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RESEARCH ARTICLE

Distribution of aromatic amines, phenols, chlorobenzenes, and naphthalenes in the surface sediment of the Dianchi Lake, China

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HIGHLIGHTS

- The total organic pollutant concentrations in sediment were 27.4 – 1620 ng/g.
- The phenol concentrations were relatively high in the sediment of the Dianchi Lake.
- Average total concentrations decreased as follows: Caohai>Waihai>Haigeng Dam.
- 1,4-dichlorobenzene, 3- or 4-methylphenol, 1,2,4-trichlorobenzene might be risks.

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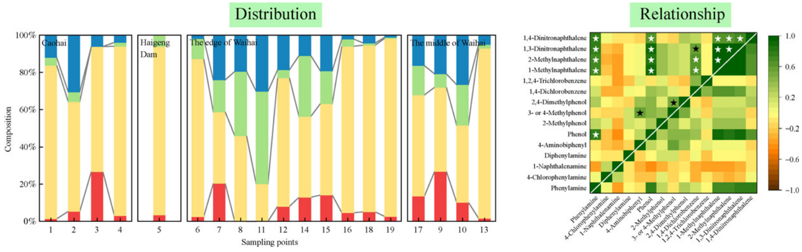
GRAPHIC ABSTRACT



ABSTRACT

Organic pollutants are widespread environmental pollutants with high toxicity, persistence, and bioaccumulation. Our aim was to investigate the distribution of aromatic amines, phenols, chlorobenzenes, and naphthalenes in the surface sediment of the Dianchi Lake, China. Nineteen surface sediment samples were collected from the Dianchi Lake, and 40 types of organic pollutants were analyzed via gas chromatography–mass spectrometry. The total organic pollutant concentrations in the surface sediment of the Dianchi Lake varied from 27.4 to 1.62×10^3 ng/g. The concentrations of phenols were much higher than those in other water bodies but still within a controllable range, whereas the concentrations of the other organic pollutant classes were similar or even lower. The detection ratio of 3- or 4-methylphenol was the highest (100.00%) among the pollutants. The average total organic pollutant concentrations decreased in the following order: Caohai (540 ng/g)>the middle of Waihai (488 ng/g)>the edge of Waihai (351 ng/g)>Haigeng Dam (90.4 ng/g). Pearson analysis showed a strong correlation among 1-methylnaphthalene, 2-methylnaphthalene, 1,3-dinitronaphthalene, and 1,4-dinitronaphthalene ($p < 0.01$). Caohai, the north lakeshore of Waihai and the south of Waihai showed higher risk because of high concentration; meanwhile, 1,4-dichlorobenzene, 3- or 4-methylphenol and 1,2,4-trichlorobenzene were more likely to cause risks.

1 Introduction

Organic pollutants (such as aromatic amines, phenols, chlorobenzenes, and naphthalenes), which are widely used in industry, agriculture, and daily living, have attracted the interest of researchers because they are widespread environmental pollutants with high toxicity, persistence, and bioaccumulation (Oliver and Nicol, 1982; Lin et al., 2015; Zhou et al., 2017; Kang et al., 2018). In terms of environmental media, they have been detected in air, water, soil, sediment, and organisms, thereby posing a great threat to ecosystems and human health (Ding et al., 1992; Zhang

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et al., 2005; Wu et al., 2013; Zhou et al., 2018). Some types of organic pollutants can be accumulated in water and surface sediment due to their nonbiodegradable and persistent characteristics (Zhong et al., 2013; Kan et al., 2015; Li et al., 2018). Most of these organic pollutants, whose water solubilities are generally poor, are likely to be adsorbed in the surface sediment. Surface sediment is recognized as one of the main sinks in the environment (Mahmood et al., 2014; Li et al., 2015). When concentrations of organic pollutants reach certain levels, surface sediment may become secondary pollution sources, and the emission of organic pollutants through the surface sediment will pose threats to the aquatic ecosystem and human health. Therefore, conducting an extensive monitoring of organic pollutants in surface sediment is necessary.

Aromatic amines, phenols, chlorobenzenes, and naphthalenes are widespread around the world. For example, phenols are detected in the surface sediment of rural and urban water in China. Phenols with concentrations of 0–234 ng/g in the surface sediment of rural watercourses in southern Jiangsu have been investigated (Feng et al., 2007). The rivers in Tianjin have also been seriously polluted with phenols whose concentrations in the surface sediment were nd (not detected)–2937 ng/g during the wet season(Zhong et al., 2018). Phenols have also been detected in waters of other countries; e.g., the concentration of phenols varied from nd to 396 ng/g in Egypt (Khairy, 2013).

The Dianchi Lake, which is located in the south-western part of China and adjacent to Kunming, is the sixth largest freshwater lake in China with an area of 309 km^2. It is the main reserve source of domestic water for 6.8 million residents in Kunming, providing support for the growing industry and agriculture of the city (Huang et al., 2013). The lake is divided into Caohai and Waihai by the Haigeng Dam. Waihai is the main section with a surface area of 290 km^2 and a mean water depth of 4.4 m; there is the only natural outlet (Haikou) on the west of Waihai. Caohai is more adjacent to Kunming City compared with Waihai and has received large amounts of untreated urban sewage and industrial wastewater before 2002 (Zhao et al., 2014). With the rapid economic growth and urban development in the previous decades, industrial, agricultural, and daily life sewage have seriously polluted 14 major inflow rivers.

Despite the regional importance and potential serious pollution of the Dianchi Lake, only a few investigations have been conducted on organic pollutants in the Dianchi Lake, such as aromatic amines, phenols, chlorobenzenes, and naphthalenes. These pollutants are widely used in daily life but harmful to the environment. Most studies on the Dianchi Lake focus on relatively classic organic pollutants, such as polychlorinated biphenyls (PCBs) and steroid estrogens in the surface sediment (Wan et al., 2011; Huang et al., 2013). The distribution of several other potentially harmful organic pollutants in the Dianchi Lake, especially in the surface sediment, has received insufficient attention. High concentrations of organic pollutants, such as phenols, have been detected in the inflow river, aquatic animals, and submerged plants in the Dianchi Lake (Yao et al., 2014; Fan et al., 2017; Fan et al., 2018). Moreover, organic pollutants have been detected in different media in the aquatic environment; hence, the surface sediment in the Dianchi Lake, which is the main sink, may have accumulated organic pollutants and thus must be focused on.

This work aims to investigate the distribution of selected organic pollutants in the surface sediment of the Dianchi Lake. Nineteen surface sediment samples from the Dianchi Lake were collected in December 2016, and 40 types were analyzed via gas chromatography–mass spectrometry (GC–MS). Considering the chemical structure, physical and chemical property parameters and general sources/use of organic pollutants, the 40 types of the detected organic pollutants were classified into the four classes (aromatic amines, phenols, chlorobenzenes and naphthalenes). Spatial characteristics of organic pollutants and distribution of each kind of organic pollutants were determined. Further, a comprehensive scoring method and PAC method was used to investigate the priority pollutants and potential source.

