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Human Activities Aggravate VOC Pollution in the Huangshui River of the Tibetan Plateau

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Abstract: Many xenobiotic compounds can threaten human health and natural ecosystems. The ability to predict the level of human activities and identify major impact factors is crucial for the design of pollutant risk-reduction plans. In this study, a total of 25 volatile organic compounds (VOCs) including eight alkenes, six alkanes, and eleven aromatics were identified at 11 monitoring locations along the Huangshui River of the Tibetan Plateau. GC-MS analysis was applied to detect the concentrations of the VOCs. The results showed that the alkene, alkane, and aromatic concentrations in the sediment were significantly higher than in the water in all seasons ($p < 0.001$). The VOC concentrations in summer were significantly higher than in spring and winter ($p < 0.01$). In addition, several VOCs were found to surpass the national standard, i.e., bromoform reached 312.43 μg/L in water during the summer (the national standard is 100 μg/L), carbon tetrachloride was 209.58 μg/L (the national standard is 2 μg/L), and vinyl chloride was 10.99 μg/L (the national standard is 5 μg/L), which were all related to human activities. Principal component analysis (PCA) was used to comprehensively evaluate the water quality and the VOCs. The total organic carbon (TOC) was found to be responsible for the presence of the VOCs in the river, accounting for 77.93%, 81.97%, and 82.13% of the total variance in the datasets in spring, summer, and winter, respectively.

Keywords: volatile organic compounds (VOCs); Huangshui River; human activities

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1. Introduction

Many volatile organic compounds (VOCs) can cause an abnormal taste and odor of water and fish [1,2], which lead customers to complain about and question the safety of the water and fish [3]. Except for biogenic sources [4,5], many VOCs in water are emitted by human activities, such as chemical manufacturing, organochlorine pesticides, leakage of petroleum, domestic waste from daily life, etc. [4,5]. These artificial VOCs usually include non-methane hydrocarbons, chlorinated hydrocarbons, oxygenated volatile organic compounds, benzene, toluene, ethylbenzene, and the different xylene isomers [6,7]. Due to their low odorant olfactory thresholds, stable chemical structures, and potential ecological risks, these artificial VOCs have been the subject of intense research.

In the water system, VOCs migrate between the water body and the sediment and become a persistent source of pollution, which not only harms the water quality but also poses serious health risks to humans and aquatic organisms [8]. For example, VOC emissions are often found in eutrophic lakes and are an important contamination factor in water pollution [9]. In rivers, VOCs strongly affect humans and aquatic organisms, such as 1,2-dichloropropane, which is used as a soil fumigant and industrial solvent, the most frequently detected type [7]. Methylene chloride, another VOC, also contaminates drinking water systems by pyrolysis and smoke intrusion from depressurization, which may be generated from the dehalogenation of disinfection byproducts stagnating in galvanized iron pipes [10].

To summarize, these artificial VOCs, as industrial byproducts, have been detected in ponds, lakes, reservoirs, rivers, and oceans, which further harm drinking water, aquatic products, and ecosystems. Therefore, artificial VOC pollution in water is inseparable from the intensity of human activities. As human activities began to thrive on the Qinghai Tibetan Plateau, this VOC pollution should have attracted attention. However, the artificial VOC pollution on the Tibetan Plateau has rarely been studied, and the details of the artificial VOC concentrations and sources are scarce, even though such findings are critical for pollution control and legislation. As we know, the Tibetan Plateau has important water systems [11]. The Huangshui River is situated in the climatically vulnerable semiarid zone of the northeastern Tibetan Plateau in Xining city, the provincial capital of Qinghai. As a major tributary of the Yellow River's upper reach, the Huangshui River flows through Xining city and has been severely polluted in the past due to rapid socioeconomic development and the discharge of domestic sewage. Thus, the Huangshui River is a typical river in which to study the artificial VOC pollution caused by human activities on the Tibetan Plateau. The goals of this study were to determine: (1) the main species of artificial VOCs in the river on the Tibetan Plateau, (2) the spatial and temporal fluctuations of the VOCs throughout the seasons, and (3) the major environmental factors affecting the artificial VOCs in the river on the Tibetan Plateau.

