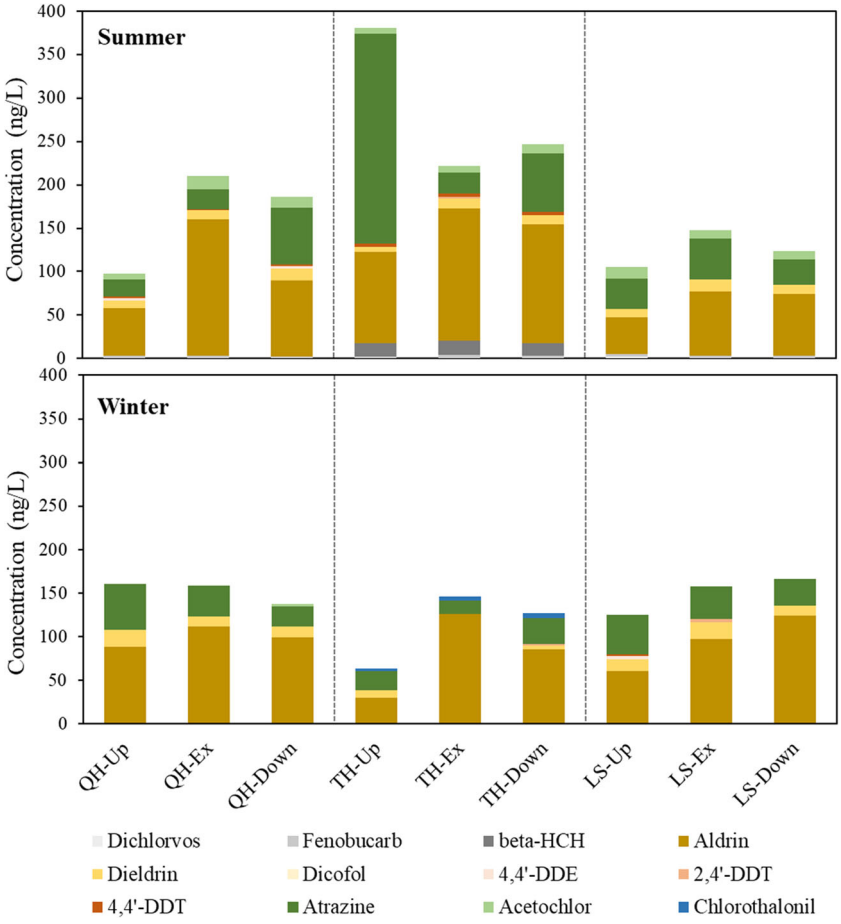

Fig. 3 Pesticide profiles in MWTP effluents upstream and downstream of the rivers in summer and winter

medium risk to fish and algae. This result was consistent with Xu, who reported that atrazine posed a potential risk in major rivers in China (Xu et al. 2016). The risks attributed to aldrin and atrazine may lead to changes in fish and algae communities. Therefore, additional measures should be taken to reduce ecological risks from these pesticides. In Germany and Switzerland, an increasing number of MWTPs are required to adopt advanced treatment technologies, including ozonation and activated carbon absorption, to reduce the discharge of micropollutants into the environment (Eggen et al. 2014, Joss et al. 2008). However, some pesticides cannot be effectively removed by ozonation (Margot et al. 2013). Therefore, to further reduce ecological risks from pesticides, additional