2 Materials and methods

2.1 Materials

All the standard chemicals, internal standards, and surrogates of the organic pollutants with purity greater than 95% were purchased from AccuStandard (New Haven, CT, USA). Deuterated PAHs (D-PAHs), including naphthalene-D_8, acenaphthene-D_{10}, phenanthrene-D_{10}, chrysene-D_{12}, and perylene-D_{12} were used as internal standards. The surrogates included 2-fluorobiphenyl and p-terphenyl-D_{14}. Pesticide grade reagents (n-hexane) with a purity of 95% were obtained from J.T. Baker (USA). Acetone of HPLC-grade and with a purity of 99% was purchased from Fisher (USA).

2.2 Site description and sample collection

The south, north and east shores of the Dianchi Lake were urban areas of Kunming City, which involved relatively complete industrial system. The farmland around these areas was mainly used for fruit/vegetable growing industries and flower cultivation. Almost all of the industrial and domestic wastewater from the above areas was disposed first before discharged into the Dianchi Lake. Before the year 2011, the industrial and domestic wastewater was first discharged into Caohai, then passed by Haigeng Dam and finally diluted in Waihai. Different from the above areas, the west shore of Dianchi Lake was located in mountainous area, where primary business were mining industry (mainly phosphate-mine) and quarrying industry. Specifically, sampling point No. 11 (Fig. A.1), which was located in Haikou Town, was near the only natural outflow channel of the Dianchi Lake. It was affected by oil inflame due to the large numbers of incoming and outgoing vessels. Sampling point No. 15 was located at the lake inlet of Nanchong River, Chenggong District, where primary business was fruit/vegetable growing industries and flower cultivation.

Nineteen surface sediment samples were collected from the Dianchi Lake, including Caohai ($n = 4$) and Waihai ($n = 15$), on the 4th–5th of December, 2016, when the lake surface was calm and breezy. On the basis of the physical and chemical properties of the Dianchi Lake (such as the current velocity, water depth, and oxidation condition), all the sampling points of the Dianchi Lake were divided into four regions in this work, as follows: 1) Caohai (sampling points Nos. 1–4); 2) Haigeng Dam (sampling point No. 5); 3) the edge of Waihai (sampling points Nos. 6, 7, 8, 11, 12, 14, 15, 16, 18, and 19); 4) the middle of Waihai (sampling points Nos. 17, 9, 10, and 13) (Li et al., 2019; Wang et al., 2019). Detailed information of the sampling locations is shown in Fig. A.1. With a columnar gravity sampler (sampling tube with a diameter of 10 cm and length of 80 cm), the surface sediment at the bottom of the Dianchi Lake were sampled at a depth of 0–20 cm, sealed with a polyethylene Ziplock bag, and frozen at -18°C. All samples were freeze-dried at approximately -50°C, sieved through a 60-mesh sieve, placed in a polyethylene Ziplock bag, and stored at 4°C prior to use.

2.3 Sample preparation

The sample preparation method referred to Hu et al. (2019). A suitable amount of samples (2.00 g) and Na_2SO_4 (2.00 g) were obtained and homogenized, wrapped in fat-free filter paper, and placed in a Soxhlet extraction tube. Surrogate mixed standard (100 ng) was placed into the tube. Then, 100 mL of n-hexane/acetone (1:1, v/v) mixed solution was added and extracted for 6–8 h, with a small amount of copper added to the flask. Each extract was transferred and concentrated, 100 ng of D-PAH mixed internal standard was added, and the volume of nitrogen was blown to 1.0 mL, as determined by the analysis. The surrogate was a mixed solution of 2-fluorobiphenyl and p-triphenyl-D_{14}. Samples were purified by silica gel SPE column.

2.4 GC-MS analysis method

The samples were determined by using QP-2010 Ultra GC–MS (Shimadzu, Japan). Electron impact source and the selected ion mode were selected as the quantitative methods. The carrier gas velocity was 1.3 mL/min with high purity helium as the carrier gas. The injection port and quadrupole temperature were 280°C, each sample splitless injection volume was 1.0 μL, and the DB-5MS capillary column (30.0 m × 0.25 mm × 0.25 μm; Agilent, USA) was used as chromatographic separation. The temperature program was set as follows: 1) beginning at 70°C and holding for 3 min; 2) increasing to 270°C with a rate of 10°C/min and holding for 1 min; 3) increasing to 285°C with a rate of 5°C/min; 4) increasing to 305°C with a rate of 10°C/min and holding for 10 min. The electron energy was 70 eV, and the ion source temperature was 240°C.

2.5 Data analysis

Pearson correlation (all experimental data followed normal distribution; SPSS 23.0, IBM, USA) was used to investigate the relationship between different organic pollutants, and the significance level was set to $p < 0.05$. Kriging interpolation method (Surfer 8, Golden Software, USA) was used to predict the organic pollutant distribution pattern in the surface sediment of the Dianchi Lake.

A comprehensive scoring method was used to determine the primary pollutants in the surface sediment of the Dianchi Lake, which was describe in Section A.1 in detail. Principal component analysis (PCA; SPSS 23.0, IBM, USA) was used to analyze the potential sources of organic pollutants in the surface sediment of the Dianchi Lake.

2.6 Quality assurance and quality control

Each batch of 20 samples contained a full process blank sample, a parallel sample, and a (blank) standard samples. During each ten samples, a continuous calibration sample was added to check the fluctuation of the standard curve. The concentrations of target contaminants in the blank samples should be below the detection limits. Requirements for the deviation of parallel samples were: $\leqslant 100\%$ when the sample concentration was no more than threefold of the method detection limit (MDL), and $< 50\%$ when the sample concentration was more than threefold of the MDL. If any conditions didn't meet the quality control requirements, the batch of samples should be analyzed again from pretreatment. The recovery percentages ranged from 60.5% to 106%. The recovery percentages of surrogate ranged from 66.4% to 71.2% (2-fluorobiphenyl) and from 105% to 127% (p-triphenyl-D_{14}), respectively. No target compounds were detected in the blanks, and the relative standard deviation of the parallel samples was lower than 10.0%.

3 Results and discussion

3.1 Concentration of organic pollutants

Among the 40 types of organic pollutants in the four classes (aromatic amines ($\lg K_{OW} = 0.940–2.97$, $K_{OC} =$

103–1.19 × 10^3), phenols (lg K_{OW} = 1.48–2.40, K_{OC} = 182–4.57 × 10^2), chlorobenzenes (lg K_{OW} = 3.34–3.82, K_{OC} = 1.47 × 10^3–3.15 × 10^3), and naphthalenes (lg K_{OW} = 2.60–3.91, K_{OC} = 763–3.29 × 10^3)) determined in the surface sediment of the Dianchi Lake, 15 types were detected, including five types of aromatic amines, four types of phenols, four types of naphthalenes, and two types of chlorobenzenes (Tables A.1 and A.2 in Appendix A). The total organic pollutant concentration in the surface sediment of the Dianchi Lake varied in a range of 27.4–1.62 × 10^3 ng/g with an average of 409 ng/g, consisting of aromatic amines (nd–43.0 ng/g), phenols (9.94–1.55 × 10^3 ng/g), chlorobenzenes (nd–33.0 ng/g), and naphthalenes (nd–146 ng/g). The mean concentrations of aromatic amines, phenols, chlorobenzenes, and naphthalenes were 19.0, 335, 17.8, and 33.8 ng/g, accounting for 4.68%, 82.6%, 4.39%, and 8.33% of the total organic pollutant concentration, respectively.

