Phenolic compounds in water, suspended particulate matter and sediment from Weihe River in Northwest China

Yuyun Chen, Junqin Zhang, Yanxia Dong, Ting Duan, Yiqiang Zhou and Wei Li

ABSTRACT

The distribution and ecological risks of 11 phenolic compounds were studied in Weihe River, Northwest China. The concentrations of phenolic compounds were determined by ultra-high performance liquid chromatography (UPLC). The total concentration of 11 phenolic compounds ($\sum PC_{11}$) ranged from 0.06 to 14.12 μg/L with an average of 5.22 μg/L in water, from 0.92 to 34,885 μg/g with an average of 4,446 μg/g in suspended particulate matter (SPM), and from 3.54 to 34.09 μg/g with an average of 11.09 μg/g in sediment. For individual phenolic compound, the mean concentration of pentachlorophenol was the highest in water (2.65 μg/L) and in SPM (3,865 μg/g), while in sediment the mean concentration of 2,4,6-trichlorophenol was the highest (3.05 μg/g). The total concentration of 5 chlorophenols ($\sum CP_5$) was significantly higher than that of 6 non-chlorophenols ($\sum NCP_6$) in all three studied compartments. The phenolic compounds in Weihe River were at moderate levels in water and at high levels in sediment. The ecological risk assessment results indicated that phenolic compounds exhibited a high ecological risk in Weihe River water. In most sites, the distribution coefficient (Kd) (SPM) was much higher than Kd (sediment), which probably suggested fresh phenolic compounds input in Weihe River.

Key words | ecological risk, phenolic compounds, sediment, SPM, water, Weihe River

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HIGHLIGHTS

- This is the first systematic study of phenolic compounds in rivers in northwest China.
- The results of ecological risk assessment indicated that phenolic compounds exhibited a high ecological risk in Weihe River water.
- The total concentration of 5 chlorophenols ($\sum CP_5$) was significantly higher than that of 6 non-chlorophenols ($\sum NCP_6$) both in water and sediment.

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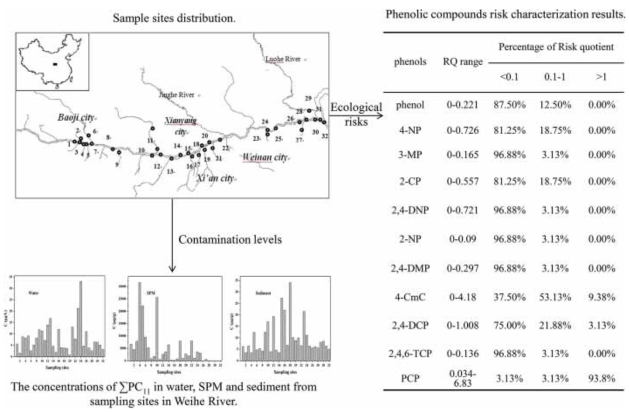
GRAPHICAL ABSTRACT



phenols	RQ range	Percentage of Risk quotient		
		<0.1	0.1-1	>1
phenol	0-0.221	87.50%	12.50%	0.00%
4-NP	0-0.726	81.25%	18.75%	0.00%
3-MP	0-0.165	96.88%	3.13%	0.00%
2-CP	0-0.557	81.25%	18.75%	0.00%
2,4-DNP	0-0.721	96.88%	3.13%	0.00%
2-NP	0-0.09	96.88%	3.13%	0.00%
2,4-DMP	0-0.297	96.88%	3.13%	0.00%
4-CmC	0-4.18	37.50%	53.13%	9.38%
2,4-DCP	0-1.008	75.00%	21.88%	3.13%
2,4,6-TCP	0-0.136	96.88%	3.13%	0.00%
PCP	0.034-6.83	3.13%	3.13%	93.8%

INTRODUCTION

Phenolic compounds are a kind of refractory organic matter whose unique chemical structures consist of an aromatic ring with one or more hydroxyl functional groups. Phenolic compounds used to produce pharmaceuticals, insecticides, cosmetics and plastics are discharged into the environment from chemical plants, oil refineries, paper and pulp mills (Wang *et al.* 2012). Many researchers have confirmed the presence of phenolic compounds in surface waters (Bolz *et al.* 2001; Gao *et al.* 2008; Song *et al.* 2013; Zhou *et al.* 2017; Zhong *et al.* 2018). The toxicity of phenols not only hinders survival and reproduction of aquatic organisms, but also endangers human health (Wang *et al.* 2012; Wolff *et al.* 2015). In particular, some phenolic compounds are known to be endocrine-disrupting compounds (EDCs), which have a detrimental effect on the endocrine system, such as 2,4,6-trichlorophenol (2,4,6-TCP). In 2011, the World Health Organization (WHO) listed 2,4,6-TCP and pentachlorophenol (PCP) as 2B pollutants with carcinogenic effects. Several phenolic compounds have been listed as priority pollutants by the US Environmental Protection Agency and European Union (EU) (Brinda *et al.* 2013). And six phenolic compounds are also listed as priority pollutants in water in China (Zhou *et al.* 1991).

Perennial rivers are major sources of freshwater for aquatic ecosystems worldwide. The phenolic compounds in rivers have been extensively researched in the world (Kawahata *et al.* 2004; Michałowicz & Duda 2007). Many scholars in China also studied these pollutants from different rivers. These studied rivers included the Pearl River (Diao *et al.* 2017), the Yellow River (Gao *et al.* 2008), the Yangtze River (Gao *et al.* 2008), rivers in Tianjin City (Zhong *et al.* 2018), Huai River (Gao *et al.* 2008), Songhua River (Wang *et al.* 2012) and Liaohe River (Li *et al.* 2015), which were all located in East, Northeast or South China. Northwest China, with an area of 3.2 million square kilometers, is an arid and semi-arid region. It belongs to a relatively undeveloped area. There are also many rivers located in this area. However, phenolic pollution in rivers over such a large area has never been studied.

Ecological risk assessment is a systematic approach that describes, explains and organizes scientific facts, laws and relationships, so as to provide a sound basis to develop adequate protective measures for the environment. It is also an essential tool for environmental management and is widely applied in environmental decision-making (Nash *et al.* 2005). Some scholars studied the ecological risk of phenolic compounds in surface waters from different regions of China (Jin *et al.* 2011; Zhong *et al.* 2018).

The Yellow River is the fifth largest river in the world, and is very important in China. Weihe River is the largest tributary of the Yellow River, with a drainage area of 134,800 square kilometers (Wang *et al.* 2016, 2019a). The river is called the 'Mother River' of the Guanzhong region, and plays an important role in the development of Northwest China and the health of the ecosystem of the Yellow River (Wei *et al.* 2012). It mainly flows through Baoji, Xianyang, Xi'an and Weinan cities in the Guanzhong region, and then flows into the Yellow River. In addition, Weihe River Basin also plays an important role in the Silk Road Economic Belt. Xi'an City in this basin was one of four ancient capitals of the world and the starting point of the ancient Silk Road. It has a population of more than 10 million now. With the rapid increase in population and economic wealth, the insufficient water supply and degradation of the water environment has become one of the most restrictive factors for Weihe River basin's economic development. Previous relevant studies on organic pollutants in Weihe River water mainly focused on polycyclic aromatic hydrocarbons (PAHs) (Chen *et al.* 2015) and organochlorine compounds (Wang *et al.* 2016), which had an adverse effect on aquatic organisms and human health. This is the first systematic study on the distribution and ecological risk of phenolic compounds in a river in Northwest China.