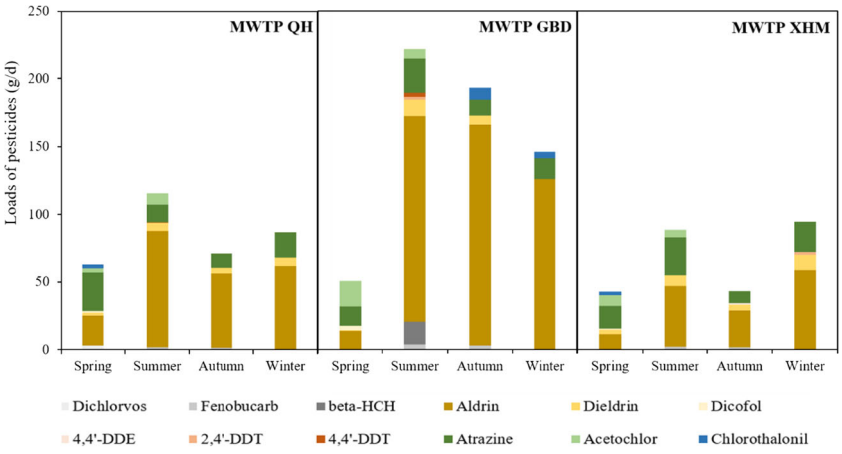

Fig. 4 Pesticide loads from the three MWTPs in the four seasons

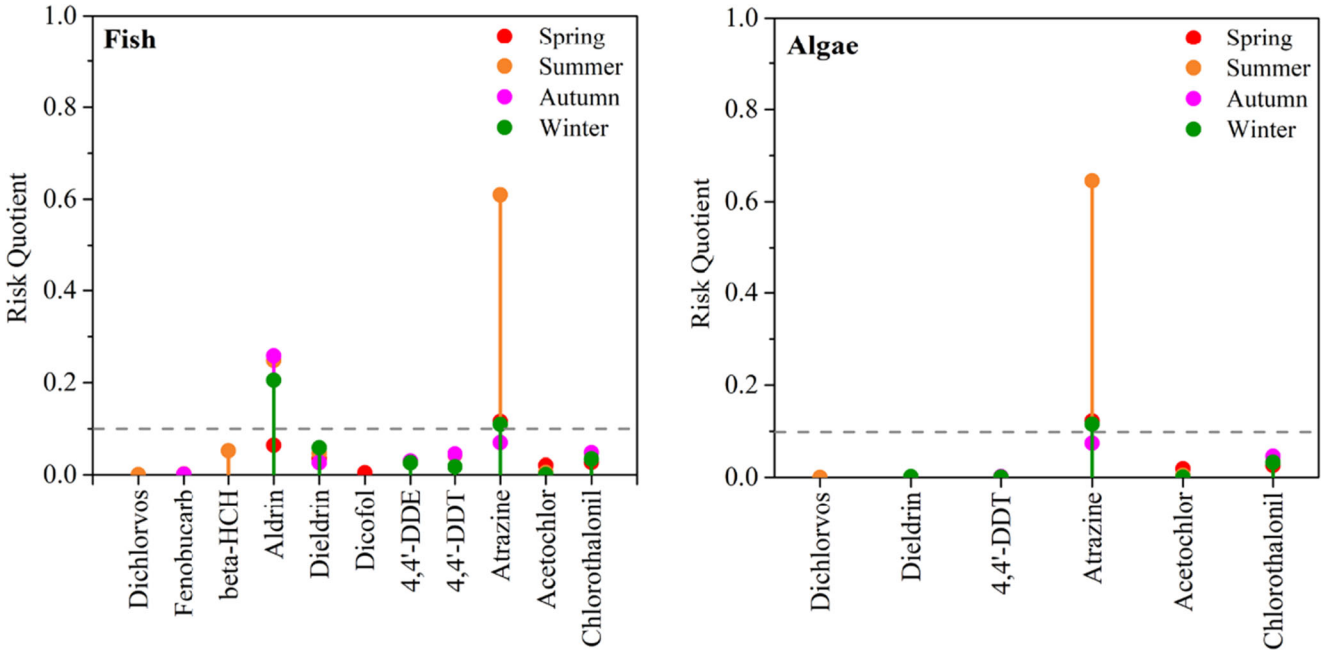

Fig. 5 Calculated risk quotients for pesticides in the three rivers ($0 \leq RQ < 0.1$, low risk; $0.1 \leq RQ < 1$, medium risk; $RQ \geq 1$, high risk)

technologies including advanced oxidation technologies (Malakootian et al. 2020; Vagi and Petsas 2020) should be considered to remove micropollutants from wastewater.