Twenty-three other water bodies located in China and USA were chosen to estimate the pollution level of the Dianchi Lake (details seen in Table A.3). Compared with the surface sediment of other water bodies, the concentrations of aromatic amines and chlorobenzenes in the surface sediment of the Dianchi Lake were at the same or even lower level. In the rural watercourses of Zhenjiang, Yixing, and Changzhou (Jiangsu, China), the concentration of aromatic amines (phenylamine and benzidine) was 0–55 ng/g (Feng et al., 2007), which was at the same level as this study (aromatic amines: nd–43.0 ng/g). The chlorobenzene concentration was lower than that in the Maowei Sea (2.5–61.5 ng/g; Qinzhou, Guangxi, China), Tonghui River (18.2–1827.7 ng/g; Beijing, China), Pearl River estuary (7.83–40.09 ng/g; Guangdong, China), Tittabawassee River (24.25–243.66 ng/g; Michigan, USA), and Saginaw River (0.06–65.88 ng/g; Michigan, USA) (details seen in Table A.3).

The concentration of naphthalenes in the Dianchi Lake was much higher than that in Liaodong Bay (1-methylnaphthalene: 7.75 ng/g, 2-methylnaphthalene: 4.29 ng/g; Liaoning, China), slightly higher than that in the Lanzhou section of the Yellow River (1-methylnaphthalene: nd–60 ng/g, 2-methylnaphthalene: nd; Lanzhou, Gansu, China) and the Yellow River estuary (1-methylnaphthalene: 0.59–33.3 ng/g, 2-methylnaphthalene: 0.71–68.80 ng/g; Shandong, China), but much lower than that in Baoshan of the Yangtze River estuary (1-methylnaphthalene: 1370 ng/g; Shanghai, China) (details seen in Table A.3).

The concentration of phenols was much higher than that of the rivers in the rural areas of Lixiahe (0–141 ng/g; Jiangsu, China), the Yinma River (188–448 ng/g (wet-season); Jilin, China), rural watercourses (nd–234 ng/g; Zhenjiang, Yixing and Changzhou, Jiangsu, China), two major rivers in Tianjin (nd–54.5 ng/g (dry-season), nd–299 ng/g (wet-season); nd–3.31 ng/g (dry-season), nd–21.9 ng/g (wet-season); China), and the Maryut Lake (nd–396 ng/g; Egypt) (details seen in Table A.3); it was only lower than that of the Dagu Drainage River during the wet season (nd–2.94 × 10^3 ng/g; Tianjin, China) (Feng et al., 2007; Khairy, 2013; Zhou et al., 2017; Zhong et al., 2018). In general, the concentration of phenols in the surface sediment of the Dianchi Lake was relatively high. To determine the pollution level of phenols, this investigation further tried to compare phenol concentrations with the sediment environmental quality standards.

At present, almost all countries have set clear limits for organic pollutant concentration of freshwater lake surface sediment. Related studies mainly focus on typical pollutants, such as PCBs and polycyclic aromatic hydrocarbons (PAHs). However, only a few studies have reported the pollution situation of aromatic amines, phenols, chlorobenzenes, and naphthalenes. An effective comparison to determine the pollution level of these organic pollutants in lake surface sediment is difficult due to the data deficiencies. Therefore, this work referred to the Sediment Management Standards (SMS) issued by the Department of Ecology of Washington State, USA (2013) to evaluate the pollution level of phenols in the surface sediment of the Dianchi Lake, and thereby provided reference for the subsequent treatment and protection of the water quality for the Dianchi Lake (Table A.4) (Department of Ecology of Washington State, 2013). According to the SMS, the concentration of phenol in the surface sediment of the Dianchi Lake exceeded the Sediment Cleanup Objectives (SCO, which is defined as “no adverse effects” level) of freshwater sediment in the sampling points Nos. 2 and 19 but did not reach the Cleanup Screening Levels (CSL, which indicates the maximum allowed concentration of any pollutant and the level of biological effects permissible) of freshwater sediment; the average concentration of phenol was below the CSL. Although the precise concentration of 4-methylphenol in Dianchi Lake sediment was unknown, it did not satisfy the freshwater sediment CSL (the measured concentrations of 3- or 4-methylphenol: 7.01–1.42 × 10^3 ng/g, the CSL of 4-methylphenol 2.00 × 10^3 ng/g). No guidelines on the concentrations of 2-methylphenol and 2,4-dimethylphenol are available in the freshwater sediment of the SMS. The concentrations of 2-methylphenol and 2,4-dimethylphenol were below the SCO according to the marine sediment standards in the SMS. The comparative results of the concentration of the SMS revealed that the concentrations of most types of phenols in the Dianchi Lake surface sediment were under the SCO, and the pollution level of phenols remained within the controllable range.

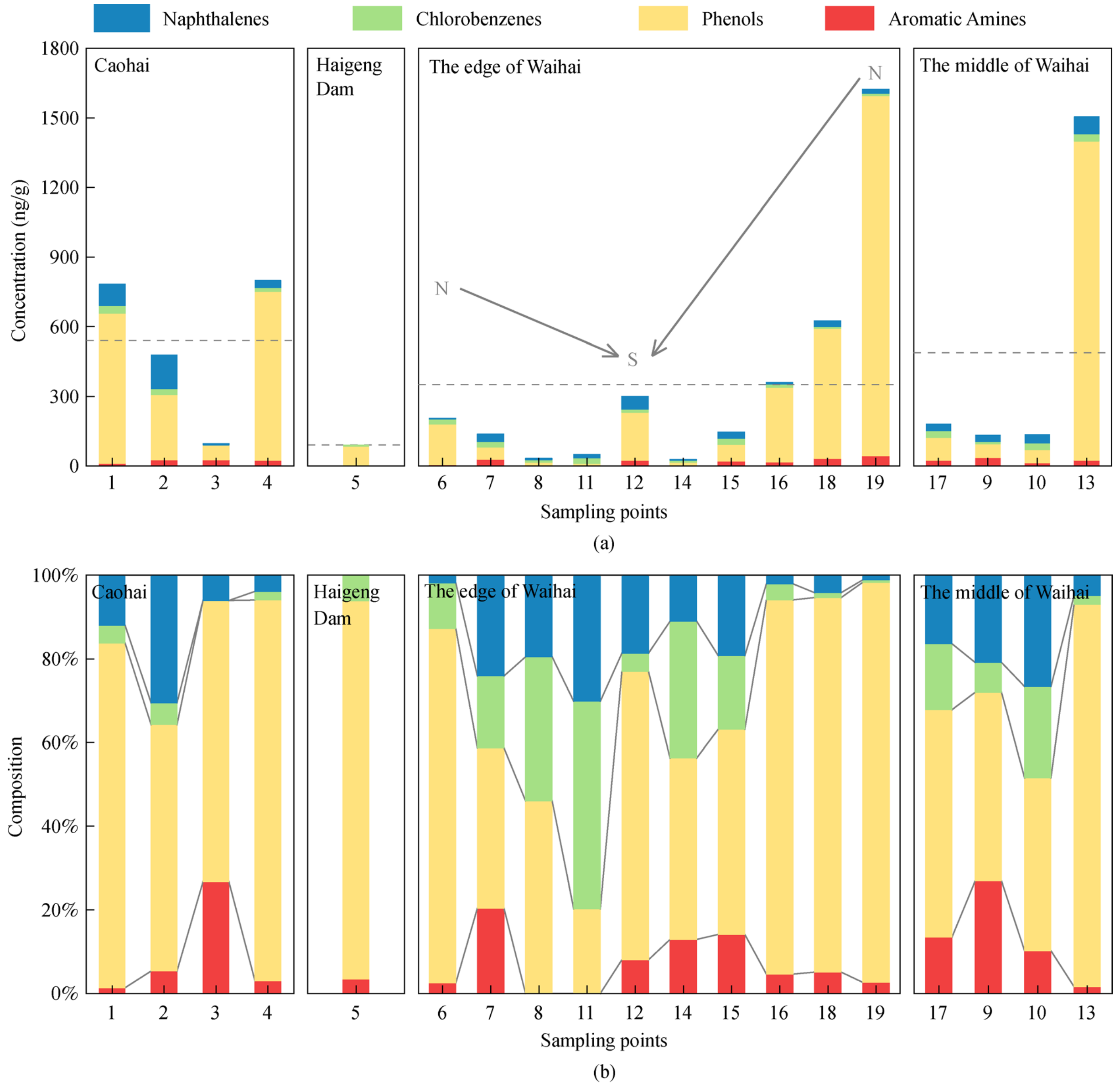
3.2 Spatial characteristics of organic pollutants

