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Dilution or enrichment: the effects of flood on pollutants in urban rivers

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Abstract

Background: Flood events increase the risk of sediment erosion and hence the release of particle-bound pollutants besides other processes that can be observed during such events like transportation, lateral distribution and other. Macropollutants, such as acids, salts, nutrients, and natural organic matter, are usually diluted by flooding, while the effect of floods on micropollutants is still unclear. To fill this gap, Qingshui Stream, a tributary of the Jialing River in the city of Chongqing that suffered 75,000 $m^3 \cdot s^{-1}$ flood in August 2020 was selected in the current study to clarify effects of flood-induced pollution transportation. 14 surface water samples and 14 sediment samples were collected to analyze the occurrence of micropollutants (including 21 organochlorine pesticides (OCPs), 34 organophosphorus pesticides (OPPs) and 3 estrogenic compounds) before, during and after the flood. Finally, the environmental risks were evaluated by risk quotient (RQ).

Results: The concentrations of total phosphorus (TP), total nitrogen (TN), chemical oxygen demand (COD) in the surface water decreased from upstream to downstream, and the amounts were diluted by flooding from 0.08 to 0.05 $mg \cdot L^{-1}$ for TP, from 0.06 to 0.02 $mg \cdot L^{-1}$ for TN and from 132 to 27 $mg \cdot L^{-1}$ for COD, respectively. The concentration of estrogenic compound was up to 90 $ng \cdot g^{-1}$, which was reduced to be lower than the limit of detection during flood. Alpha-endosulfan, delta-BHC, mirex, dichlorvos, phosdrin, thionazine, tetraethyl pyrophosphate, diazinon, methyl parathion, malathion, chlorpyrifos, famphur, and EPN were diluted by flooding, i.e., the concentration of delta-BHC reduced from 6.67 to 0.09 $ng \cdot g^{-1}$; whereas, pp′-DDD, heptachlor epoxide, o,o,o-triethylphosphorothioate, dimethoate, rabon and fensulfothion were enriched after the flood. The environmental risk was observed to be mainly arise from the presence of OPPs, which increased after flooding. The RQ values of OPPs and OCPs increased after the flood, and the potential environmental risk of OPPs accounted for the majority portion of the risk.

Conclusions: The concentrations of macropollutants in surface water and sediments, and 14 micropollutants in sediments were diluted, while pesticides such as pp′-DDD, heptachlor epoxide, o,o,o-triethylphosphorothioate, dimethoate, rabon and fensulfothion were enriched after the flood. These results suggested management on urban river should focus on potential risk of OPPs. The current study therefore could provide scientific evidence and regulatory reference for urban river ecosystem protection.

Keywords: Flood, Macropollutants, Micropollutants, Environmental risk, Urban River management

Background

With the rapid development on economy and technology, the intensification of human activities increased the release of pollutants into environments. Pollutants which were transported and transformed through air subsidence, river transportation, groundwater as well as surface runoff in environments [1], may lead to large-scale

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ecosystem damages. The wide use of pesticides around the world, have reported to cause adverse effects on water quality, biodiversity, and human health, including migration and transformation processes [2]. As one of the important transportation pathways, flooding erodes larger amounts of sediments than that of the non-flooding flow, and even introduce old sediment to the environment again [3]. Hence, pollutants accumulated in the sediments may also be mobilized and transformed as well during such events. Many studies illustrated the importance of pollutants transportation and transformation through rivers during flooding [4, 5].

Most studies of macropollutants focus mainly on, such as acids, salts, nutrients, and natural organic matter, occurring at $\mu g \cdot L^{-1}$ to $mg \cdot L^{-1}$ concentrations [6–8]. While the micropollutants that presented in water at low to very low concentrations ($\mu g \cdot L^{-1}$ to $ng \cdot L^{-1}$) may raise considerable toxicological concerns at environmental concentrations. For instance, pesticides, which are developed to increase crop production, were detected in surface water [9, 10], sediment [11], groundwater [12] and drinking water [13] at varying degrees. In considering the discrepancy of physical and chemical properties of micropollutants, they may lead to different migration rules and ecological effects in the environment [14, 15]. A study on trace element and pesticide dynamics indicated that pesticides and endocrine disruptor chemicals (EDCs) can be transported through air subsidence, river transportation, groundwater, and surface runoff [1]. Hence, urban rivers, some of which are previously as rural and/or natural rivers, have accumulated significant amounts of many micropollutants during urbanization process. And simultaneously, the natural hydrological regimen of urban rivers have been altered, which may result in unexpected environmental risk, in particularly during flooding events [16]. It is, therefore, of importance to understand the dynamic of pollutants, particularly for these micropollutants.