The aims of the present work were to identify and quantify 11 phenolic compounds in water, SPM and sediment samples and to assess the ecological risk associated with phenolic compounds present in Weihe River. The results not only contribute to a better understanding of the status of phenolic compounds pollution in rivers in arid, semi-arid and underdeveloped regions of the world, but also provide data for the development of countermeasures and management programmes for polluted rivers.

MATERIALS AND METHODS

Chemicals and instruments

Mixture standard solutions containing 11 kinds of phenolic compounds including phenol, 2-chlorophenol (2-CP), 4-chloro-m-cresol (4-CmC), 2,4-dichlorophenol (2,4-DCP), 2,4,6-TCP, PCP, 4-nitrophenol (4-NP), 3-methylphenol (3-MP), 2,4-dinitrophenol (2,4-DNP), 2-nitrophenol (2-NP), 2,4-dimethyl phenol (2,4-DMP) were purchased from Putian Tongchuang Biotechnology Co. Ltd (Beijing, China). All chemical solvents (methanol, dichloromethane, glacial acetic acid, ethyl acetate and hydrochloric acid etc.) used for sample processing and analysis were of high-performance liquid chromatography (HPLC) grade or equivalent.

The phenolic compounds were analyzed using an ultra-high performance liquid chromatography (Waters H-class) coupled with UV detector (Waters Corp., USA). Chromatographic separation and resolution was achieved by using an ACQUITY UPLC® HSS T3 column (2.1 mm × 150 mm, 1.8 μm particle size, Waters Corp., USA). The mobile phase consisted of water with 0.5% formic acid (A) and acetonitrile with 0.5% acetic acid (B). The flow rate of the mobile phase was kept at 0.2 mL/min and the wavelength of determination was 280 nm. The gradient program was as follows: 0 min, 20% B; 10 min, 60% B; 13 min, 80% B.

Sampling area and sample collection

The Weihe River is located in northwest China, and supplies the drinking water and irrigation water for the cities along the river. There has been a dramatic increase in the emissions of industrial wastewater and urban domestic sewage in this area in recent years (Song *et al.* 2018). The Weihe River has many tributaries. The Jinghe River is the largest tributary of Weihe River, which has annual sediment runoff of approximately 9.46×10^6 t. The large tributaries including Qianhe River, Jinling River, Jinghe River and Beiluo River have high sediment concentrations. There are many industrial enterprises in the basin, such as machinery, electronics, coal, and chemical industry. In Chencang District of Baoji section in the upper reaches of Weihe River, livestock farms are more common in the nearby Dazhangsi village. There are sewage treatment plants and sewage outlets along the middle reaches of Weihe River. The lower reaches of Weihe River is a traditional farming area. Chemical fertilizer is frequently used and the wastewater from the surrounding chemical fertilizer plants is directly discharged without treatment. Land use in the Guanzhong section of the Weihe River Basin is mainly dominated by cropland, forestland and grassland.

Based on the natural environmental conditions and the overall layout of the urban planning, a total of 32 sampling sites along Weihe River and its tributaries were selected for this sample collection (Figure 1). Nine, twelve and eleven sites were located in the upper (sites 1–9), middle (sites 10–21) and lower (sites 22–32) reaches of Weihe River, respectively. All samples were collected on August 30–31, 2017. On 31 August, the Weihe river flow at site 30 was 215 m^3/s. During the whole sampling process global position system (GPS) was used to locate the sampling stations. In each sampling site, water samples were taken from 50 cm below the surface level with 4 L pre-cleaned brown glass bottles. All water samples were transported to the laboratory directly after sampling and kept at 4 °C before analysis.

The SPM samples are derived from water samples in the laboratory. Water samples were filtered through a previously kiln-fired (400 °C overnight) GF/F glass fibre filter (47 mm × 0.7 μm; Whatman, Maidstone, UK). Filters (suspended particulate matter, SPM) were kept in the dark at −20 °C until analysis. Dissolved phase refers to the fraction of contaminants passing through the filter. This includes the

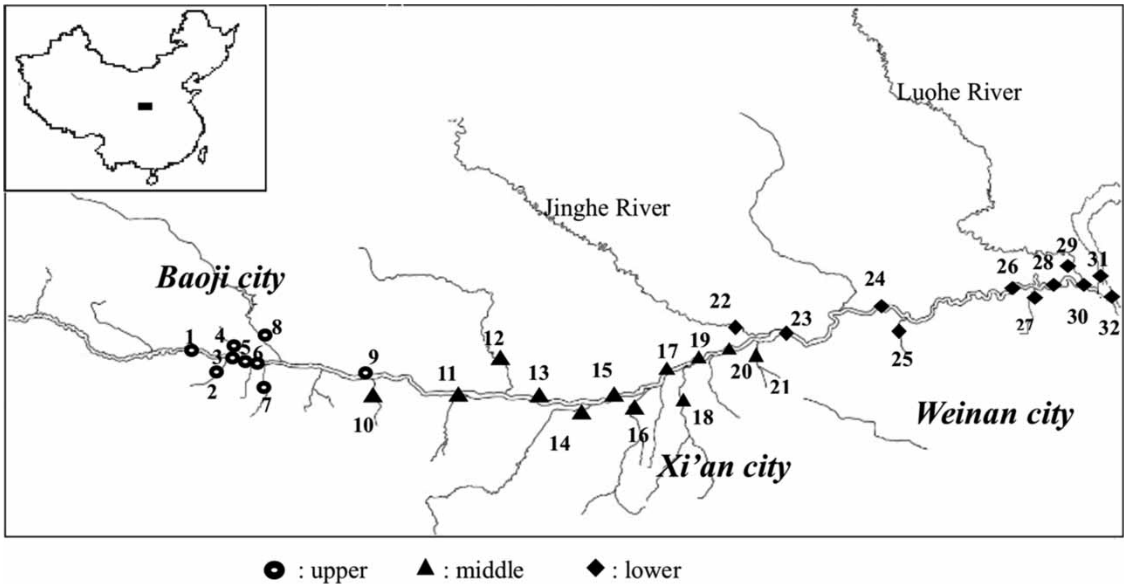


Figure 1 | Sample sites distribution.

compounds that are both truly dissolved as well as those associated with colloidal organic matter. These filtrates were kept in the dark at 4 °C and extracted within 24 h.

Surface sediment (0–20 cm) samples were collected by using a grab sampler (Van VeenBodemhappe 2 L, Kiel, Germany) and put into aluminium containers. The sediments were transported to the laboratory and kept at −20 °C before analysis.

Phenolic compounds extraction

Water

A solid phase extraction (SPE) cartridges system from Supelco (Sigma Aldrich Corp., Saint Louis, MO, USA) was used for the enrichment of phenolic compounds in water. A volume of 1 L of water sample was filtered through a GF/F glass fiber filter in the laboratory. Next, 3 g of NaCl was dissolved in water, and samples were acidified with hydrochloric acid to pH 5. SPE columns containing 500 mg of styrene-divinyl benzene copolymer (Poly-Sery PSD) were activated with 6 mL of ethyl acetate, 6 mL of methanol and 6 mL of ultra-pure water successively. Then 1 L of water sample was percolated through the cartridges with a flow rate of 5 mL/min under a vacuum pump. The phenolic compounds were eluted to a glass tube by 5 mL ethyl acetate. The solvent fractions were then evaporated on a rotary evaporator at 35 °C, and exchanged by acetonitrile to a final volume of 1 mL.