For all sampling points, the detection ratios of aromatic amines, phenols, chlorobenzenes, and naphthalenes were 89.5%, 100%, 94.7%, and 94.7%, respectively. At least one organic pollutant was detected in each sampling point. The organic pollutants with the highest detection ratio were 3- or 4-methylphenol (100%), 1,4-dichlorobenzene (94.7%), and phenol (89.5%) (Table A.1).

The detection ratio of phenylamine (100%) in Caohai was much higher than that in Waihai (57.1%), whereas the detection ratio of 4-aminobiphenyl (0.00%) in Caohai was relatively lower than that in Waihai (64.3%) and especially lower than that in the middle of Waihai (the middle of Waihai with sampling points Nos. 17, 9, 10, and 13, the detection ratio of which was 100%) and in the near middle area (the near middle area with sampling points Nos. 12, 18, and 19; the detection ratio of which was 100%).

The highest concentration of the total organic pollutants was detected in surface sediment sampling point No. 19 (1.62×10^3 ng/g), and the lowest was detected in sampling point No. 14 (27.4 ng/g). The average total organic pollutant concentrations in the different regions of the Dianchi Lake decreased in the following order: Caohai (540 ng/g)>the middle of Waihai (488 ng/g)>the edge of Waihai (351 ng/g)>Haigeng Dam (90.4 ng/g) (Fig. 1(a)). In the middle of Waihai, the total organic pollutant concentrations were higher than those near the lakeshore, and the total organic pollutant concentrations of the samples collected near the south and north lakeshore were higher than those near the east and west lakeshore.

These phenomena were consistent with the spatial distribution of lake current velocity, indicating that the hydraulic characteristics were important factors that affected the distribution of organic pollutants. The velocity



(a)

(b)

Fig. 1 Concentration (a) and composition (b) of organic pollutants in the surface sediment of the Dianchi Lake (sampled in December 2016). N, north; S, south. Dashed lines mean average total organic pollutant concentrations in the different regions.

of the lake current was relatively fast at the east and west lakeshore of Waihai, whereas the hydrodynamic condition in the south lakeshore of Waihai was weak, and the current velocity of the north lakeshore of Waihai was slow (Ma et al., 2013). The lake current velocity was small when close to the Haigeng Dam; driven by the wind, a large counterclockwise circulation forms at the east lakeshore of Waihai (Ma et al., 2013). The organic pollutants in the lake water moving with the lake current began to settle in the sediment in the south and north lakeshore of Waihai where the current velocity was slow, especially in the north lakeshore, because of the slow current velocity. The organic pollutant concentration was low when the velocity was fast, and vice versa.

The total organic pollutant concentration in the surface sediment of the edge of Waihai was relatively high at sampling points Nos. 6, 7, 15, 16, 18, and 19. These findings were evident at sampling points Nos. 14, 15, 16, 18, and 19 (from the south to the north) where the concentration increased from 27.4 ng/g to 1.62×10^3 ng/g. The fluctuation of concentration was mainly caused by varied phenol concentrations. The concentration of phenols, accounted for the largest percentage, because of their own characteristics, such as solubility and potential migration in water (Fig. 1(b)). If the lake current slowed down, the phenols carried by the lake current would easily attach to the surface sediment, thereby increasing the concentration of organic pollutants.

Kriging interpolation is a good linear unbiased estimator or predictor and a commonly used spatial interpolation algorithm that has been widely applied in geoscience, environmental science, and atmospheric science (Cressie, 1990). Thus, the Kriging interpolation method was used to predict the organic pollutant distribution pattern in the surface sediment of the Dianchi Lake. The distribution of various organic pollutants in the surface sediment of the Dianchi Lake was different (Figs. 2(a)–2(e)). The concentrations of all the four classes of organic pollutants in Caohai were the highest among the entire lake (Figs. 2(a)–2(e)), and the concentrations of several classes of organic pollutants were high in the northern part of Caohai (Figs. 2(a) and 2(c)–2(e)). The concentrations of the total organic pollutants, aromatic amines, and phenols were substantially increased in the north lakeshore of Waihai, especially at sampling point No. 19 (Figs. 2(a)–2(c)). Sampling point No. 19 was adjacent to the inlet of two rivers, and the organic pollutants may have been brought in by the input water.

Simultaneously, a high concentration of each class of organic pollutants was found in the southern part of Waihai (Figs. 2(a)–2(e)). The total organic pollutants and phenols had similar distribution. Phenols had the highest concentration among all the classes of organic pollutants; thus, they largely determined the distribution of the total organic pollutants. The concentration distribution of aromatic amines and naphthalenes in the southern section of Waihai was largely consistent mainly because phenylamine, with the highest proportion of aromatic amine concentration, had a significant correlation with every type of naphthalene ($p < 0.01$) (Fig. 2(f)).