It is known that even though the concentration of EDCs is at the concentration level of $ng \cdot L^{-1}$, they could still show strong adverse biological effects [17]. Some EDCs exhibited toxicity, teratogenicity, carcinogenicity, and mutagenicity, such as interfering with fetal gender differences, causing genital cancer, changing glucose, and leading to fat metabolism [18, 19]. It is noticed that some micropollutants are persistent. The half-life of chlorpyrifos, dichloro diphenyl trichloroethane (DDT) and ring diene pesticide (aldrin, dieldrin, heptachlor, chlordane and mirex and endosulfan) range from a few months to a few years, in some cases for decades [20]. DDT has been estimated to degrade to 1,1-dichloro-2,2-bis(p-chlorophenyl) ethane (DDD), 1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene (DDE) and other metabolites in soil for 4 to 30 years, and some chlorinated organochlorine pesticides may remain stable for many years after use [21]. Although these pesticides have been banned for decades in the global scope, they caused serious environmental pollution due to its persistence [22]. A study by Wang et al. even showed that OCPs in sediments from urban river were higher than that in rural river [23]. Hence, urban rivers, some of which are previously as rural and/or natural rivers, have accumulated significant amounts of micropollutants during urbanization processes. Meanwhile, the hydraulic situation of urban rivers has been altered, which may result in unexpected environmental risk, in particular during flooding events [16]. Rivers are considered as sink and source of many pollutants. The role of sink and/or source depends on the dilution and enrichment dynamic of pollutants mixture which may change, for instance, by flooding erosion. When contaminates are re-mobilized and enter the water, the environmental risk might increase. More systematic studies on the effects of flooding to environmental risk in urban rivers are needed.

To answer the questions above, an urban river, named Qingshui Stream as a tributary of the Jialing River in Chongqing district was selected as the study area. This urban river, as many urban rivers in China and around the world, has been found to accumulate many pollutants, such as estrogens and pesticides [24–27]. A total of 28 surface water and sediment samples were collected before, during and after the flood to investigate macropollutants of total nitrogen (TN), total phosphorus (TP), total carbon (TC), chemical oxygen demand (COD). To clarify the transportation of micropollutants during the flood, 21 organochlorine pesticides (OCPs), 34 organophosphorus pesticides (OPPs) and 3 estrogenic compounds were analyzed in sediment samples. The risk quotient (RQ) was applied to evaluate the dynamic of potential environmental risks before, during and after flood. The current study could provide the scientific underpinnings and regulatory reference for urban river management and protection.

Methods

Study area

In August 2020, to study the effect of flood on the transportation and potential risk of pollutants in urban rivers, we selected the Qingshui Stream as the target (Fig. 1), in which five sites were set up from upstream to downstream (Additional file 1: Table S1). The Qingshui Stream originates in the Shapingba district of Chongqing, China and joins the Jialing River at Ciqikou. The length of the main stream amounts to 15.88 km, with a total basin area of 35 km^2 and the annual average flow is about 0.47 $m^3 \cdot s^{-1}$ [28]. The city of Chongqing has a

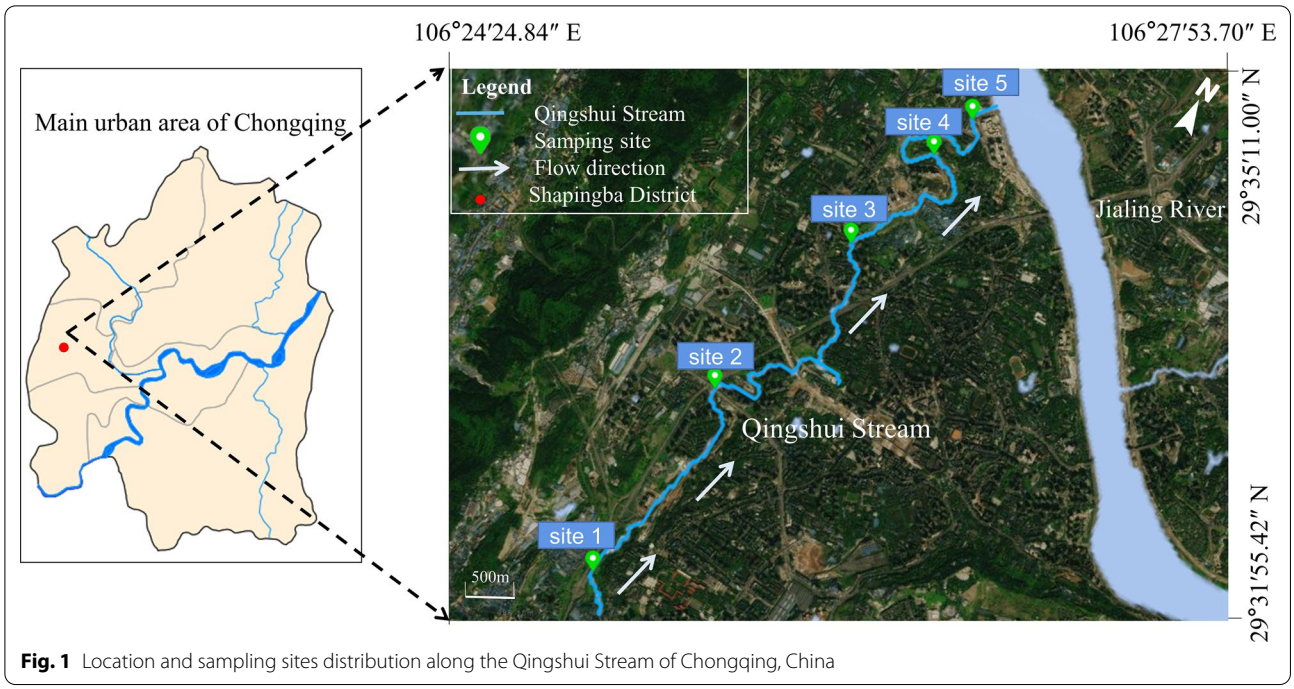

Fig. 1 Location and sampling sites distribution along the Qingshui Stream of Chongqing, China

subtropical humid climate, with annual average temperature of 17.8–18.6 ℃ and annual average precipitation of 1085–1141 mm. About 70% of the rainfall is concentrated in May to September. The pollution sources are mainly domestic sewage and urban surface runoff [29]. With urbanization process, the in conversion of natural surfaces to relatively impermeable ones in Chongqing urban area made more rainfall directly enter urban rivers through surface runoff and drainage pipe network transportation, which increased the flood intensity in Qingshui Stream. In addition, global climate change has led to increased extreme rainfall events and intensities [30]. When Chongqing city suffered about 75,000 $m^3 \cdot s^{-1}$ flood in August 2020, which raised the depth of the flooding in Qingshui Stream up to about 30 m.