SPM

SPM content was determined by gravimetry, after drying the glass fibre filter in an air-heated oven (55 °C until constant weight) and equilibrated at 25 °C in a desiccator. SPM containing glass fibre filter was cut into pieces, and then extracted three times by ultrasonic-assisted solvent extraction in 20 mL of dichloromethane for 1 h followed by centrifugation at 5,000 r/min for 10 min. Then 10 mL of supernatant was filtered through a silica gel column (3 g) with 10 mL (5 mL each time) elution of dichloromethane. The solvent fractions were then evaporated at 35 °C on a rotary evaporator, and exchanged by acetonitrile with a final volume of 0.5 mL and transferred into a vial through an organic phase filter membrane (0.22 μm) for subsequent testing.

Sediment

Sediments were oven dried at 40 °C. Then the dry sediment samples were carefully collected, homogenized and passed through a 250 μm standard sieve. Phenolic compounds in 3 g sediment were extracted three times by ultrasonic-assisted solvent extraction with 20 mL of dichloromethane for 1 hour followed by centrifugation at 5,000 r/min for 10 min. Then 10 mL of supernatant was filtered through a silica gel column (3 g) with 10 mL (5 mL each time) elution of dichloromethane. The solvent fractions were then evaporated at 35 °C on a rotary evaporator, and exchanged by acetonitrile with a final volume of 1 mL and transferred into a vial through an organic phase filter membrane (0.22 μm) for subsequent testing. In this experiment, 3 parallel samples were made for each sample and 3 parallel blanks were made for each batch of samples.

Parameters determination

Physiochemical parameters such as chemical oxygen demand (COD), electrical conductivity (EC), total dissolved solids (TDS), salinity and pH value in water samples were measured immediately after arrival at the laboratory. The pretreatment process of the collected water sample was completed in 24 hours. The total organic carbon (TOC) of sediment was determined by TOC analyzer (TOC-VCPH; Shimadzu Corp., Shimadzu, Japan). The COD of water samples were determined by COD determinator (Shanghai, China). The EC, TDS and salinity were determined by a HQ30D water quality analyzer (Shanghai, China). The pH value was determined by a pH meter (Mettler Toledo, Columbus, OH, USA).

Quality assurance/control (QA/QC)

After every 5 samples, a procedural blank and a spike sample consisting of all reagents was run to check for interference and cross contamination, and no interferences or cross contamination were found in the whole test process. The limit of detection (LOD) and limit of quantification (LOQ) were calculated as having signal-to-noise ratios of above 3 and 10, respectively, by seven replicate analyses. The LODs of 11 phenolic compounds ranged from 0.005 to 0.02 μg/L in water and from 0.006 to 0.02 μg/g in sediment samples, respectively. The LOQs were in the range of 0.02–0.05 μg/L in water and 0.02–0.5 μg/g in sediment samples, respectively. The matrix spike recoveries for 11 phenolic compounds in water, SPM and sediment samples ranged from 82.7 to 112.5%, 58.5 to 126.2% and 75.6 to 116.2%, respectively. The relative standard deviations (RSD) for three kinds of samples were all below 5.0%.

Risk assessment method of phenolic compounds

Ecological risk assessment of phenolic compounds was based on the US EPA ecological risk assessment framework, according to the method by Chakraborty *et al.* (2016) and Chen *et al.* (2014). The risk quotient (RQ) method was used to estimate the ecological risk of 11 phenolic compounds from Weihe River water. The RQ value was estimated as follows:

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

where RQ was the risk characterization coefficient or the quotient value; PNEC was the predicted no effect concentration of compounds (μg/L); MEC was the measured environmental concentration of the compounds in water samples (μg/L).

The PNEC values for 11 phenolic compounds were obtained by using a species sensitivity distribution (SSD) approach. It was mainly performed in four steps: toxicity data screening and collecting for the pollutants, distribution model selection and SSD curve fitting, HC_5 and PNEC calculation, and estimation of the ecological risk. First, the acute toxicity data (LC_{50} or EC_{50}) and chronic toxicity data (NOEC, LOEC, EC_{10} and MATC) used in the current study for ecological risk assessment of 11 phenolic compounds in Weihe River water were obtained from the Ecotoxicology Database of the US EPA (https://cfpub.Epa.Gov/ecotox/[OL].) These selected datas involved three aquatic organisms (algae, invertebrates and vertebrates). According to principles for screening toxicological data for organic pollutants, when the experimental environment is fresh water such as lakes or rivers, the minimum exposure time for acute toxicological data is 96 h for vertebrates, 48 h for invertebrates and 24 h for algae, and the minimum exposure time for chronic toxicological data is 14 d for vertebrates, 7 d for invertebrates and 3 d for algae. Finally, the chronic toxicity datas of 5 phenolic compounds (phenol, 2,4-DNP, 2,4-DCP, 2,4,6-TCP and PCP) and the acute toxicity datas of the remaining 6 phenolic compounds (4-NP, 3-MP, 2-CP, 2-NP, 2,4-DMP and 4-CmC) were screened and used for the SSD model (Tables S1 and 2). Then, the SSD model curves were constructed using the National Institute of Public Health and the Environment, Bilthoven, Netherlands, based on a normal distribution (log-normal) software ETX 2.1. The HC_5 (hazardous concentration for 5% of species) value was calculated based on the SSD curve and the PNEC value was obtained from the ratio between the HC_5 and an assessment factor (AF).

The ecological risk levels were classified into three levels according to the RQ values. $RQ > 1$ indicates a high ecological risk, RQ values between $0.1 < RQ < 1$ mean a median risk, and $RQ < 0.1$ suggests a minimal environmental risk (Wang *et al.* 2019a, 2019b).

RESULTS AND DISCUSSION

Phenolic compounds in water

The concentration ranges and mean values of 11 phenolic compounds in water samples collected from the Weihe River are summarized in Table 1. The concentrations of $\sum PC_{11}$ ranged from 0.06 to 14.12 μg/L with a mean value of 5.22 μg/L. The concentration range of $\sum CP_5$ was 0.03–11.6 μg/L with an average concentration of 4.19 μg/L, which accounted for 80.12% of the concentration of $\sum PC_{11}$. And the concentrations of $\sum NCP_6$ ranged from nd to 10.53 μg/L with a mean value of 1.04 μg/L, accounting for 19.88% of the total amount. The contents of phenol and chlorophenols were relatively higher than those of other phenolic compounds. The mean concentration of PCP was the highest (2.65 μg/L), accounting for more than half of the concentration of $\sum CP_5$. The detection frequencies of five phenolic compounds including 4-NP, 2,4-DNP, 2,4-DMP, 4-CmC, 2,4,6-TCP and PCP exceeded 50%, and the detection frequencies of PCP even reached 100%.

The data obtained in this study were compared with the data in published researches. It is difficult to directly compare our data with literature data due to the differences in compounds, sample number, sampling location and sampling season considered in these studies. However, the comparison can still provide useful information to understand the pollution levels of phenolic compounds in Weihe River.

The total concentrations of 2,4-DNP, 2,4,6-TCP and PCP in water from the Weihe River (0.03–12.20 μg/L) were higher than those in Yangtze River (0.0036–1.004 μg/L) (Gao *et al.* 2008). The maximum of total concentrations of 2,4,6-TCP and PCP in water from the Weihe River (8.44 μg/L) were much higher than those in Huaihe River (421 ng/L) and Haihe River (110 ng/L) (Gao *et al.* 2008). However, compared with rivers such as the Beitang Drainage River (nd–43.1 μg/L) and Dagu Drainage River (nd–106.1 μg/L) (Zhong *et al.* 2018), the total concentrations of phenol and 2,4-DMP in Weihe River (nd–4.68 μg/L) were lower. The total concentrations of 2,4-DNP, 2,4,6-TCP and PCP in Weihe River were also lower than those in the Yellow River basin (48.68 μg/L) (Gao *et al.* 2008). Weihe River in this study is a tributary of the Yellow River. However, the research area for Gao *et al.* (2008) was located in the main stream of the Yellow River. It may be due to this reason that the sources of phenolic compounds in Weihe River and main stream of the Yellow River are different. The concentration of phenol in Weihe River (nd–3.84 μg/L) was much lower than that in Messinian Rivers (0.02–1.108 mg/L) (Anastasopoulou *et al.* 2015). The above comparisons suggested that the concentration of phenolic compounds in water from Weihe River was at a moderate level.