Conclusions

This study found 27 pesticides, including legacy and current use pesticides, in 3 MWTP effluents and their corresponding receiving rivers over a period of 4 seasons in Beijing. Among the 27 pesticides, more than half were observed with concentrations less than the LOD. In general, legacy pesticides, including heptachlor, HCHs, 4,4′-DDE, 4,4′-DDT and endosulfans, were no longer found in the rivers owing to the implementation of the Stockholm Convention on POPs. However, aldrin and dieldrin, which are banned in China, still exhibited high levels. Moreover, high loads of both pesticides were found in the wastewater effluents, indicating that MWTP discharge may be a potential point source in the receiving rivers. Low concentrations of the currently used pesticides, such as dichlorvos, fenobucarb, dicofol and chlorothalonil, were also found in the 3 receiving rivers. However, atrazine has the greatest concentration due to its overuse in urban landscapes. Additionally, there was an ecological risk to river aquatic organisms from the legacy and currently used pesticides, and aldrin and atrazine posed medium risks to fish and algae. Therefore, efforts should be devoted to identifying the potential sources of aldrin and dieldrin and upgrading of the MWTPs to improve the ecological safety of the rivers.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-021-13140-0.

Availability of data and materials All data analysed during the current study are available in the supplementary material.

Author contribution Yangping Zhang analysed and processed all sample data and was a major contributor in writing the manuscript. Min Yang and Haifeng Zhang reviewed and edited the original draft. All authors read and approved the final manuscript.

Funding This work was supported by the project of Chinese Academy of Sciences (No. QYZDY-SSW-DQC004) and Major Science and Technology Program for Water Pollution Control and Treatment (No. 2017ZX07502003).

Declarations

Ethics approval and consent to participate Not applicable for ethics approval and consent to participate.

Consent for publication Not applicable for consent for publication.

Competing interests The authors declare that they have no competing interests.

References

Amiard J-C, Amiard-Triquet C (2015) Chapter 2—conventional risk assessment of environmental contaminants. In: Amiard-Triquet C, Amiard J-C, Mouneyrac C (eds) Aquatic Ecotoxicology. Academic Press, Cambridge, pp 25–49

Arisekar U, Shakila RJ, Jeyasekaran G, Shalini R, Kumar P, Malani AH, Rani V (2019) Accumulation of organochlorine and pyrethroid pesticide residues in fish, water, and sediments in the Thamirabarani river system of southern peninsular India. Environ Nanotechnol Monitor Manag 11:100194

Barco-Bonilla N, Romero-González R, Plaza-Bolaños P, Martínez Vidal JL, Garrido Frenich A (2013) Systematic study of the contamination of wastewater treatment plant effluents by organic priority compounds in Almeria province (SE Spain). Sci Total Environ 447: 381–389

Barion A, Balsaa P, Werres F, Neuhaus U, Schmidt TC (2018) Stability of organochlorine pesticides during storage in water and loaded SPE disks containing sediment. Chemosphere 210:57–64

Bollmann UE, Tang C, Eriksson E, Jönsson K, Vollertsen J, Bester K (2014) Biocides in urban wastewater treatment plant influent at dry and wet weather: concentrations, mass flows and possible sources. Water Res 60:64–74

Bourgin M, Beck B, Boehler M, Borowska E, Fleiner J, Salhi E, Teichler R, von Gunten U, Siegrist H, McArdell CS (2018) Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: abatement of micropollutants, formation of transformation products and oxidation by-products. Water Res 129:486–498

Chen J, Liu C, Yang Z, Wang J (2008) Residues and characteristics of organochlorine pesticides in the surface water in the suburb of Beijing. Earth Sci Front 15:242–247

Chen Y, Yu K, Hassan M, Xu C, He Y (2018) Occurrence, distribution and risk assessment of pesticides in a river-reservoir system. Ecotoxicol Environ Saf 166:320–327

Cruz-Alcalde A, Sans C, Esplugas S (2018) Priority pesticide dichlorvos removal from water by ozonation process: reactivity, transformation products and associated toxicity. Sep Purif Technol 192:123–129

Derco J, Dudáš J, Valičková M, Šimovičová K, Kecskés J (2015) Removal of micropollutants by ozone based processes. Chem Eng Process Process Intensif 94:78–84

Donna G, Thomas PS, Van Meter RJ, Black CM, Henderson MW (2018) Analysis of pesticides in surface water, stemflow, and throughfall in an agricultural area in South Georgia, USA. Chemosphere 209:496–507

Eggen RIL, Hollender J, Joss A, Schärer M, Stamm C (2014) Reducing the discharge of micropollutants in the aquatic environment: the benefits of upgrading wastewater treatment plants. Environ Sci Technol 48:7683–7689

EPA USEPA (2017) Atrazine ecological exposure monitoring program data and results. https://www.epa.gov/ingredients-used-pesticide-products/atrazine-ecological-exposure-monitoring-program-data-and-results. Accessed Nov 2020