Sampling and analysis preparation

Water was sampled at 50 cm below the surface, and sediments were collected by a Peterson dredger from the bottom of the river, samples were tripled treatments in each site and then combined into one sample mixture. The sampling times included three periods, that is, before (August 16, 2020), during (August 21, 2020), and after the flood (August 24, 2020). Each water or sediment sample consists of three sub-samples, a total of 28 samples including 14 surface water samples and 14 sediment samples, were finally collected during the course of the study. Besides, samples of site 5 after the flooding could not be collected due to river management regulations. Each water or sediment sample was taken into a 500-mL wide-mouth amber glass container that was pre-cleaned by ultrapure water. Samples were transported to the laboratory under 4 °C and stored in a refrigerator at − 20 °C.

Surface water samples of stream water was filtered by 0.45-μm syringe filter (Jinteng, Tianjin, China) and were stored at 4 °C in glass vials. The supernatant was filtered by 0.45-μm syringe filter (Jinteng, Tianjin, China) and stored at 4 °C. While the residue of sediments were freeze-dried and ground through a 60-mesh sieve, followed by weighting 20 g pre-treated sediment sample for Soxhlet extraction with 120 mL solvent mixture (*n*-hexane:acetone; *v*:*v* = 1:1) for 12 h. Afterwards, the extract was concentrated by a vacuum rotary evaporator (R201D, Yinggu, China) under the conditions of 40 °C and 60 rpm to 1–2 mL. Then, the extracts were further dried under nitrogen and re-dissolved with 1 mL methanol.

The re-dissolved extracts were filtered with a 0.22-μm glass fiber membrane. After filtration, samples were purified using Oasis HLB SPE cartridges (200 mg, 1 mL). The cartridges were activated with 6 mL methanol and 6 mL ultrapure water, followed by rinsing with 6 mL ultrapure water and vacuum dried for 30 min. The cartridges were eluted with 6 mL methanol, the eluent was dried with nitrogen at 35–40 °C, and finally the volume was concentrated to 1 mL with methanol.

Chemicals and materials

HPLC-grade solvents include methanol, acetone, and *n*-hexane, which were obtained from Sigma-Aldrich (China). The mixture of standard substances includes

21 organochlorine (alpha-BHC, hexachlorobenzene, beta-BHC, gamma-BHC, delta-BHC, heptachlor, aldrin, isodrin, heptachlor epoxide, o,p′-DDE, alpha-endosulfan, p,p′-DDE, o,p′-DDD, dieldrin, endrin, p,p′-DDD, o,p′-DDT, beta-endosulfan, p,p′-DDT, methoxychlor, mirex) (99% of purity) and 34 organophosphorus (o,o,o-triethylphosphorothioate, dichlorvos, phosdrin, tetraethyl pyrophosphate, thionazine, demeton o&s, prophos, dibrom, tetraethyl dithiopyrophosphate, monocrotophos, phorate, dimethoate, simazine, atrazine, propazine, diazinon, disulfoton, methyl parathion, fenchlorphos, malathion, chlorpyrifos, fenthion, parathion, trichloronate, merphos, anilazine, rabon, tokuthion, fensulfothion, sulprofos, famphur, EPN, guthion, coumaphos) (99% of purity), respectively, were purchased from ANPEL Laboratory Technologies, China. The standards of estradiol (E2), bisphenol a (BPA), and 17 alpha-ethynylestradiol (EE2) were purchased from Sigma-Aldrich (Germany), with the purity of HPLC grade. The mixture of organochlorine was prepared as 500 mg·L^{-1} with *n*-hexane, and that for organophosphorus was 400 mg·L^{-1} with *n*-hexane:acetone (*v*:*v* = 1:1). Estrogens were prepared with methanol at a concentration of 1 mg·L^{-1} as stock solution. All stock solutions were stored in a refrigerator at − 20 °C prior to use.

Measurement of sample physical and chemical properties

The TN concentration of surface water was detected by ultraviolet spectrophotometry with basic potassium persulfate [31]. The TP concentration of surface water was analyzed by ammonium molybdate spectrophotometric method with potassium persulfate as the digestion oxidant [32]. The COD concentration of the sample was determined by ultraviolet spectrophotometry [33]. Regarding the sediment samples, TN was determined by a Kjeldahl nitrogen determinator (UPT-K1800) according to the Kjeldahl method, and that for TP was a UV–vis spectrophotometer (TU-1901) by molybdenum–antimony resistance colorimetric method [34]. The total carbon concentration of sediments was measured in a TOC analyzer (Shimadzu TOC-L, Japan) by high-temperature combustion and oxidation method [35].