Compared with other phenolic compounds, the concentrations of 2,4-DCP, 2,4,6-TCP and PCP were higher in Weihe River water. However, none of them exceeded the limit values in Standard Limits for Specific Projects of

Table 1 | Concentration ranges and mean values of phenolic compounds in water, SPM and sediment samples from Weihe River

	Water (μg/L)		SPM (μg/g)		Sediment (μg/g)	
Phenolic compounds	**Range**	**Mean ± SD**	**Range**	**Mean ± SD**	**Range**	**Mean ± SD**
phenol	nd-3.84	0.66 ± 1.11	0.02–1,715	101 ± 122	0.03–1.99	0.24 ± 0.38
4-NP	nd-1.15	0.11 ± 0.23	0.01–34.1	3.45 ± 4.22	0.001–8.28	0.57 ± 1.53
3-MP	nd-1.74	0.07 ± 0.31	0.06–13,449	954 ± 548	0.04–3.47	1.81 ± 0.85
2,4-DNP	nd-2.69	0.12 ± 0.47	0.01–97.3	13.0 ± 24.0	0.004–1.24	0.13 ± 0.29
2-NP	nd-0.38	0.03 ± 0.08	0.01–74.9	9.83 ± 4.29	0.003–0.08	0.04 ± 0.02
2,4-DMP	nd-0.84	0.05 ± 0.15	0.03–121	13.6 ± 24.8	0.01–0.35	0.07 ± 0.06
2-CP	nd-1.74	0.24 ± 0.45	0.02–940	66.1 ± 142	0.01–2.86	0.17 ± 0.54
4-CmC	nd-4.53	0.54 ± 1.01	0.03–441	36.9 ± 21.0	0.01–1.52	0.19 ± 0.28
2,4-DCP	nd-3.76	0.39 ± 0.88	0.12–1,639	155 ± 47.5	0.01–15.58	2.15 ± 4.28
2,4,6-TCP	nd-2.48	0.35 ± 0.56	0.16–2,028	194 ± 101	0.03–22.72	3.05 ± 4.71
PCP	0.03–5.96	2.65 ± 1.29	0.37–22,021	2,902 ± 1,245	0.43–7.79	2.66 ± 2.21
$\sum NCP_6$	nd-10.53	1.04 ± 1.99	0.15–13,993	1,091 ± 425	0.80–12.32	2.87 ± 2.01
$\sum CP_5$	0.03–11.6	4.19 ± 2.77	0.76–20,892	3,355 ± 1,416	0.76–32.21	8.22 ± 8.43
$\sum PC_{11}$	0.06–14.12	5.22 ± 3.46	0.92–34,885	4446 ± 1,424	3.54–34.09	11.09 ± 8.68

Surface Water Sources of Centralized Drinking Water (SLSPSWCDW) (GB 3838 2002), as shown in Table 2.

Phenolic compounds in SPM

As shown in Table 1, the concentrations of $\sum PC_{11}$ in SPM samples ranged from 0.92 to 34,885 μg/g with a mean value of 4,446 μg/g. The concentrations of $\sum NCP_6$ ranged from 0.15 to 13,993 μg/g with a mean value of 1,091 μg/g, accounting for 24.5% of the concentrations of $\sum PC_{11}$. And the concentration range of $\sum CP_5$ was 0.76–20,892 μg/g, accounting for 75.5% of the concentrations of $\sum PC_{11}$. The detection frequencies of all the 11 phenolic compounds reached 100%, while in the water samples, only the detection frequency of PCP reached 100%. For individual phenolic compounds, the average concentration of PCP was also the highest (2,902 μg/g), accounting for 65.3% of the total amount.

Phenolic compounds in sediment

The results of phenolic compounds in Weihe River sediments were shown in Table 1. The concentrations of $\sum PC_{11}$ in all sampling sites ranged from 3.54 to 34.09 μg/g with a mean value of 11.09 μg/g. Similar to the pollution characteristics of phenolic compounds in water and SPM, the concentrations of $\sum CP_5$ were higher than those of $\sum NCP_6$. The concentration range of $\sum CP_5$ was 0.76–32.21 μg/g with an average concentration of 8.22 μg/g, accounting for 74.15% of the total amount. The concentration range of $\sum NCP_6$ was 0.80–12.32 μg/g with an average concentration of 2.87 μg/g, accounting for 25.85% of $\sum PC_{11}$. The concentration range of 2,4,6-TCP was from 0.03 to 22.72 μg/g with a mean concentration of 3.05 μg/g, which was the highest among the 11 phenolic compounds. The concentration of PCP was the second highest (range: 0.43–7.79 μg/g; mean ± SD: 2.66 ± 2.21 μg/g). The reason why the content of chlorophenol compounds was much higher than that of non-chlorophenol may be that chlorophenol compounds were widely used as raw materials such as for disinfectants, organic pesticides, resins and surfactants in the production of paper, printing, anti-corrosion, dyes, pharmaceuticals and other industries. Industrial wastewater has been discharged into rivers in more and more ways, resulting in a higher concentration in Weihe River sediments.

Table 2 | The standard limits of phenolic compounds in SLSPSWCDW (μg/L)

Phenolic compounds	Limit value	Maximum value in Weihe River water
2,4-DCP	93	3.76
2,4,6-TCP	200	2.48
PCP	9	5.96

The concentration of phenolic compounds in sediment from Weihe River was lower than that in Liaohe River basin (Li *et al.* 2015). However, the total concentration ranges of phenol, 2-CP and 2,4-DMP in Weihe River sediments were 0.05–5.20 μg/g, which were much higher than those in Beitang Drainage River (nd–16.79 μg/kg) (Zhong *et al.* 2018). The total concentration of phenol and PCP in Weihe River sediments (0.46–9.78 μg/g) were much higher than those in Dagu Drainage River (nd–71.07 μg/kg) (Zhong *et al.* 2018). The concentration range of $\sum CP_5$ (0.76–32.21 μg/g) in Weihe River sediments was much higher than that in Lake Mariut, Egypt (24.9–1,246 μg/kg) (Khairy 2013). These comparisons indicated that the concentrations of phenolic compounds in Weihe River sediments were at a relatively high level. This may be due to the fact that the water body had been greatly influenced by industries such as the dyeing and chemical industries for a long time, which caused the pollutants in the water to settle into the river sediment, thus resulting in the higher concentration of phenolic compounds in sediments of Weihe River.