Florian H, Heinz S, Beno TPC, Weixiao Q, Huijuan L, Philipp L, Beat M, Michael B (2012) Organic micropollutants in rivers downstream of the megacity Beijing: sources and mass fluxes in a large-scale wastewater irrigation system. Environ Sci Technol 46:8680–8688

Gaur N, Narasimhulu K, PydiSetty Y (2018) Recent advances in the bioremediation of persistent organic pollutants and its effect on environment. J Clean Prod 198:1602–1631

Ge J, Cong J, Sun Y, Li G, Zhou Z, Qian C, Liu F (2010) Determination of endocrine disrupting chemicals in surface water and industrial wastewater from Beijing, China. Bull Environ Contam Toxicol 84: 401–405

Glinski DA, Purucker ST, Meter RJV, Black MC, Henderson WM (2018) Analysis of pesticides in surface water, stemflow, and throughfall in an agricultural area in South Georgia, USA. Chemosphere 209:496–507

Grung M, Lin Y, Zhang H, Steen AO, Huang J, Zhang G, Larssen T (2015) Pesticide levels and environmental risk in aquatic environments in China—a review. Environ Int 81:87–97

He W, Kong X, Qin N, He Q, Xu F (2019) Combining species sensitivity distribution (SSD) model and thermodynamic index (exergy) for system-level ecological risk assessment of contaminates in aquatic ecosystems. Environ Int 133:105275

Heeb F, Singer H, Pernet-Coudrier B, Qi W, Liu H, Longrée P, Müller B, Berg M (2012) Organic micropollutants in rivers downstream of the megacity Beijing: sources and mass fluxes in a large-scale wastewater irrigation system. Environ Sci Technol 46:8680–8688

Heinz-R K, Rita T (2013) Wildlife ecotoxicology of pesticides: can we track effects to the population level and beyond? Science 341:759–765

Hernando MD, Mezcua M, Fernández-Alba AR, Barceló D (2006) Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. Talanta 69:334–342

Iturburu FG, Calderon G, Amé MV, Menone ML (2019) Ecological Risk Assessment (ERA) of pesticides from freshwater ecosystems in the Pampas region of Argentina: legacy and current use chemicals contribution. Sci Total Environ 691:476–482

Jhamtani RC, Shukla S, Sivaperumal P, Dahiya MS, Agarwal R (2018) Impact of co-exposure of aldrin and titanium dioxide nanoparticles at biochemical and molecular levels in Zebrafish. Environ Toxicol Pharmacol 58:141–155

Jiujiang S, Xiaoping W, Ping G, Joswiak DR, Lide T, Tandong Y, Jones KC (2013) Monsoon-driven transport of organochlorine pesticides and polychlorinated biphenyls to the Tibetan Plateau: three year atmospheric monitoring study. Environ Sci Technol 47:3199–3208

Joss A, Siegrist H, Ternes TA (2008) Are we about to upgrade wastewater treatment for removing organic micropollutants? Water Sci Technol 57:251–255

Kan K-C, Gu X-H, Li H-M, Chen H-H, Mao Z-G, Zeng Q-F (2020) Distribution and risk assessment of OCPs in surface water, sediments, and fish from Lake Gucheng and inflow and outflow rivers. Huan jing ke xue=Huanjing kexue 41:1346–1356

Katsoyiannis A, Samara C (2004) Persistent organic pollutants (POPs) in the sewage treatment plant of Thessaloniki, northern Greece: occurrence and removal. Water Res 38:2685–2698

Lewis M, Thursby G (2018) Aquatic plants: test species sensitivity and minimum data requirement evaluations for chemical risk assessments and aquatic life criteria development for the USA. Environ Pollut 238:270–280

Li X, Zhang Q, Dai J, Gan Y, Zhou J, Yang X, Cao H, Jiang G, Xu M (2008a) Pesticide contamination profiles of water, sediment and aquatic organisms in the effluent of Gaobeidian wastewater treatment plant. Chemosphere 72:1145–1151

Li X, Zhang Q, Dai J, Gan Y, Zhou J, Yang X, Cao H, Jiang G, Xu M (2008b) Pesticide contamination profiles of water, sediment and aquatic organisms in the effluent of Gaobeidian wastewater treatment plant. Chemosphere 72:1145–1151