Determination of organic pollutants

The organochlorine and organophosphorus pesticides were measured by a gas chromatography–mass spectrometer (GC–MS) (Agilent 7890/5977MSD). The column was CD-5 MS (30 m × 0.25 mm × 0.25 um: GAEQ-554421). Helium (≥ 99.999%) was used as the carrier gas at a flow rate of 1 mL·min^{-1}. For measurement of organochlorine pesticides, the oven temperature was programmed from 100 °C for 2 min, raised to 250 °C at 25 °C·min^{-1}, and then raised to 300 °C at 20 °C min^{-1} and maintained for 5 min. The sample volume was 1 μL in splitless injection mode with an inlet temperature of 280 °C. The source temperature was set at 250 °C and the transfer line was at 280 °C. The oven temperature of organophosphorus was programmed from 60 °C for 2 min, raised to 180 °C at 5 °C·min^{-1} and maintained for 3 min, and then raised to 310 °C at 10 °C·min^{-1} and maintained for 10 min. The sample volume was 1μL in splitless injection mode with an inlet temperature of 250 °C. The source temperature was set at 250 °C and the transfer line was at 280 °C. Details of the OCPs and OPPs determination are shown in Additional file 1: Table S2, S3.

Estrogenic compounds were determined by a high-performance liquid chromatography (HPLC) coupled to a fluorescence detector (FLD) (Agilent 1260 Infinity II). The column is ZORBAX SB-C18 (4.6 mm × 250 mm, 5 μm) with a pre-column (SB-C18 Guard Cartridges 4.6 × 12.5 4/PK). The operating conditions were as follows: acetonitrile:water, gradient elution, 0–6 min 45% acetonitrile, 6–10 min acetonitrile increased from 45 to 65%, 10–20 min acetonitrile increased from 65 to 75%. The flow rate was 1 mLmin^{-1} and the injection volume was 10 μL [36]. The column temperature was 30 °C, the excitation wavelength of estrogenic compound in the fluorescence detector was 280 nm and emission wavelength was 310 nm [37]. Details of the estrogenic compounds determination are shown in Additional file 1: Table S4.

The limits of detection (LOD) for OCPs, OPPs and estrogen compounds are shown in Additional file 1: Table S2–S4. For quality assurance and control, soils did not contain those compounds were used as blank sample, which the study pollutants were added as internal standards to evaluate the recovery rates. The recovery rates of target substances in sediments were between 88.6% and 104.7%.

Environmental risk assessment

In order to assess the potential environmental risk, the toxicology data of organic pollutants were mainly obtained from the existing toxicology database (American ECOTOX database, http://cfpub.epa.gov/ecotox/) [38], in which the data were selected according to the principles of reliability, correlation and accuracy [39, 40]. The toxic effects of each micropollutant were studied using aquatic organisms, algae (phototrophic level), crustaceans (invertebrates) and fish (vertebrates). To cover sub-lethal endpoints and lethal endpoints, median effect concentration (EC_{50}) and median lethal concentration (LC_{50}) were selected for each species [39]. If multiple values are reported for the same toxicity endpoint, the intermediate data will be selected. The risk was calculated only for those chemicals for which EC_{50} or LC_{50} is available. Among the 20 detected

micropollutants, o,o,o-triethylphosphorothioate and famphur cannot find EC_{50} or LC_{50} values in the American ECOTOX database, and thus were eliminated during risk assessment process.

In the current study, the risk assessment of the sediments was performed by quotient method [41]. The RQ value was calculated according to Eq. 1 and Eq. 2. The RQ was used to classify the organic pollutant as low risk ($0.01 \leq RQ < 0.1$), medium risk ($0.1 \leq RQ < 1$, or high risk ($RQ \geq 1$) [42]:

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

$$PNEC = \frac{EC_{50} or LC_{50}}{AF}, \tag{2}$$

where MEC is the measured environmental concentration of organic pollutants in Qingshui Stream. In this study, MEC was based on the concentration of micropollutants in pore water, rather than utilizing micropollutants directly measured in sediments. PNEC is the predicted no effect concentration, which is obtained by dividing the acute toxicity test result (LC50) by assessment factor (AF), in which the value of AF is 1000 [43].

However, for most of the organic toxic pollutants, their toxicity data in sediments are still scarce. The pore water is the primary route of sediment-bound pollutants exposure for fish, Daphnia, and alga. The equilibrium distribution method proposed by Di Toro et al. was used to estimate the concentration of micropollutants in pore water [44, 45]. Equation 3 and Eq. 4 were adopted to convert the concentration of organic matter in sediments to that in pore water [45, 46], and then the risk assessment of organic pollutants in the samples was carried out:

$$C_{PW} = \frac{C_{SE}}{F_{OC} \cdot K_{OC}}, \tag{3}$$

$$LogK_{OC} = 0.623 LogK_{OW} + 0.873, \tag{4}$$

where C_{PW} is pore water concentration; C_{SE} is sediment concentration; F_{OC} is organic carbon mass fraction (%); K_{oc} is the normalized organic carbon to water partition coefficient scalarization partition coefficient, when the K_{oc} value of the substance cannot be obtained, the transformation is carried out by the K_{ow} value [47], K_{ow} is the octanol/water partition coefficient.

The risk quotients of mixtures were calculated according to the mixture interaction analysis. In the current study, the risk quotient of organic micropollutant mixtures was evaluated based on concentration addition (CA) model [48]. First, the quotient method was used to calculate the RQ value of a single pollutant, and then the risk quotients of similar pollutants were superimposed according to Eq. 5:

$$RQ_{MEC/PNEC} = \sum_{i=1}^{n} \frac{MEC_i}{PNEC_i}, \tag{5}$$

where MEC_i is the environmental exposure concentration of a single organic pollutant; $PNEC_i$ is the predicted concentration of no effect.