The spatial distribution of phenolic compounds

The spatial distribution of phenolic compounds in water, SPM and sediments were studied by comparing the concentrations of 11 phenolic compounds among upper (sites 1–9), middle (sites 10–21) and lower (sites 22–32) reaches (Figure 2). It could be observed that both in water and sediment, the highest concentrations of $\sum PC_{11}$ were observed in the middle reach, while the lowest concentrations of $\sum PC_{11}$ were found in the lower reach. This may be due to the sampling time being August, which belongs to the wet season of the river. Moreover, the largest tributary of Weihe River, Jinghe River and Weihe River, intersects between site 22 and site 23, which increased the runoff of the lower reach. Therefore, the content of phenolic compounds in the water of the lower reach was relatively lower than that of the middle and upper reaches. The higher concentrations of $\sum PC_{11}$ in water were observed in site 12, Xingping Sewage Plant (site 13), Luohe River (site 23) and site 24 (Figure 3(a)). These sampling sites were all located near sewage outlets. Large quantities of waste water contained phenolic compounds were discharged into the middle reach of Weihe River, which caused the $\sum PC_{11}$ in water to be highest in the middle reach. The

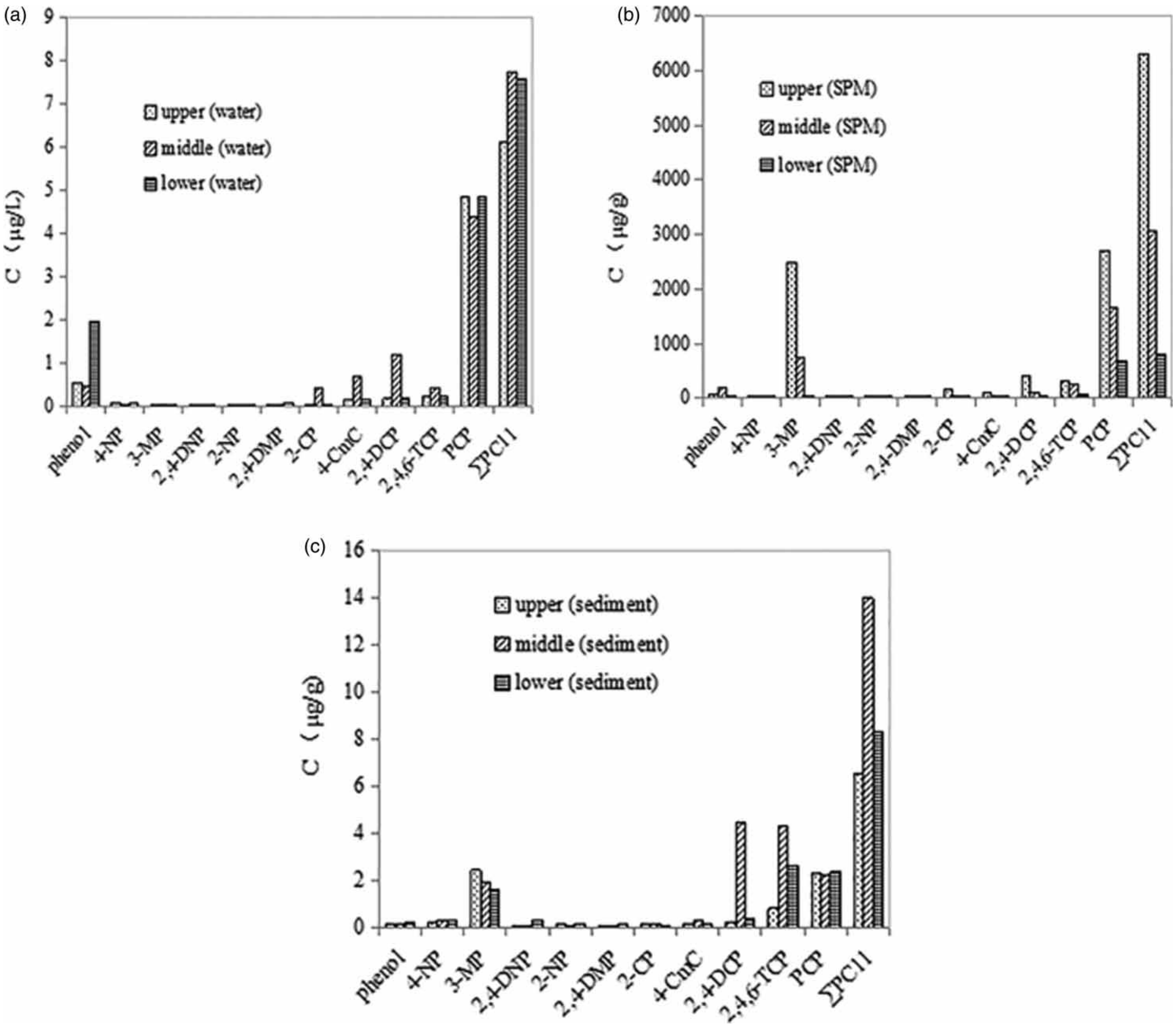


Figure 2 | The concentration of phenolic compounds in water, SPM and sediment in different reaches of Weihe River.

highest concentrations of $\sum PC_{11}$ were observed in site 15, site 16 and site 19 in sediment (Figure 3(c)). These sites were all located in the Xianyang or Xi'an areas, which were the most developed areas in this basin with some sewage treatment plants nearby. The results may be caused by the discharge of urban domestic sewage and industrial wastewater. Also, the water in the middle reach was flat and the SPM adsorbed phenolic compounds from water, then sank to the bottom of the river, which caused the $\sum PC_{11}$ in sediment to increase. For SPM, however, the highest concentrations were found in the upper reach and the lowest concentrations were found in the lower reach. The SPM content in the lower reach was the highest (Figure 3(b)).

For individual phenolic compounds, the mean concentration of PCP in water was the highest in each of the three reaches (Figure 2(a)). In the upper and lower reaches, the phenol concentration was the second highest, while in the middle reaches 2,4-DCP concentration was the second highest. For SPM samples, the mean concentration of PCP was the highest too (Figure 2(b)). Also, the 3-MP concentration was the second highest in the upper and middle reaches, differing from that in water samples. The concentration of each phenolic compound was lowest in the lower reaches. For sediment samples, the highest concentrations of individual phenolic compounds were 3-MP in upper reaches, 2,4-DCP in middle reaches and PCP in lower reaches, respectively.