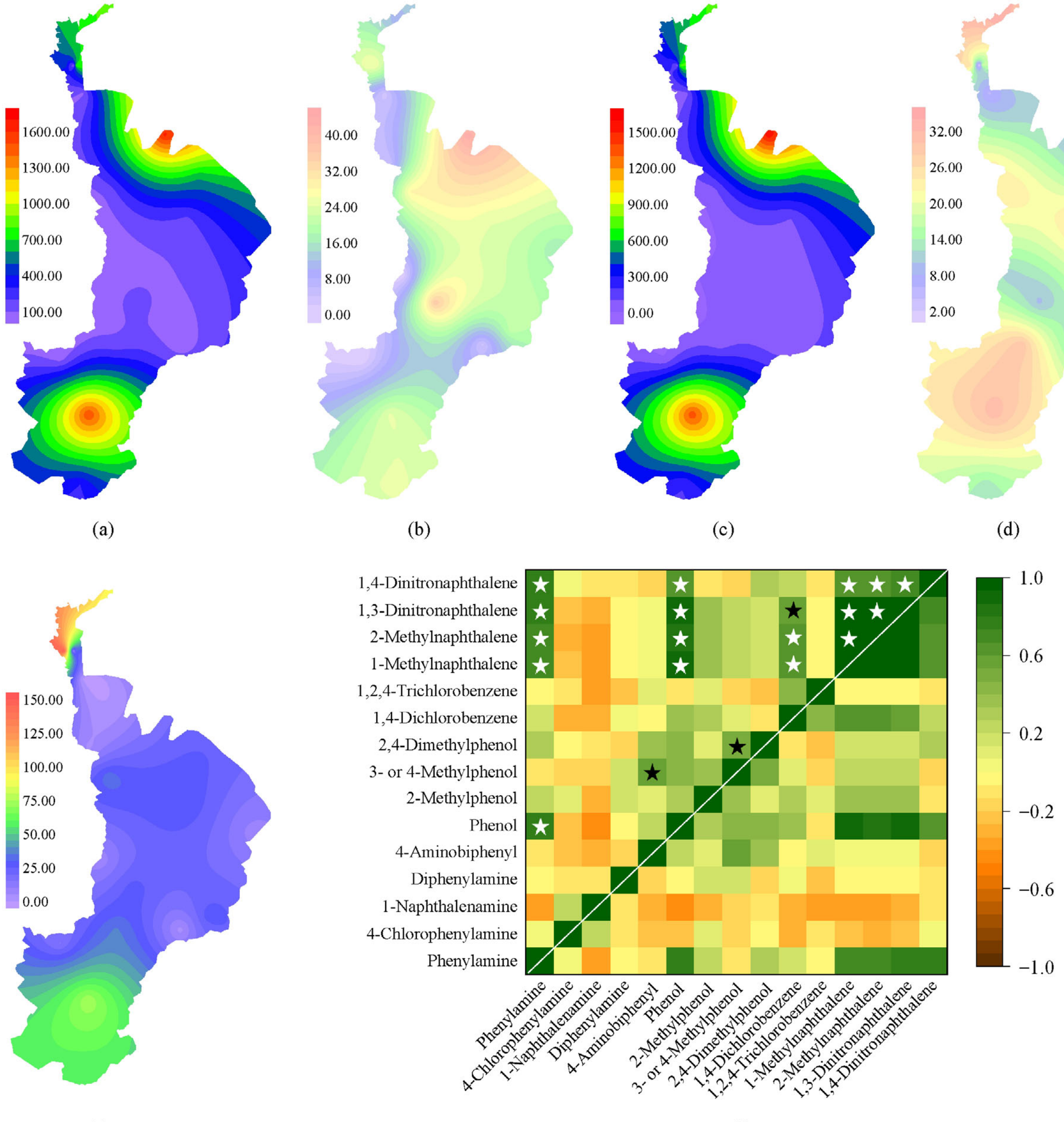
In summary, the concentrations of organic pollutants in Caohai, the north lakeshore of Waihai, and the southern part of Waihai were higher than those in the other areas of Dianchi. It was reported that the PAH concentration in the north lakeshore of Caohai (sampling year: 2012) was the highest in the entire lake (Zhao et al., 2014). The results were in accord with the author’s previous research which took samples in the year of 2016 (Hu et al., 2019). In the research of Wan et al. (2011), PCB pollution was serious in the water of the southern section of Waihai (sampling year: 2008). In this work, the area with a high concentration of pollutants in the surface sediment of the Dianchi Lake was similar to previous research results. The follow-up water quality control project of the Dianchi Lake should focus on these areas for treatment.

3.3 Spatial distribution of each kind of organic pollutant

The distribution of each type of aromatic amine varied greatly (Fig. 3). Among the five types of aromatic amines detected, phenylamine is the most soluble in water ($\lg K_{\mathrm{OW}} = 0.940$); moreover, it was easier to migrate with the lake current compared with other organic pollutants. However, the organic pollutants with poor water solubility tended to accumulate in the surface sediment, and their distribution was determined by the surface sediment. The water could spread in a wider range compared with sediment; thus, the detection ratio of phenylamine in the Dianchi Lake was higher than that of other aromatic amines.

The detection ratios of 4-chlorophenylamine, 1-naphthylamine, and diphenylamine were low (16.0% for all), of which most were found in areas where no phenylamine was detected. For example, phenylamine was not detected at the points where 1-naphthalenamine presented (sampling points Nos. 5, 14, and 16). Diphenylamine, 4-chlorophenylamine, and 1-naphthylamine mainly appeared near the river entrance along the lakeshore of the Dianchi Lake, indicating that they presumably came from the rivers entering the lake. These organic pollutants (4-chlorophenylamine, 1-naphthylamine, and diphenylamine) were difficult to dissolve in water and tended to accumulate in sediment. Thus, the spread ranges of these pollutants were small, and the detection points were few.

Among aromatic amines, 4-aminobiphenyl is one of the substances which was the most difficult to dissolve in water ($\lg K_{\mathrm{OW}} = 2.83$). The distribution of 4-aminobiphenyl was relatively similar to that of phenylamine, especially at sampling points Nos. 12, 18, 19, 17, 9 and 10, where aromatic amines were composed of phenylamine and 4-aminobiphenyl. The sampling points were distributed in the core area of Waihai from north to south.



(a) (b) (c) (d)