Statistical analysis

Microsoft Excel 2016 was used to organize data in spreadsheet. Data collation and mapping of inorganic pollutants, organic pollutants and environmental risk assessment were completed by Origin 2018. In case of the assumption of homogeneity of variance was met, one-way ANOVA was used to test for statistically significant differences in all data sets of different treatments. Tukey's test was used to identify significant differences between different treatments at $P < 0.05$, in other case, the Kruskal–Wallis H test was employed.

Results and discussion

Effect of flood on inorganic pollutants

The concentrations of TP, TN, and COD in surface water are shown in Fig. 2a–c, where the results are similar to other urban rivers in Chongqing [49]. The concentrations of TP, TN, and TC in sediments are shown in Fig. 2d–f. Before the flood, the concentrations of C, N and P in the upper reaches were higher than those in the middle and lower reaches, both in surface water and sediment. During the flood, the TP content in the upstream surface water decreased significantly, i.e., the concentration of sample site 2 decreased from 0.21 to 0.06 $mg \cdot L^{-1}$, while TP content in the downstream increased slightly, which may be that part of TP was carried to the downstream with the water flow during the flood. However, the decrease of TN and COD concentrations at each sampling site indicated that the flood had a diluting effect on them. TP in sediment did not change during and after flood, while TN and TC showed the same trend as surface water, and both concentrations decreased during the flood. Interestingly, after the flood, TP content in the upstream and downstream surface water slightly increased, but was still lower than before the flood. The contents of TN and TC in the sediment also increased, surface runoff in the urban area, erosion of upland and riparian zone of the river as well as remobilization are reasonable. The different inorganic and organic components of suspended particles (e.g., clay minerals and humic substances) provide many binding sites for dissolved chemicals, such as metals and lipophilic organic chemicals. As a

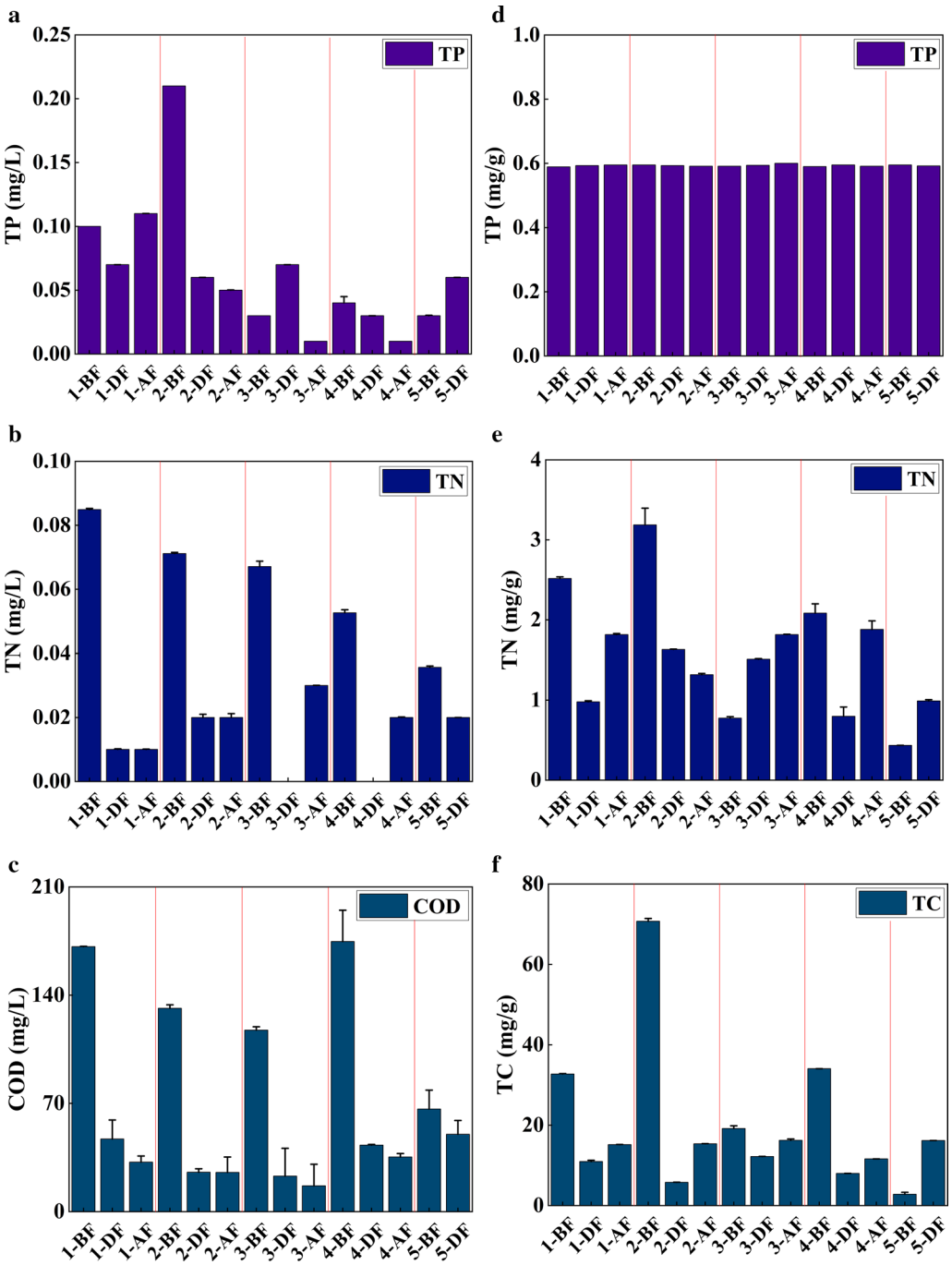

Fig. 2 Concentrations of total phosphorus (TP) (**a**), total nitrogen (TN) (**b**), chemical oxygen demand (COD) (**c**) in surface water and in sediments (d: TP; e: TN and f: TC) from each sampling site of Qingshui Stream before (BF) during (DF) and after the flood (AF). $n = 3$