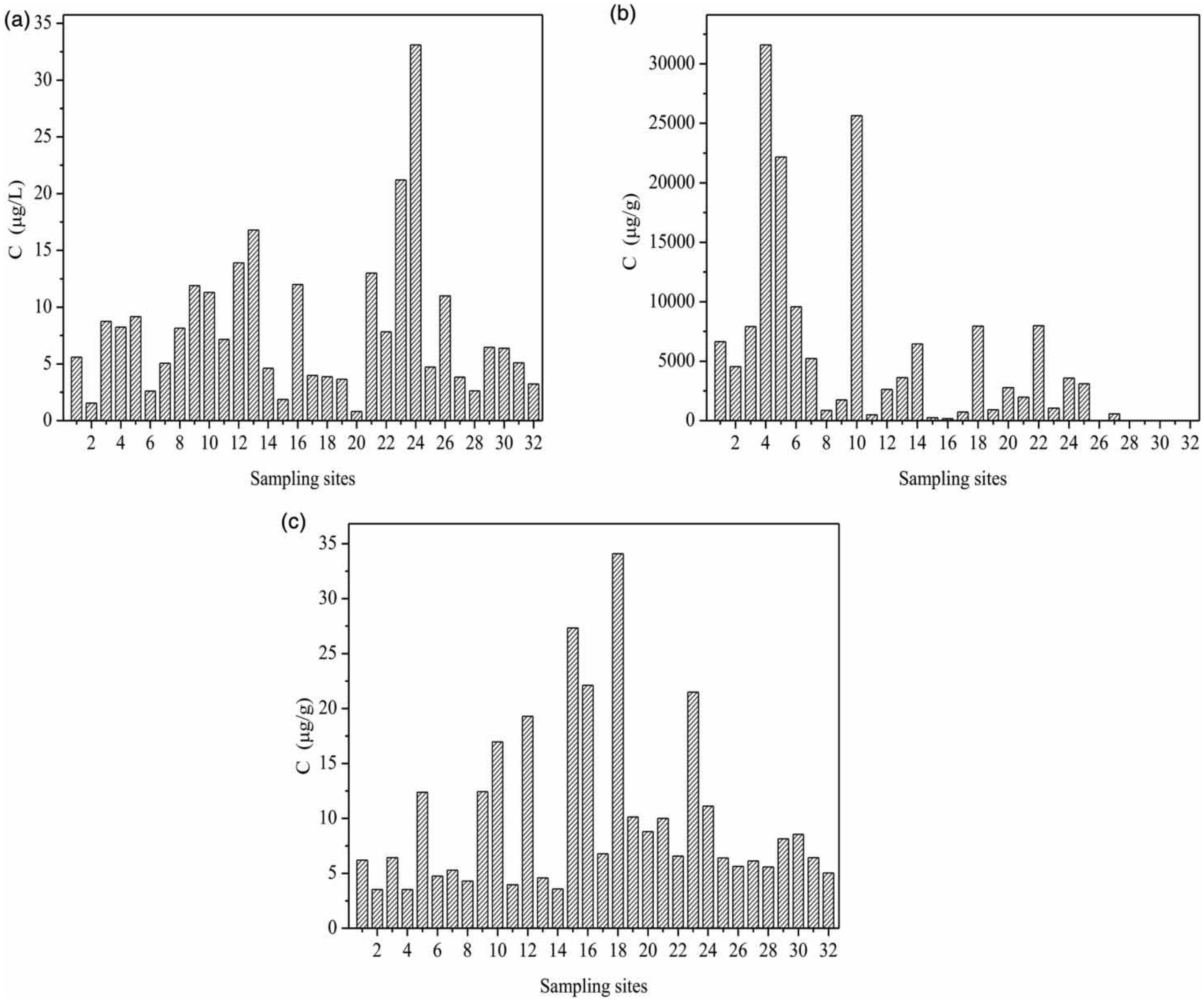


Figure 3 | The concentrations of $\sum PC_{11}$ in water, SPM and sediment from sampling sites in Weihe River.

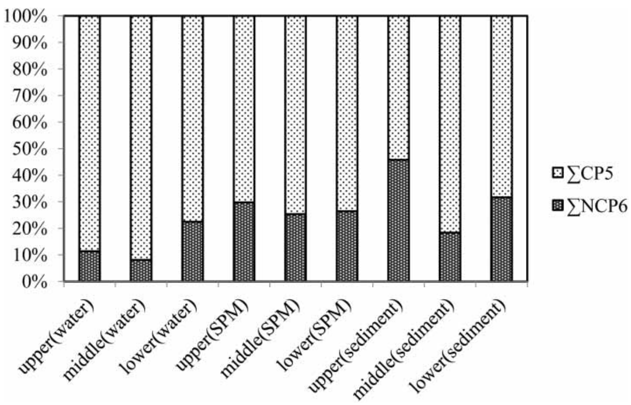


Figure 4 | The percentage of $\sum NCP_6$ and $\sum CP_5$ in water, SPM and sediment in different reaches of Weihe River.

The percentages of $\sum NCP_6$ and $\sum CP_5$ in water, and SPM and sediment in different reaches, were also calculated (Figure 4). In any reach of Weihe River, the percentage of $\sum CP_5$ was higher than that of $\sum NCP_6$. So it can be concluded that the chlorophenol pollution in the Weihe River was more serious than non-chlorophenol pollution. The highest percentages of $\sum CP_5$ were found in the middle reaches in every kind of sample.

The distribution of phenolic compounds between water, SPM and sediment

It is believed that the environmental fate and behavior of hydrophobic organic compounds is ultimately determined by the physicochemical properties of each compound and sediment, such as organic content, size distribution, partition coeffficient and salinity (Chen et al. 2015). Physiochemical parameters such as COD (7.14–1,023 mg/L), EC (512–1,565 us/cm), TDS (214–1,432 mg/L), salinity (0.23–0.62 ppt) and pH (7.46–9.84) in water samples from Weihe River were detected, but no significant correlations were observed between concentrations of phenolic compounds and these physiochemical parameters.

Many researchers hold that the TOC value determined the concentrations of hydrophobic organic compounds in sediment and positive linear relations could be found between hydrophobic organic compound concentrations and the TOC values in sediment (Witt 1995; Kannan et al. 2001; Chen et al. 2015). The TOC of sediments in Weihe River ranged from 0.91 to 8.06% (Table 3) with a mean value of 2.1%. But no linear relationship was found between phenolic compounds concentrations and TOC (Figure S1). This may be due to the following reasons. First, the phenolic compounds and TOC come from different sources. Second, the hydrophobicities of some phenolic compounds are weak. Although sediments and water in river systems such as Weihe River undergo dynamic sorption and desorption and may not have reached chemical equilibrium, an analysis of the distribution of phenols between sediment and water can still provide useful insight into the processes that control the transport and fates of phenols. To realize this objective, the mean apparent distribution coefficient (K_d) of individual phenols, which is defined as the ratio of phenols concentrations in sediment or SPM to those in water, was calculated (Table 3). No correlations existed between K_d (sediment) and sediment TOC values. Also no correlation between K_d for organic contaminants and sediment TOC values was found in Qiantang River (Zhu et al. 2008) and the Humber Estuary (Zhou et al. 1999). The possible reason was that the sorption of phenolic compounds to sediments will be affected by both organic matter content and the inorganic matrix (e.g. clay minerals) when sediment TOC values were low. The highest SPM contents were found in site 26 and site 28–32 in the lower reach, which even reached 7.58, 2.23, 7.42, 17.9, 22.7 and 5.21 g/L, respectively. In these sites, the $\sum PC_{11}$ concentrations in SPM and K_d (SPM) were relatively low. Except for these sites, the K_d (SPM) was much higher than K_d (sediment) (Table 3), which probably indicated fresh phenolic compounds input in Weihe River.

Table 3 | The $\sum PM_{11}$ in SPM, TOC in sediment, the K_d (SPM) and K_d (sediment) in sampling sites