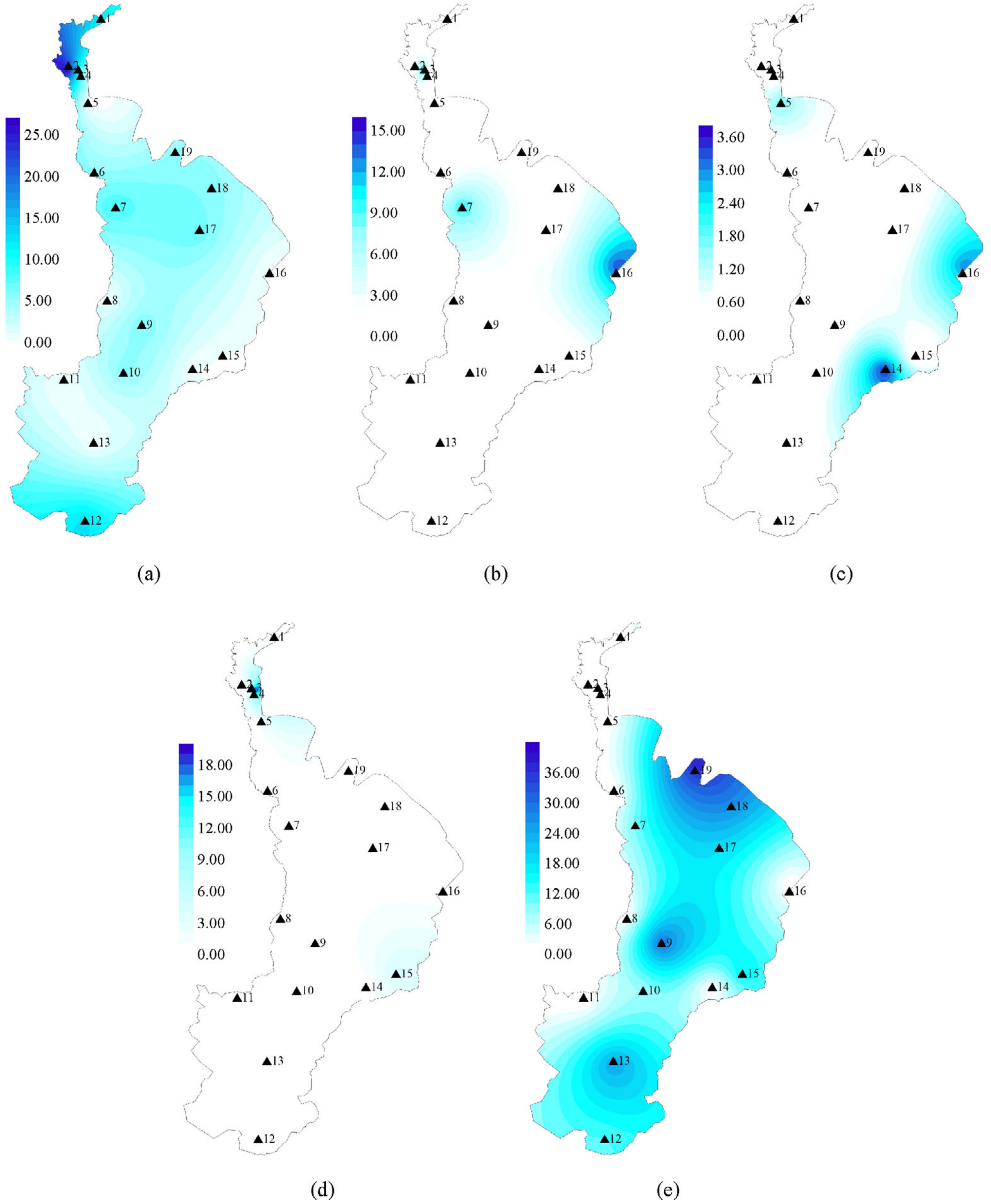
(e) (f)

Fig. 2 Concentration distribution of organic pollutants (the total four classes of organic pollutants (a), aromatic amines (b), phenols (c), chlorobenzenes (d) and naphthalenes (e)) and Pearson analysis (f) in the surface sediment of the Dianchi Lake. The concentration unit in this figure is ng/g. In subfigure (f), ☆ stands for the 0.01 level (double-tailed), showing that the correlation is significant; ★ stands for the 0.05 level (double-tailed), showing that the correlation is significant.

Wilcoxon rank sum test was conducted between the paired samples of the ratios that obtained by concentrations of phenylamine or 4-aminobiphenyl divided by the average value of the corresponding substrate concentrations among the above 6 sampling points, and the result significance was 0.893, indicating that there were no significant differences between the two population distributions of the paired samples. Phenylamine and 4-aminobiphenyl might come from the same pollution source.

The high concentration of phenols was mainly distributed in the following three regions of Danchi Lake: Caohai (Figs. 4(a) and 4(b)), the southern section of Waihai (Figs. 4(a)–(c)), and the north lakeshore of Waihai or near sampling point No. 19 (Figs. 4(a)–4(d)). Phenols were similar in biodegradability (phenylamine: 0.598; 4-chlorophenylamine: 0.271; 1-naphthalenamine: 0.446; diphenylamine: 0.689; 4-aminobiphenyl: 0.561; the probability of rapid biodegradation was obtained from ChemSpider), and lg K_{OW} of phenol (1.46) was the smallest among all types of phenols, thereby resulting in its high detection ratio (89.5%) (Lu et al., 2013).

The 1,4-dichlorobenzene and 1,2,4-trichlorobenzene are



(a) (b) (c)

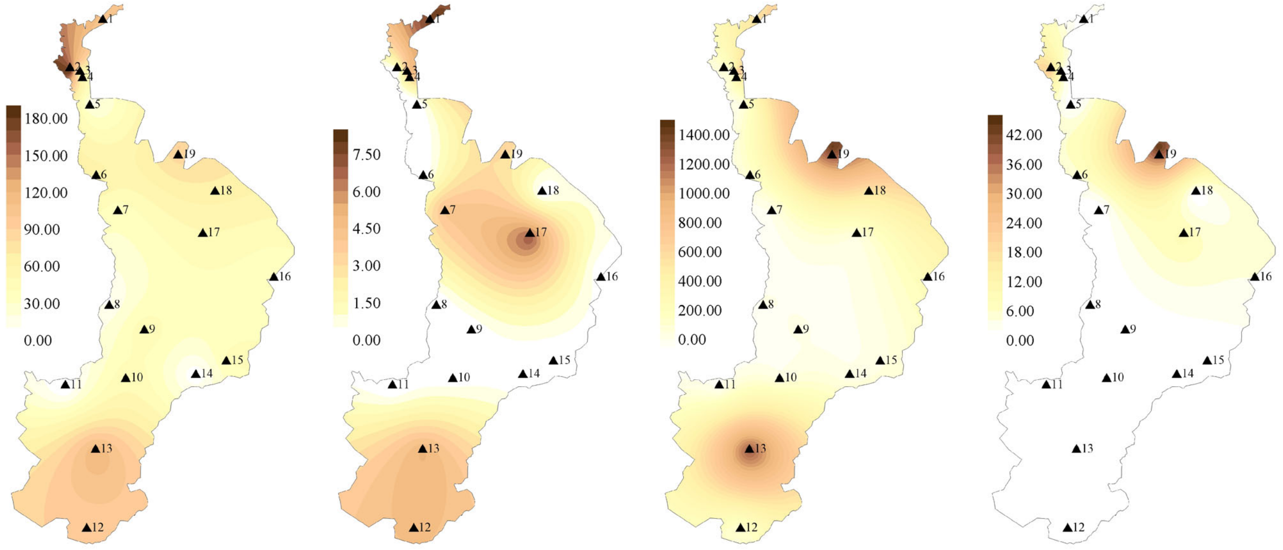
(d) (e)

Fig. 3 Concentration and distribution of aromatic amines (Phenylamine (a), 4-Chlorophenylamine (b), 1-Naphthalenamine (c), Diphenylamine (d) and 4-Aminobiphenyl (e)) in the surface sediment of the Dianchi Lake (ng/g). The triangular symbols mean sampling points.

insoluble in water but widely distributed in the surface sediment (Figs. 5(a) and 5(b)). The concentration of 1,4-dichlorobenzene was stratified from north-east to south-west in Waihai of the Dianchi Lake without a consistent increasing or decreasing trend. The concentration of 1,4-dichlorobenzene was high in Caohai and the south of Waihai. The concentration of 1,2,4-trichlorobenzene decreased gradually from the west to the east in Waihai. The distribution trend and high concentration area of chlorobenzenes were different from the other classes.