result, these suspended particles tend to accumulate various organic and inorganic pollutants from the environment, which are then deposited in the sediment with the suspended solids [50]. Under the extreme conditions of flood, not only more suspended solids were deposited in the sediments, but also the pollutants in the previous sediments are released again. It may cause the concentrations of pollutants in surface water and sediment increased.

Effect of flood on organic pollutants

Among the 58 tested organic micropollutants, 20 compounds were detected in the sediment samples, including estradiol, 5 organochlorine pesticides, and 14 organophosphorus pesticides. It is noteworthy that a number of pesticides were detected in urban river sediments. Sediments are one of the main sinks of organic pollutants due to their hydrophobicity, residues of organic pollutants in sediments can reflect the historical input of pollutants [51]. The concentration of estradiol ranged from 20 ng g^{-1} to 90 ng g^{-1} before the flood (Fig. 3a), while during the flood the concentration was lower than the LOD, indicating the dilution effect of flood to estradiol. After the flood, the concentration of estradiol was detectable again, while it was still lower than that before the flood. It was probably due to the hydrophobicity and imbalance between the solid and dissolved phases during the flood event [52]. Estradiol showed relatively high octanol–water partition constant, therefore, it may be easily bound to sediment and particles suspended solids, as compared to water [53]. After the flood receded, estradiol was enriched in sediment, which is consistent with what has been observed in the Ebro River [54].

Before the flood, the highest concentrations of mirex, heptachlor epoxide, alpha-endosulfan and delta-BHC in sediments of the five sites were 7.44 ng·g^{-1}, 4.12 ng·g^{-1}, 4.24 ng·g^{-1}, and 6.67 ng·g^{-1}, respectively (Fig. 3b). It is noticed that pesticides such as pp ’-DDD, delta-BHC and mirex that have been prohibited for more than two decades by authority [55]. Thus, the detectable of those persistence pollutants could still be potential risk to ecosystem and even human being [56]. The occurrence and concentrations of those pollutants varied significantly, which was mainly because of the complexity of hydrology during the flood. During the flooding, the concentration of alpha-endosulfan was lower than the LOD, and delta-BHC decreased to 0.09 ng·g^{-1}. These two compounds were not detected after the flood subsided. The pp’-DDD was detectable in the sediment in flood period. After the flood receded, the concentrations of pp’-DDD