Site No.	$\sum PM_{11}$ in Water (μg/L)	SPM C_{SPM} (g/L)	SPM $\sum PM_{11}$ (μg/g)	SPM K_d (L/g)	Sediment TOC (%)	Sediment $\sum PM_{11}$ (μg/g)	Sediment K_d (L/g)
1	5.59	0.013	6,635	1,187	2.53	6.20	1.1
2	1.54	0.018	4,536	2,951	2.73	3.54	2.3
3	8.74	0.024	7,903	904	1.91	6.42	0.7
4	8.25	0.002	31,595	3,829	1.75	3.54	0.4
5	9.17	0.010	22,167	2,417	1.29	12.38	1.4
6	2.60	0.024	9,579	3,679	1.62	4.76	1.8
7	5.06	0.006	5,228	1,032	1.55	5.28	1.0
8	8.14	0.052	871	107	1.51	4.29	0.5
9	11.9	0.077	1,743	146	2.07	12.43	1.0
10	11.3	0.007	25,638	2,269	1.26	16.96	1.5
11	7.17	0.234	498	69	2.39	3.96	0.6
12	13.9	0.064	2,624	189	2.24	19.30	1.4
13	16.8	0.043	3,616	215	2.13	4.58	0.3
14	4.61	0.013	6,453	1,399	0.91	3.58	0.8
15	1.86	0.659	241	130	1.61	27.33	14.7
16	12.0	1.06	171	14	1.79	22.11	1.8
17	4.00	0.080	722	180	3.10	6.77	1.7
18	3.88	0.027	7,956	2,051	1.28	34.09	8.8
19	3.65	0.106	918	252	2.01	10.12	2.8
20	0.80	0.078	2,785	3,461	2.11	8.80	10.9
21	13.0	0.058	1,980	152	1.54	9.99	0.8
22	7.83	0.022	7,989	1,020	1.73	6.57	0.8
23	21.2	0.116	1,046	49	1.38	21.49	1.0
24	33.1	0.126	3,590	108	1.48	11.12	0.3
25	4.71	0.023	3,107	660	8.06	6.41	1.4
26	11.0	7.58	7.8	0.71	1.60	5.64	0.5
27	3.83	0.214	581	152	3.27	6.13	1.6
28	2.63	2.23	26	10	1.38	5.57	2.1
29	6.46	7.42	2.6	0.41	1.43	8.15	1.3
30	6.37	17.9	4.0	0.63	2.07	8.56	1.3
31	5.09	22.7	0.9	0.18	2.59	6.42	1.3
32	3.23	5.21	16	4.9	1.98	5.04	1.6

Distribution of contaminants such as phenolic compounds between sediment/soil and water at equilibrium is widely considered as a partition process (Zhong et al. 2018); as a result, the distribution coefficient tends to be closely related to the properties of contaminants, in particular their octanol-water partition coefficient (K_{ow}). The organic carbon normalized partition coefficient of phenols (i.e. $K_{oc} = K_d/f_{oc}$) in Weihe River were plotted against K_{ow} values (Figure 5). Some reports agreed that $\log K_{oc}$ increased with $\log K_{ow}$ of organic compounds, consistent with the

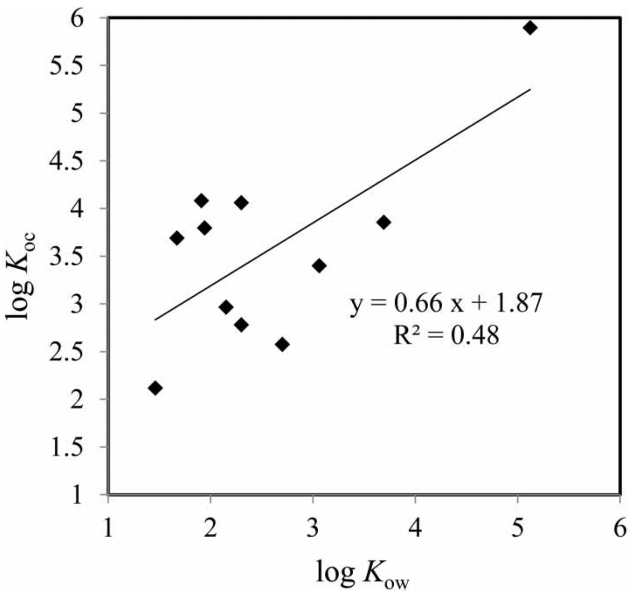


Figure 5 | The mean logK_{oc} of 11 phenolic compounds against logK_{ow}.

so-called linear free energy relationship (Zhou & Maskaoui 2003; Zhu *et al.* 2008). However, no significant linear correlation between logK_{oc} and logK_{ow} was found in Weihe River. As shown in Figure 5, the slope, intercept and square determination coefficient were 0.66, 1.87 and 0.48, respectively. The significant difference between *in situ* logK_{oc} is perhaps related to the disequilibrium between the concentrations of sediment samples and surface water samples. Many reasons including dilution, high surface runoff and atmospheric fallout could produce the disequilibrium (Zhong *et al.* 2018).

Ecological risk assessment of phenolic compounds in Weihe River

The specific risk characterization results were shown in Table 4. Among the 11 phenolic compounds, 8 phenolic compounds exhibited minimal (RQ < 0.1) or median (RQ: 0.1–1) ecological risks in all sampling sites. For these 8 phenolic compounds, the sampling sites with RQ < 0.1 accounted for more than 80%, with 0.1 < RQ < 1 accounted for a small proportion (below 20%) and with RQ > 1 accounted for 0%, that was, these 8 phenolic compounds did not pose high ecological risks to aquatic organisms in the study area. However, RQ values of 4-CmC, 2,4-DCP and PCP in some sites were more than 1.0 (meaning a high ecological risk). The proportions of high risk of 4-CmC and 2,4-DCP were 9.38% and 3.13%, respectively. And the proportions of median

Table 4 | Phenolic compounds risk characterization results

		Percentage of Risk quotient		
Phenols	**RQ range**	**<0.1**	**0.1–1**	**>1**
phenol	0–0.221	87.50%	12.50%	0.00%
4-NP	0–0.726	81.25%	18.75%	0.00%
3-MP	0–0.165	96.88%	3.13%	0.00%
2-CP	0–0.557	81.25%	18.75%	0.00%
2,4-DNP	0–0.721	96.88%	3.13%	0.00%
2-NP	0–0.09	96.88%	3.13%	0.00%
2,4-DMP	0–0.297	96.88%	3.13%	0.00%
4-CmC	0–4.18	37.50%	53.13%	9.38%
2,4-DCP	0–1.008	75.00%	21.88%	3.13%
2,4,6-TCP	0–0.136	96.88%	3.13%	0.00%
PCP	0.034–6.83	3.13%	3.13%	93.8%

risk of 4-CmC and 2,4-DCP were 53.13% and 21.88%, respectively. The RQ value of PCP ranged from 0.034 to 6.834 and the rate of high risk was the highest among 11 phenolic compounds, reaching 93.75%, which indicated that the Weihe River suffered serious ecological risk from PCP. Based on the above analysis, 4-CmC, 2,4-DCP and PCP should be selected as priority phenolic compounds for Weihe River and some effective measures should be taken to control and reduce the pollution of these phenolic compounds.

CONCLUSIONS

In this study, we conducted single sampling due to insufficient funding and some other reasons. However, analyses of 11 phenolic compounds still provided very useful information for the evaluation of the contamination levels, spatial distribution and ecological risks that are located in Northwest China. The results obtained in this study showed that the levels of phenolic compounds in Weihe River were at a moderate level for water and at a relatively high level for sediment in the world, respectively. In any reach of Weihe River, the concentration of ∑CP5 was higher than that of ∑NCP6. For individual phenolic compounds, PCP pollution was the most serious. The results of ecological risk assessment of phenolic compounds by RQs indicated a high ecological risk in Weihe River water. 4-CmC, 2,4-DCP and PCP had higher contribution to the total phenols in the study area. Thus, more attention should be paid to these phenolic compounds, and preventing greater risks to the environment. In most sites, the distribution coefficient (K_d) (SPM) was much higher than K_d (sediment), which probably suggested fresh phenolic compounds input in Weihe River. The existence of these fresh phenolic compounds and their potential risk should also be given more rigorous evaluation.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Anastasopoulou, E., Katsogiannou, I., Georgiopoulos, N. & Gritzalis, K. 2015 Distribution of total phenols in Messinian Rivers. In: *International Conference on Environmental Management, Engineering, Planning and Economics*.

Bolz, U., Hagenmaier, H. & Körner, W. 2001 Phenolic xenoestrogens in surface water, sediments, and sewage sludge from Baden-Württemberg, south-west Germany. *Environmental Pollution* **115** (2), 291–301.