Liu C, Li K, Yu L, Xu Y, Huang B, Wu J, Wang Z (2013) POPs and their ecological risk in sewage sludge of waste water treatment plants in Beijing, China. Stoch Env Res Risk A 27:1575–1584

Liu Z, Demeestere K, Van Hulle S (2019) Enhanced ozonation of trace organic contaminants in municipal wastewater plant effluent by adding a preceding filtration step: comparison and prediction of removal efficiency. ACS Sustain Chem Eng 7:14661–14668

Ma Y, Yun X, Ruan Z, Lu C, Shi Y, Qin Q, Men Z, Zou D, Du X, Xing B, Xie Y (2020) Review of hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) contamination in Chinese soils. Sci Total Environ 749:141212

Malakootian M, Shahesmaeili A, Faraji M, Amiri H, Silva Martinez S (2020) Advanced oxidation processes for the removal of organophosphorus pesticides in aqueous matrices: a systematic review and meta-analysis. Process Saf Environ Prot 134:292–307

Man YB, Chow KL, Wang HS, Lau KY, Sun XL, Wu SC, Cheung KC, Chung SS, Wong MH (2011) Health risk assessment of

organochlorine pesticides with emphasis on DDTs and HCHs in abandoned agricultural soils. J Environ Monit 13:2250–2259
Man YB, Chow KL, Cheng Z, Kang Y, Wong MH (2018) Profiles and removal efficiency of organochlorine pesticides with emphasis on DDTs and HCHs by two different sewage treatment works. Environ Technol Innov 9:220–231
Margot J, Kienle C, Magnet A, Weil M, Rossi L, Alencastro LFD, Abegglen C, Thonney D, Chèvre N, Schärer M (2013) Treatment of micropollutants in municipal wastewater: ozone or powdered activated carbon? Sci Total Environ 461-462:480–498
Metcalfe CD, Sultana T, Li H, Helm PA (2016) Current-use pesticides in urban watersheds and receiving waters of western Lake Ontario measured using polar organic chemical integrative samplers (POCIS). J Great Lakes Res 42:1432–1442
Nguyen TX, Nguyen BT, Tran HTT, Mai H, Bach Q-V (2019) Seasonal, spatial variation, and potential sources of organochlorine pesticides in water and sediment in the lower reaches of the Dong Nai river system in Vietnam. Arch Environ Contam Toxicol 77:514–526
Ormad MP, Miguel N, Lanao M, Mosteo R, Ovelleiro JL (2010) Effect of application of ozone and ozone combined with hydrogen peroxide and titanium dioxide in the removal of pesticides from water. Ozone Sci Eng 32:25–32
Palma P, Kock-Schulmeyer M, Alvarenga P, Ledo L, Barbosa IR, López de Alda M, Barceló D (2014) Risk assessment of pesticides detected in surface water of the Alqueva reservoir (Guadiana basin, southern of Portugal). Sci Total Environ 488-489:208–219
Pan H, Lei H, He X, Xi B, Xu Q (2019) Spatial distribution of organochlorine and organophosphorus pesticides in soil-groundwater systems and their associated risks in the middle reaches of the Yangtze River Basin. Environ Geochem Health 41:1833–1845
Pernet-Coudrier B, Qi W, Liu H, Müller B, Berg M (2012) Sources and pathways of nutrients in the semi-arid region of Beijing–Tianjin, China. Environ Sci Technol 46:5294–5301
Qi W, Singer H, Berg M, Müller B, Pernet-Coudrier B, Liu H, Qu J (2015) Elimination of polar micropollutants and anthropogenic markers by wastewater treatment in Beijing, China. Chemosphere 119:1054–1061
Qiao M, Zheng Y-M, Zhu Y-G (2011) Material flow analysis of phosphorus through food consumption in two megacities in northern China. Chemosphere 84:773–778
Qiao M, Bai Y, Cao W, Huo Y, Zhao X, Liu D, Li Z (2018) Impact of secondary effluent from wastewater treatment plants on urban rivers: polycyclic aromatic hydrocarbons and derivatives. Chemosphere 211:185–191
Rani L, Thapa K, Kanojia N, Sharma N, Singh S, Grewal AS, Srivastav AL, Kaushal J (2020) An extensive review on the consequences of chemical pesticides on human health and environment. J Clean Prod 283:124657