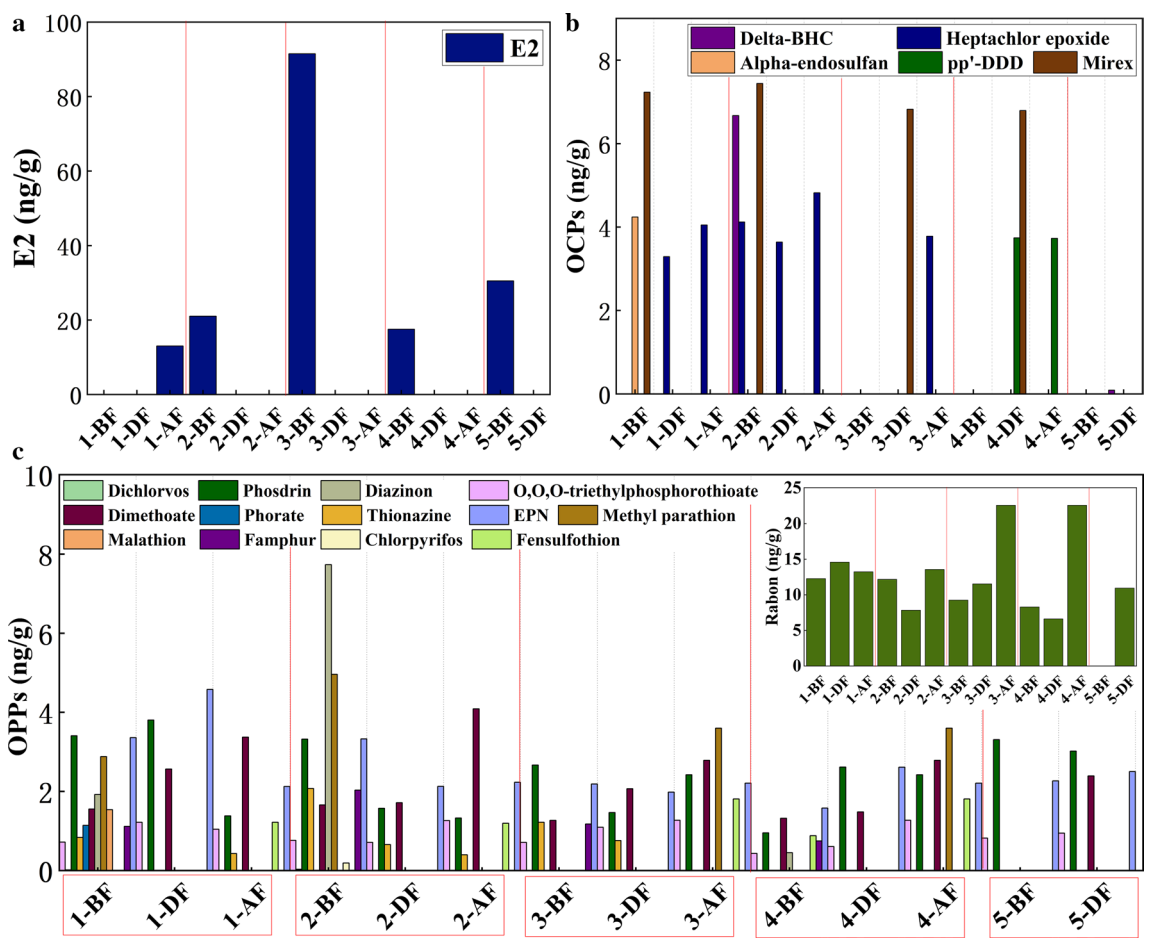

Fig. 3 Concentrations of estradiol (E2) (**a**), organochlorine pesticides (OCPs) (**b**) and organophosphorus pesticides (OPPs) (**c**) in sediments before (BF), during (DF) and after flood (AF)

and heptachlor epoxide remained unchanged or even increased slightly. Those compounds were absorbed by sediment particulates, and therefore increased the concentrations in sediment.

The concentrations of OPPs before, during and after the flood are shown in Fig. 3c. Banned organophosphorus pesticides such as methyl parathion and phorate were detected in sediments, which proved the persistence of such micropollutants. The detected frequency of o,o,o-triethylphosphorothioate, phosdrin and EPN was as high as 100%, indicating the wide usages of these substances in Chongqing area. Before the flood, the highest content of organophosphorus pesticide in the sediment was rabon, with a concentration of 12.72 $ng{\cdot}g^{-1}$. The concentrations of o,o,o-triethylphosphorothioate, dimethoate, rabon and EPN increased in flood period due to the chemical properties of pesticides and the migration and transformation of pesticides caused by floods. However, the concentrations of tetraethyl pyrophosphate, diazinon, methyl parathion, famphur decreased or even fall below the LOD during flood period. After the flood receded, the concentrations of dichlorvos, phosdrin[tm], thionazine, tetraethyl pyrophosphate, diazinon, methyl parathion, malathion, chlorpyrifos, fanpur and EPN decreased while that for o,o,o-triethylphosphorothioate, dimethoate, rabon and fensulfothion increased. In addition, floods increased the concentrations of POPs in water and sediment columns were also reported in many studies [57]. Apart from the results showed above, it is also interesting that the concentrations of some OCPs did not change significantly by flooding, such as heptachlor epoxide, implying the normal background ranges of these compounds in the river basin area. These phenomena showed that flooding altered the migration process of POPs [58].

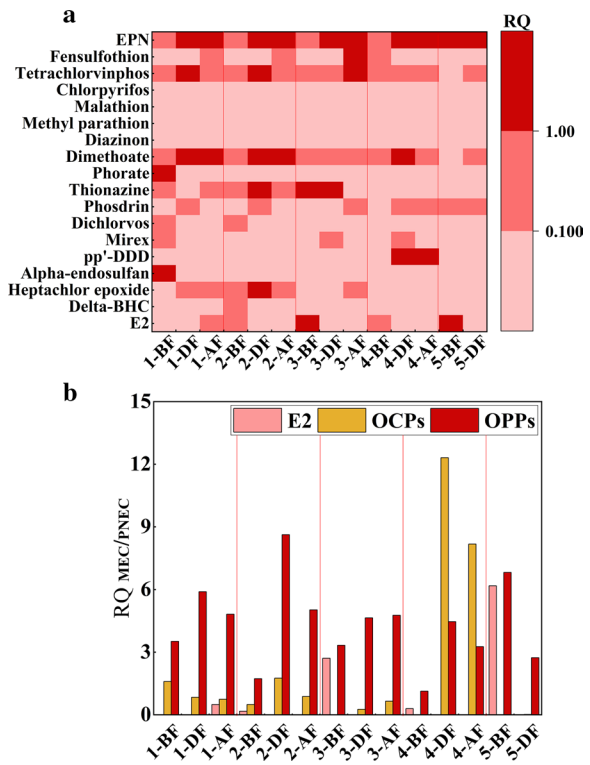

Fig. 4 Risk values of 18 organic pollutants in sediment samples before (BF), during (DF) and after flood (AF) (**a**); The RQMEC/PNEC of OCP mixture, OPP mixture and RQ of E2 in sediment samples before (BF), during (DF) and after flood (AF) (**b**)

Environmental risk assessment of organic pollutants

The risk quotients (RQ) were obtained and presented as a heat map in Fig. 4a. RQ values ranged from 0 to 11.915. It was found that flooding changed RQ values of organic pollutants at different sampling sites, thus changing environmental risks. The concentration of pp'-DDD, EPN and dimethoate increased after the flood, changing the risk level from low and middle risk to high risk. While opposite appearances were observed for E2, the environmental risks were changed from medium and high-risk level to low-risk level. The RQMEC/PNEC of OCP mixture, OPP mixture and RQ of E2 in sediments are shown in Fig. 4b. The potential environmental risk of OPPs accounted for the main part of the risk, mainly because the high concentrations of OPPs in sediments. The RQ values of OPPs and OCPs increased after flood, while the potential risk of E2 reduced. Therefore, our study showed that flooding changed the patterns of organic pollutants in urban rivers, and thus altered the potential environmental risks. The changes of environmental risks caused by the adsorption or desorption of pollutants in river sediments after flood events deserve our attention [59, 60]. Einsporn et al. studied the toxic effects of transported organic pollutants in flatfish and mussels after the Elbe flood in 2002, and found a significant impairment in the function of cell organelles (lysosomes) involved in the detoxification and elimination of pollutants in fish liver [61]. It has been demonstrated by Brinkmann et al. that flood caused sediment re-suspension, which can lead to accumulation of POPs in fish and thus resulting in potentially adverse toxicological effects [62]. Lim and Foo assessed the hazard index for exposure and health risk of organic and inorganic contaminants in the water samples, and found the value exceeded the USEPA maximum limit after the flood incidence [63].