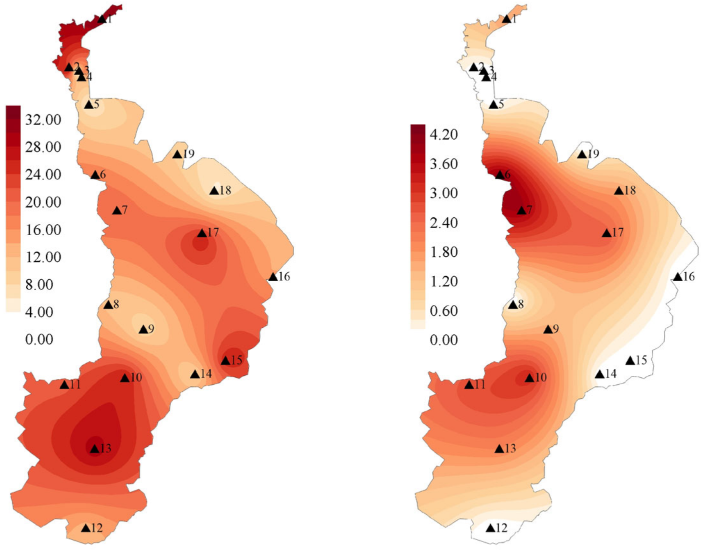
The concentration of 1,2,4-trichloronaphthalene decreased as 1,4-dichloronaphthalene increased, and the trend was particularly evident in sampling points Nos. 5-19-18-16, Nos. 6-7-17-16-15, and Nos. 8-9-14. The three groups of sampling points belonged to the different concentration levels of 1,4-dichlorobenzene (Fig. 6). The results indicated that 1,4-dichlorobenzene might be related to the anaerobic dechlorination of 1,2,4-trichlorobenzene (Wu et al., 2002).

Except for 1,4-dinitronaphthalene, the detection ratios of naphthalenes were extremely high (at 80.0%, but 1,4-dinitronaphthalene was excluded) with similar concentra-



(a) (b) (c) (d)

Fig. 4 Concentration and distribution of phenols (Phenol (a), 2-Methylphenol (b), 3- or 4-Methylphenol (c) and 2,4-Dimethylphenol (d)) in the surface sediment of the Dianchi Lake (ng/g). The triangular symbols mean sampling points.



(a) (b)

Fig. 5 Concentration distribution of chlorobenzenes (1,4-Dichlorobenzene (a) and 1,2,4-Trichlorobenzene (b)) in the surface sediment of the Dianchi Lake (ng/g). The triangular symbols mean sampling points.

tion distribution trends (Figs. 7(a)–7(c)). The high concentration mainly occurred in two regions of the Dianchi Lake, namely, Caohai (Figs. 7(a)–7(d)) and the southern section of Waihai (Figs. 7(a)–7(c)). Pearson analysis showed a strong correlation among 1-methylnaphthalene, 2-methylnaphthalene, 1,3-dinitronaphthalene, and 1,4-dinitronaphthalene ($p < 0.01$) (Fig. 2(f)). Hence, the four types of naphthalene might be homologous or have mutual transformation relation. Further, the more detailed generation, emission and transformation mechanisms of the mentioned four types of naphthalene should be investigated deeply for the future control of naphthalenes class.

In summary, the distribution of organic pollutants in

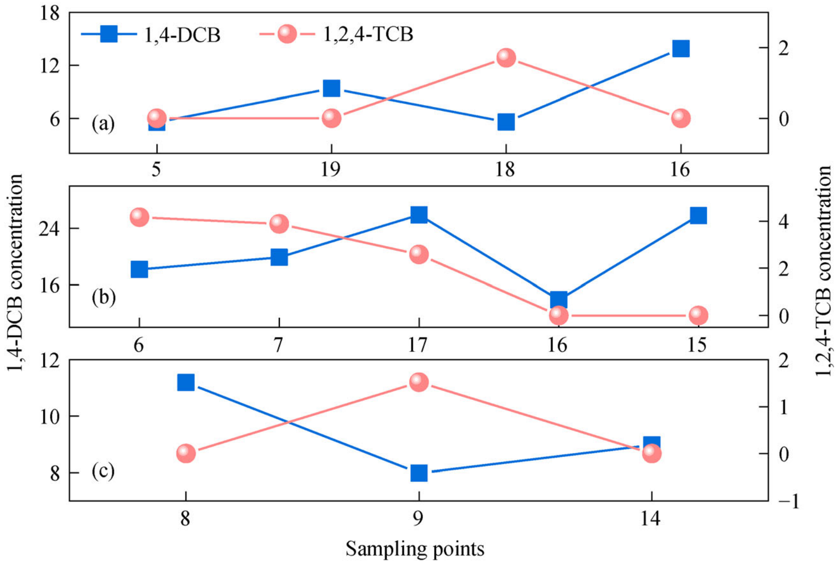
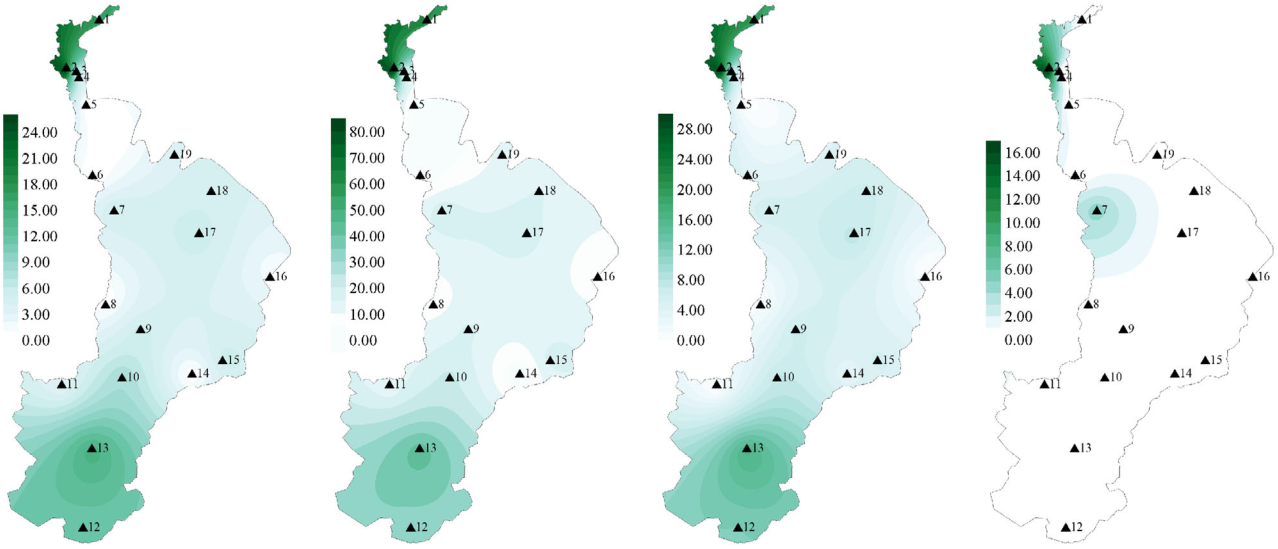


Fig. 6 Variation trend of chlorobenzenes in the surface sediment of the Dianchi Lake (ng/g).