2. Materials and Methods

2.1. Sampling Sites

The Huangshui River flows through Xining city. Its source is the Baohutu Mountain in Haiyan County, Qinghai Province, and the entire basin spans an area of 17,733 km^2 between the longitudes 100°42′ to 103°01′ and latitudes 36°02′ to 37°28′. From upstream to downstream along the river, paired water and sediment samples were collected during the spring (April), summer (August), and winter (November) of 2020 at 11 monitoring locations (L1 to L11, Figure 1), and the information about the sampling sites is provided in Table S1 (Supplementary Materials).

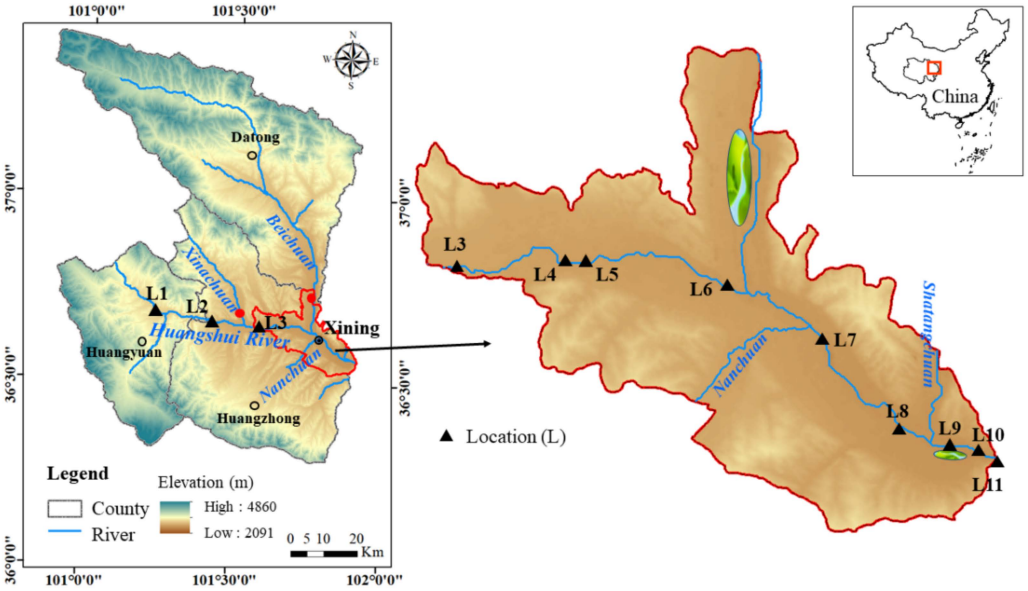

Figure 1. Map of sampling locations.

2.2. Sample Processing

The water samples were collected by hydrophore (1 L) from the middle of the river and slowly poured into brown 40-mL purge and trap bottles that were pre-treated with four drops of 6 mol/L hydrochloric acid. Sediment samples were obtained by a UWITEC sediment corer from the bottom of the river and accurately weighed to 10.00 milligrams using the same type of bottles. All samples were transferred from the purge and trap

autosampler (CDS-7000E, CDS Analytical LLC, Oxford, PA, USA) to the instrument for GC-MS analysis (GC-MS-QP2020, Shimadzu, Japan). The purge and trap technique and GC-MS detected method were used following Cheng [12]. Twenty-five VOCs were separated on the column (60 m × 0.25 mm × 1 μm, InertCap AQUATIC, Japan) and detected using electron ionization and selected ion monitor modes (SIM). Standard and duplicate samples were used to check the accuracy of the analysis. The concentrations of total organic carbon (TOC), NH_4^+-N, NO_3^--N, NO_2^--N, and total phosphorus (TP) were common hydrochemical parameters [13], determined according to our previous studies [14].

2.3. Statistical Analysis

In order to evaluate the VOC levels in different sources and identify their distribution, the water quality datasets were further analyzed with different multivariate statistical techniques to explore their spatial trends and source apportionments. This study used one-way ANOVA for VOC analysis with SPSS version 25.0. The statistical significance level (alpha level) was set at 0.05. PCA (Principal Component Analysis) was carried out with CANOCO (version 5).