Flood implications for urban river management

In recent years, the rapid urbanization process has led to the expansion of urban area. The effects of urbanization on river hydrological and hydraulic conditions have been frequently documented, i.e., flow rate, discharge as

well as flood duration are closely relevant to the dynamics of pollution [64]. The rapid development in urban watershed and human-caused intervention in riparian forest systems and riparian corridors lead to poor flood diversion and discharge, resulting in fluvial flood disasters [65]. Urban flooding has become a common problem faced by many countries [66, 67]. Current flood control policy, such as the European Floods Directive (2007/60/EC) (EC, 2007), emphasizes the retention of flood to reduce its adverse impact on the environment, human health, economy, and cultural activities [50]. For which relocating the existing dikes, construction of flood polders, and combination of various prevention and control measures to prevent the damage caused by extreme flooding events [68]. These measures mainly focus on regulating hydraulic condition, i.e., flood flow, erosion resistance, hydraulic retention time, etc.; whereas, ecosystem safety is rare in consideration. However, water quality and ecological river development are important factors in water management in recent decades [69]. The existing river landscape ecological restoration mainly focuses on river bank shape, bank slope structure, landscape plant configuration of river buffer zone [70]. Although biodiversity conservation is one of the most important purposes in river ecological restoration, and some successful cases were reported [71], many restorations are still insufficient [72]. The changes in patterns of composition and concentrations of pollutants and their corresponding environmental risks with hydrological regime, in particular for flooding has not been considered in urban river management. In fact, understanding the dynamics of environmental risk by flooding is critical for successfully restoring urban river ecosystem and human well-being [73].

The current study, provided insights for risk dynamic with various pollutants during flooding event, which could be an important reference for river management. Because both dilution and enrichment effects existed during flooding, pollution source tracing based on risk identification and optimization on pollution dynamic with urban river hydrology become essential for river restoration [74, 75]. Our study may provide useful information on guiding where measures need to be taken to reduce pollution. For OPPs and OCPs that are easy to adhere to sediments and thus increase the environmental risk, silt cleaning after floods is particularly important. Although dredging has been used for removing silt [76], it is, in fact not recognized by many ecologists. On one hand, it shifts the problem to a downstream site, on the other hand, the dredging of river reaches is also an ecological disaster. Hence, for better maintaining the ecosystem vitality, the above-mentioned measures should be conducted carefully [77]. Besides, regarding urban rivers that have high frequency of human exposure, special concerns should be taken to assess the health risks [78].

Conclusion

The current study explored the flood influence by analysis of the distribution and concentration changes of macropollutants (C, N, P) as well as micropollutants such as 3 estrogenic compounds, 34 organophosphorus pesticides, and 21 organochlorine pesticides in the Qingshui Stream, which is a typical urban stream. Banned pesticides, such as pp'-DDD and delta-BHC, were detected in sediments. Although the concentrations of macropollutants in surface water and sediments, and 14 micropollutants in sediments were diluted, pesticides such as pp'-DDD, heptachlor epoxide, o,o,o-triethylphosphorothioate, dimethoate, rabon and fensulfothion were enriched after the flooding. It is noticed that flooding increased the environmental risk, which was mainly contributed by OPPs. Hence, the specific microorganic pollutants within the rivers are suggested to be taken into river pollution management. The current study could provide scientific evidence and regulatory reference for the management of similar urban rivers.

Abbreviations

BF: Before the flood; DF: During the flood; AF: After the flood; TN: Total nitrogen; TP: Total phosphorus; COD: Chemical oxygen demand; TC: Total carbon; E2: Estradiol; OCPs: Organochlorine pesticides; OPPs: Organophosphorus pesticides; DDT: Dichlorodiphenyltrichloroethane; BHC: Benzene hexachloride; RQ: Risk quotient; SD: Standard deviation; EC_{50}: Cause effective drug concentration in 50% of individuals; LC_{50}: The concentration of a substance that is lethal to 50 percent of the organisms in a toxicity test.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s12302-022-00639-7.

Additional file 1: Table S1. Coordinates of sampling sites. **Table S2.** Information of 21 organochlorine pesticides. **Table S3.** Information of 34 organophosphorus pesticides. **Table S4.** Information of 3 estrogenic substances.

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Author contributions

MZ performed the majority of data evaluations and wrote the first draft of the manuscript; SQW supported data management and visualization; CJ and GCZ identified organic pollutants in samples; ZLC, YXJ and YS supervised, reviewed and edited the manuscript; ZLZ, YMEJAHMT and LY contributed on field sampling and sample analysis. All authors read and approved the final manuscript.

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Availability of data and materials
The data sets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
All authors agreed to publish the paper.

Competing interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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