(a) (b) (c) (d)

Fig. 7 Concentration and distribution of naphthalenes (1-Methylnaphthalene (a), 2-Methylnaphthalene (b), 1,3-Dinitronaphthalene (c) and 1,4-Dinitronaphthalene (d)) in the surface sediment of the Dianchi Lake (ng/g). The triangular symbols mean sampling points.

sediment was extremely complicated, which was affected by several factors. Except for the emission source strength, the chemical properties and reactions of organic pollutants, such as the K_{ow}, biodegradability and anaerobic dichlorination process, would have great impacts on pollutants distribution in sediment (Lu et al., 2013). Besides, the external environment factors, such as flow velocity and hydraulic retention time, might also affect the distribution of organic pollutants in sediment (Ma et al., 2013).

3.4 Priority pollutants and potential source analysis

A comprehensive scoring method was used to determine the primary pollutants in the surface sediment of the Dianchi Lake. Three principles were carefully chosen in this work to screen the priority pollutants: 1) high emission, which meant it would be detected frequently; 2) carcinogenic, teratogenic and mutagenic effect and genetic toxicity, which had great harm on human health and ecosystems; and 3) high stability and bioaccumulation, thus, it could exist widely in environment. Five subindices (concentration score (S_C), detection ratio score (S_D), diffusivity score (S_T), biodegradability score (S_B), toxicity score (S_P)) and one overall index (total pollution score (T_S)) were used to calculate and obtain the primary pollutants (the calculating methods were detailed in Section A.1). Five types of organic pollutants were selected as priority pollutants, and the risk order was as follows: 1,4-dichlorobenzene (3.43)>3- or 4-methylphenol (3.38)>1,2,4-trichlorobenzene (3.16)>1,3-dinitronaphthalene (3.15)>2-methylnaphthalene (3.05) (Table A.5). These organic pollutants mostly scored high on S_D and S_P, indicating that the environmental risk of the above-mentioned pollutants was mainly due to the high emission and toxicity. Generally, chlorobenzenes are mainly used in the production of pesticides, dyes, medicine, plastics and daily chemical products, and also can be used as termite control reagents, grease removal solvents, lubricating oil additives, functional additives of special engineering plastics, etc. The 3- or 4-methylphenol are from many industrial manufacturing processes such as coal gas, coking, oil refining, metallurgy, machinery manufacturing, glass, petrochemical, wood fiber, plastics, medicines, and pesticides. However, Kunming has complicated industrial layout, further investigation should be undertaken to focus on the main pollutants sources, which will be more helpful for local government to make pollutants control strategy.

Principal component analysis (PCA) was used to analyze the potential sources of organic pollutants in the surface sediment of the Dianchi Lake. The overlapping area between clusters indicated that the sampling points had similar sources (Wang et al., 2018). The PCA results of organic pollutant concentration in each sampling point of the Dianchi Lake surface sediment are shown in Fig. 8. Principal component 1 and principal component 2 accounted for 63.1% and 23.5% of the total variance, respectively, and summed up to 86.6% of the total variance.

The majority of the surface sediment sampling points in the Dianchi Lake were arcuate in the first and fourth quadrants, indicating that most surface sediment sampling points in the Dianchi Lake had similar organic pollutant sources. The offshore sampling points were concentrated along the arc, whereas some sampling points close to the lakeshore, such as sampling points Nos. 11, 14, 8, and 3, were scattered. Sampling point No. 11 was the most different from the other sampling points. The main reason was speculated that sampling point No. 11 was the only one close to the outlet of the Dianchi Lake, and the hydraulic condition was special. Therefore, the composition of pollutants was different from that of other sampling points. In addition, sampling points Nos. 3, 8 and 14 were also quite different. Sampling points Nos. 8 and 14 were located on the shore, which were greatly affected by human activities. Sampling point No. 3 was located in Caohai, with a long history and complicated causes of pollution. In general, the sampling points approaching the center of the lake were almost all clustered together, presumably due to the slow velocity and relatively uniform mixing of pollutants.

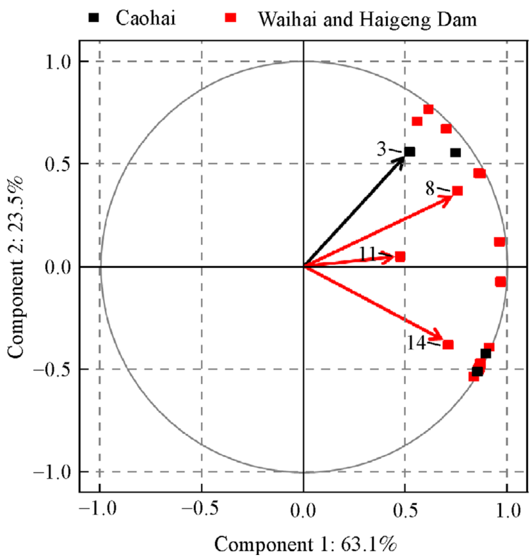


Fig. 8 PCA of organic pollutants in the surface sediment of the Dianchi Lake.

4 Conclusions

Nineteen surface sediment samples were collected from the Dianchi Lake in December 2016, and 40 types of aromatic amines, phenols, chlorobenzenes, and naphthalenes were analyzed via GC-MS. The main conclusions are as follows:

1) The total concentration of the four classes (aromatic amines, phenols, chlorobenzenes, and naphthalenes) of organic pollutants in the surface sediment of the Dianchi Lake varied from 27.4 ng/g to 1.62×10^3 ng/g. The concentrations of phenols were much higher than those in other water bodies but still within a controllable range. The detection ratio of 3- or 4-methylphenol was the highest (100.00%) among the pollutants.

2) The average total organic pollutant concentrations in the Dianchi Lake were listed by decreasing order, as follows: Caohai (540 ng/g)>the middle of Waihai (488 ng/g)>the edge of Waihai (351 ng/g)>Haigeng Dam (90.4 ng/g). Pearson analysis showed a strong correlation among 1-methylnaphthalene, 2-methylnaphthalene, 1,3-dinitronaphthalene, and 1,4-dinitronaphthalene ($p < 0.01$). Hydraulic characteristics may affect the distribution of organic pollutants.

3) Caohai, the north lakeshore of Waihai and the south of Waihai showed higher risk because of high concentration. The priority control pollutants should be 1,4-dichlorobenzene, 3- or 4-methylphenol and 1,2,4-trichlorobenzene.

PCA results suggested that most surface sediment sampling points in the Dianchi Lake were contributed by similar organic pollutant sources.

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