Revankar PR, Shyama SK (2009) Genotoxic effects of monocrotophos, an organophosphorous pesticide, on an estuarine bivalve, *Meretrix ovum*. Food Chem Toxicol 47:1618–1623
Shao Y, Han S, Ouyang J, Yang G, Liu W, Ma L, Luo M, Xu D (2016) Organochlorine pesticides and polychlorinated biphenyls in surface water around Beijing. Environ Sci Pollut Res 23:24824–24833
Shi P, Zhou S, Xiao H, Qiu J, Li A, Zhou Q, Pan Y, Hollert H (2018) Toxicological and chemical insights into representative source and drinking water in eastern China. Environ Pollut 233:35–44
Tang X-Y, Yang Y, Tam NF-Y, Tao R, Dai Y-N (2018) Pesticides in three rural rivers in Guangzhou, China: spatiotemporal distribution and ecological risk. Environ Sci Pollut Res 26:3569–3577
Thomatou AA, Zacharias I, Hela D, Konstantinou I (2013) Determination and risk assessment of pesticide residues in lake Amvrakia (W. Greece) after agricultural land use changes in the lake's drainage basin. Int J Environ Anal Chem 93:780–799
UNEP (2009) Stockholm Convention on persistent organic pollutants. http://chm.pops.int/TheConvention/ThePOPs/AllPOPs
Vagi MC, Petsas AS (2020) Recent advances on the removal of priority organochlorine and organophosphorus biorecalcitrant pesticides defined by Directive 2013/39/EU from environmental matrices by using advanced oxidation processes: an overview (2007–2018). J Environ Chem Eng 8:102940
Vryzas Z, Alexoudis C, Vassiliou G, Galanis K, Papadopoulou-Mourkidou E (2011) Determination and aquatic risk assessment of pesticide residues in riparian drainage canals in northeastern Greece. Ecotoxicol Environ Saf 74:174–181
Wang H-S, Chen Z-J, Cheng Z, Du J, Man Y-B, Leung H-M, Giesy JP, Wong CKC, Wong M-H (2014) Aquaculture-derived enrichment of hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) in coastal sediments of Hong Kong and adjacent mainland China. Sci Total Environ 466-467:214–220
Wang W, Bai J, Zhang G, Wang X, Jia J, Cui B, Liu X (2017) Depth-distribution, possible sources, and toxic risk assessment of organochlorine pesticides (OCPs) in different river sediment cores affected by urbanization and reclamation in a Chinese delta. Environ Pollut 230:1062–1072
Wu L, Kim SK (2020) Health outcomes of urban green space in China: evidence from Beijing. Sustain Cities Soc 65:102604
Wu C, Luo Y, Gui T, Huang Y (2014) Concentrations and potential health hazards of organochlorine pesticides in shallow groundwater of Taihu Lake region, China. Sci Total Environ 470-471:1047–1055
Xu X, Li C, Sun J, Wang H, Wang D, Song H, Wang Z (2016) Residue characteristics and ecological risk assessment of twenty-nine pesticides in surface water of major river-basin in China. Asian J Ecotoxicol 11:347–354
Xue N, Xu X, Jin Z (2005) Screening 31 endocrine-disrupting pesticides in water and surface sediment samples from Beijing Guanting reservoir. Chemosphere 61:1594–1606
Xue N, Zhang D, Xu X (2006) Organochlorinated pesticide multiresidues in surface sediments from Beijing Guanting reservoir. Water Res 40: 183–194
Yang W, Wang R, Zhou C, Li F (2009) Distribution and health risk assessment of organochlorine pesticides (OCPs) in industrial site soils: a case study of urban renewal in Beijing, China. J Environ Sci 21:366–372
Yang G, Ma L, Xu D, Liu L, Jia H, Chen Y, Zhang Y, Chai Z (2012) Temporal variations of organochlorine pesticides in precipitation in Beijing, China. Atmos Environ 61:614–619
Zhang Z, Jun H, Gang Y, Huasheng H (2004) Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. Environ Pollut 130:249–261
Zheng S, Chen B, Qiu X, Chen M, Ma Z, Yu X (2016) Distribution and risk assessment of 82 pesticides in Jiulong River and estuary in South China. Chemosphere 144:1177–1192