3. Results and Discussion

3.1. Comparisons of VOCs

The 25 volatile organic compounds (VOCs) were classified into three groups: eight alkenes, six alkanes, and eleven aromatics. The comparison of the VOC concentrations in the water and sediment samples is shown in Table 1. The average concentrations of alkenes in the sediment were 2.45, 648.50, and 23.96 μg/g in the spring, summer, and winter, respectively, which were all higher than the paired water samples ($p < 0.001$). The average concentrations of alkanes in the sediment were 31.23, 13,052.27, and 28.37 μg/g, which were all higher than the corresponding water samples ($p < 0.001$). The aromatic contents in the sediment were 7.54, 1372.73, and 60.47 μg/g, respectively, which were 5.8, 15.4, and 11.3 times higher than the corresponding water samples. Liu's research showed that higher concentrations of VOCs were detected in the surface water than in the sediment, because pollutants with relatively higher boiling points and lower solubilities have higher detection frequencies in sediment [15]. However, in our study, the ratio of the concentrations of the total VOCs (TVOCs) in the sediment and in the water was greater than 7.7, 50.7, 10.2 in spring, summer, and winter, respectively. Large amounts of VOCs were deposited in the sediment and continuously released into the water as the temperature rose. Asma suggested that the flux changes of VOCs under dynamic temperatures could be increased by the volatilization–dissolution interactions of VOCs with water and affect soil VOC emissions [16], which was coincident with our results. The Tibetan Plateau has the lowest summer temperature in China, a cooler summer ushers in a large increase in tourism and industrial production, leading to a significant increase in VOCs' release. We hypothesize that human activities aggravate VOC pollution in the Huangshui River during the summer, and the VOCs could be deposited in the sediment and not easily volatilized because of the distinctive geography and lower temperatures of the Tibetan Plateau.

Table 1. Comparison of VOC concentrations (μg/L or μg/g) in the Huangshui River.

Seasons	Samples	Alkenes	Nonparametric Tests	Alkanes	Nonparametric Tests	Aromatics	Nonparametric Tests
spring	water	1.01 ± 0.11	$p < 0.001$	3.19 ± 0.24	$p < 0.001$	1.31 ± 0.02	$p < 0.001$
	sediment	2.45 ± 0.15		31.23 ± 1.30		7.54 ± 0.31	
summer	water	62.66 ± 4.66	$p < 0.001$	145.57 ± 9.47	$p < 0.001$	89.22 ± 4.30	$p < 0.001$
	sediment	648.50 ± 42.34		13,052.27 ± 66.69		1372.73 ± 52.24	
winter	water	3.67 ± 0.20	$p < 0.001$	2.05 ± 0.22	$p < 0.001$	5.36 ± 0.14	$p < 0.001$
	sediment	23.96 ± 4.01		28.37 ± 2.78		60.46 ± 3.48	

There is no national standard for VOC detection in sediment; the high concentration of VOCs in the sediment combined with our previous research on antibiotic contamination in the Huangshui River suggest that this area is a typical urban river on the Tibetan Plateau and requires long-term monitoring [14]. We worry that excessive levels of VOC deposition could threaten aquatic organisms and have lasting ecological implications due to the health risks of VOCs and other contaminants.