Brinda, L. A., Balasubramanian, A. & Venkatesan, S. 2013 Extraction of phenol and chlorophenolsusing ionic liquid $[Bmim]^+[BF^4]^-$dissolved in tributylphosphate. *CLEAN-Soil Air Water* **41** (4), 349–355.

Chakraborty, P., Khuman, S. N., Selvaraj, S., Sampath, S., Devi, N. L., Bang, J. J. & Katsoyiannis, A. 2016 Polychlorinated biphenyls and organochlorine pesticides in River Brahmaputra from the outer Himalayan Range and River Hooghly emptying into the Bay of Bengal: occurrence, sources and ecotoxicological risk assessment. *Environmental Pollution* **219**, 998–1006.

Chen, R., Yin, P., Zhao, L., Yu, Q., Hong, A. & Duan, S. 2014 Spatial–temporal distribution and potential ecological risk assessment of nonylphenol and octylphenol in riverine outlets of Pearl River Delta, China. *Journal of Environmental Science* **26** (11), 2340–2347.

Chen, Y., Jia, R. & Yang, S. 2015 Distribution and source of polycyclic aromatic hydrocarbons (s) in water dissolved phase, suspended particulate matter and sediment from Weihe River in Northwest China. *International Journal of Environmental Research and Public Health* **12** (11), 14148–14163.

Diao, P., Chen, Q., Wang, R., Sun, D., Cai, Z., Wu, H. & Duan, S. 2017 Phenolic endocrine-disrupting compounds in the Pearl River Estuary: occurrence, bioaccumulation and risk assessment. *Science of the Total Environment* **584–585**, 1100–1107.

Gao, J., Liu, L., Liu, X., Zhou, H., Huang, S. & Wang, Z. 2008 Levels and spatial distribution of chlorophenols–2,4-Dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol in surface water of China. *Chemosphere* **71**, 1181–1187.

GB 3838-2002 2002 *Quality Standard for Surface Water in China*. Ministry of Environmental Protection of the People's Republic of China, Beijing, China.

Jin, X., Gao, J., Zha, J., Xu, Y., Wang, Z., Giesy, J. P. & Richardson, K. L. 2011 A tiered ecological risk assessment of three chlorophenols in Chinese surface waters. *Environmental Science and Pollution Research* **19**, 1544–1554.

Kannan, K., Kober, J. L., Kang, Y. S., Masunaga, S., Nakanishi, J., Ostaszewski, A. & Giesy, J. P. 2001 Polychlorinated naphthalenes, biphenyls, dibenzop-dioxins, and dibenzofurans as well as polycyclic aromatic hydrocarbons and alkylphenols in sediment from the Detroit and Rouge Rivers, MI, USA. *Environmental Toxicology and Chemistry* **20**, 1878–1889.

Kawahata, H., Ohta, H., Inoue, M. & Suzuki, A. 2004 Endocrine disrupter nonylphenol and bisphenol A contamination in Okinawa and Ishigaki Islands, Japan – within coral reefs and adjacent river mouths. *Chemosphere* **55**, 1519–1527.

Khairy, M. A. 2013 Assessment of priority phenolic compounds in sediments from an extremely polluted coastal wetland (Lake Maryut, Egypt). *Environmental Monitoring and Assessment* **185**, 441–455.

Li, B., Hu, X., Liu, R., Zeng, P. & Song, Y. 2015 Occurrence and distribution of phthalic acid esters and phenols in Hun River Watersheds. *Environmental Earth Sciences* **73**, 5095–5106.

Michałowicz, J. & Duda, W. 2007 Phenols - sources and toxicity. *Polish Journal of Environmental Studies* **16**, 347–362.

Nash, C. E., Burbridge, P. R. & Volkman, J. K. 2005 *Guidelines for Ecological Risk Assessment of Marine Fish Aquaculture*. U.S. Department of Commerce, National Oceanic and Atmospheric Administration (NOAA), National Marine Fisheries Service, Washington, DC.

Song, X. Y., Hu, X. J., Liang, R. J. & Sun, W. J. 2013 Spatial distribution and seasonal variations of volatile phenols in the surface water of the Taizi River. *Advanced Materials Research* **791–793**, 155–158.

Song, J., Tang, B., Zhang, J., Dou, X., Liu, Q. & Shen, W. 2018 System dynamics simulation for optimal stream flow regulations under consideration of coordinated development of ecology and socio-economy in the Weihe River Basin, China. *Ecological Engineering* **124**, 51–68.

Wang, C., Feng, Y., Gao, P., Ren, N. & Li, B.-L. 2012 Simulation and prediction of phenolic compounds fate in Songhua River, China. *Science of the Total Environment* **431**, 366–374.

Wang, D., Yang, S., Wang, G., Gao, L., Wang, Y., Jiang, Q. & Chen, Y. 2016 Residues and distributions of organochlorine pesticides in China's Weihe River. *Polish Journal of Environmental Studies* **25**, 1285–1292.

Wang, J., Wei, H., Zhou, X., Li, K., Wu, W. & Guo, M. 2019a Occurrence and risk assessment of antibiotics in the Xi'an section of the Weihe River, northwestern China. *Marine Pollution Bulletin* **146**, 794–800.

Wang, L., Yang, X., Zhang, A., Bidegain, G., Li, R., Na, G. & Yuan, X. 2019b Distribution patterns and ecological risk of endocrine-disrupting chemicals at Qingduizi Bay (China): a preliminary survey in a developing maricultured bay. *Marine Pollution Bulletin* **146**, 915–920.

Wei, S., Yang, H., Song, J., Abbaspour, K. C. & Xu, Z. 2012 System dynamics simulation model for assessing socio-economic impacts of different levels of environmental flow allocation in the Weihe River Basin, China. *European Journal of Operational Research* **221**, 248–262.

Witt, G. 1995 Polycyclic aromatic hydrocarbons in water and sediment of the Balic Sea (Alaska). *Marine Pollution Bulletin* **31**, 237–248.

Wolff, M. S., Teitelbaum, S. L., McGovern, K., Pinney, S. M., Windham, G. C., Galvez, M., Pajak, A., Rybak, M., Calafat, A. M. & Kushi, L. H. 2015 Environmental phenols and pubertal development in girls. *Environment International* **84**, 174–180.

Zhong, W., Wang, D. & Wang, Z. 2018 Distribution and potential ecological risk of 50 phenolic compounds in three rivers in Tianjin, China. *Environmental Pollution* **235**, 121–128.

Zhou, J. L. & Maskaoui, K. 2003 Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. *Environmental Pollution* **121** (2), 269–281.

Zhou, W. M., Fu, D. Q. & Sun, Z. G. 1991 Determination of black list of China's priority pollutants in water. *Research of Environmental Science* **4**, 9–12 (in Chinese).

Zhou, J. L., Fileman, T. W., Evans, S., Donkin, P., Readman, J. W., Mantoura, R. F. C. & Rowland, S. L. 1999 The partition of fluoranthene and pyrene between suspended particles and dissolved phased in the Humber Estuary: a study of the controlling factors. *Science of the Total Environment* **243–244**, 305–321.

Zhou, M., Zhang, J. & Sun, C. 2017 Occurrence, ecological and human health risks, and seasonal variations of phenolic compounds in surface water and sediment of a potential polluted river basin in China. *International Journal of Environmental Research & Public Health* **14** (10), 1140.

Zhu, L., Chen, Y. & Zhou, R. 2008 Distribution of polycyclic aromatic hydrocarbons in water, sediment and soil in drinking water resource of Zhejiang Province, China. *Journal of Hazardous Materials* **150**, 308–316.

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