3.2. Influence of Seasons on the VOCs in Different Samples

In addition, comparisons of the VOC concentrations in different seasons are shown in Figure 2. In summer, the average alkene concentrations in water and sediment were 57.54 μg/L and 720.97 μg/g, respectively, which were higher than those in spring (1.038 μg/L, 2.87 μg/g) and winter (4.24 μg/L, 25.67 μg/g) (Figure 2A,D) ($p < 0.01$). The results of the alkanes were similar: the average concentration in the water samples was 141.58 μg/L in summer, which was much higher than in spring (3.56 μg/L) and winter (1.73 μg/L); the average sediment concentration was 13,588.21 μg/g (summer), which was higher than in spring (32.08 μg/g) and winter (35.77 μg/g) (Figure 2B,E) ($p < 0.01$). The average aromatic content in water samples was higher in summer (93.67 μg/L) than in spring (1.38 μg/L) and winter (5.63 μg/L); the average sediment concentration was similarly higher in the summer (1418.15 μg/g) than in spring (7.63 μg/g) and winter (62.53 μg/g) (Figure 2C,F) ($p < 0.01$). It is known that ambient temperature often influences VOCs, and the VOC chemical reactivity increases as the ambient temperature increases [17]. In our study, the average water temperature was 6.7, 10.7, and 4.61 °C in spring, summer and winter, respectively, which verified that the temperature obviously affected the VOCs. VOCs are a type of odor compound produced mostly by aquatic organisms such as algae and bacteria in water bodies [18]. Microorganisms excrete a versatile array of metabolites with different physico-chemical properties and biological activities during the stable period of growth [19]. The high temperature in summer can increase algal and microbial metabolism and affect the evaporation rate, resulting in the highest concentrations of VOCs. In order to illustrate the possible human factor in the largest concentrations of VOCs discovered during the summer, we identified that Xining, located on the edge of the Tibetan Plateau, is a popular destination for summer travel; the tourist numbers reach their peak in summer, which leads to a boom in many businesses [20]. For example, Xining had a population of 2.476 million in 2021 and received a total of 240.39 million tourists during the same year. The significant increase in human activities has introduced a tremendous burden to the ecological environment of the Huangshui River [21]. In 2022, agriculture and animal husbandry were also found to be contaminating the Huangshui River [22]. As a result, we consider that the long-term monitoring of VOCs in water bodies and sediments in the Xining sector of the Huangshui River is critical.

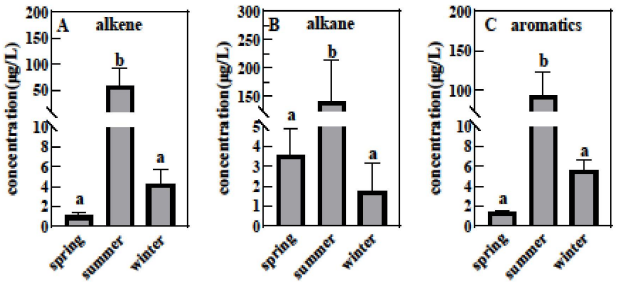

Figure 2. *Cont.*

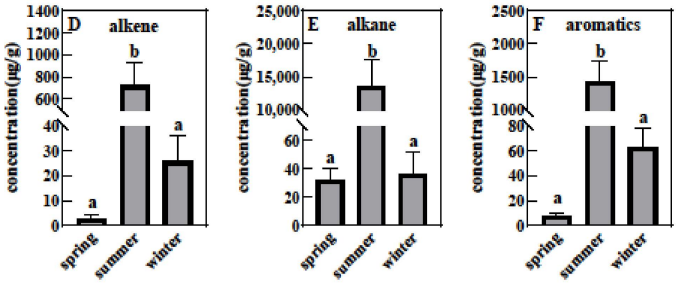

Figure 2. The comparisons of the VOCs in the water samples (**A**–**C**) and sediment samples (**D**–**F**) in different seasons.

3.3. Analysis of the Main VOCs in Different Seasons

The results of the top 10 species of VOCs in different seasons are shown in Figure 3. We found that chloroform had the highest concentrations in sediment in spring (180.06 μg/g) and summer (128,311.97 μg/g), respectively (Figure 3B). Chloroform as a kind of organic chlorine is generally harmful to human health [23,24]; it is widely used in the manufacture of refrigerants, pharmaceuticals, and household cleaning products, and is also formed as a byproduct of chlorination disinfection in drinking water, wastewater, and swimming pools [25]. In our research, we found that the residential areas, factories, and recreational parks close to the sampling sites provided evidence that human activities aggravate chloroform accumulation, as shown in other papers [26–28].

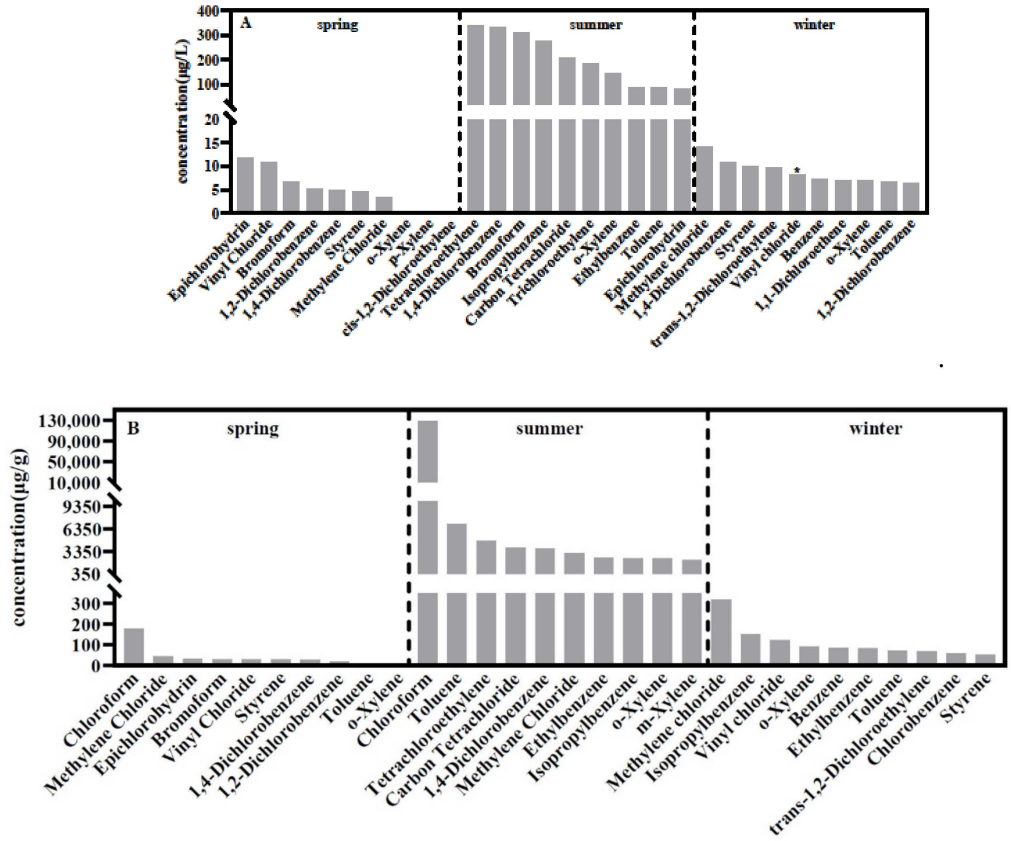

Figure 3. The top 10 species of VOCs in water samples (**A**) and sediment samples (**B**).

Methylene chloride was another main VOC found in the water samples during the spring and winter with the highest concentration of 14.29 μg/L (near the national standard for 20 μg/L). It was also detected in all seasons' sediment samples and had a maximum quantity of 318.27 μg/g (Figure 3). Methylene chloride was classified as a Group 2A carcinogen in a preliminary aggregated reference to the list of carcinogens [29] and is a major

chemical solvent and raw material, likely to originate from industry emissions [30]. We also found that 1,4-dichlorobenzene (1,4-DCB) and o-Xylene were the two VOCs detected in all samples and seasons (Figure 3). The maximum concentration of 1,4-DCB in water reached 330.28 μg/L (the national standard was 300 μg/L), which is a common organic contaminant in water bodies that can bioaccumulate in aquatic species, polluting the environment and food [31,32]. Although the amounts of o-Xylene were all below the national standard (500 μg/L) with maximum average concentrations of 142.08 μg/L, we should still consider the sediment's cumulative harmful effects because it has been related to dizziness, nausea, blurred vision, poor liver function, cellular DNA damage, and embryonic death [33,34]. Other VOCs species were also discovered, such as vinyl chloride (VC) and bromoform (Figure 3). VC was found as a major contaminant in some wells in Japan and can accumulate in the groundwater [35]. The highest concentration of VC in our analysis was 120.65 μg/L, which surpassed the national standard (50 μg/L). Because the carcinogenic potential and human carcinogenic effects of VC have already been proved (WHO, 2004) [36], its retention in the sediment should be monitored over time. Bromoform reached 312.43 μg/L in summer in our study, which surpassed the national standard (100 μg/L). Bromoform comes from the disinfection of water with chlorine, which produces large volumes of VOC byproducts. The widespread use and storage of these chemicals over the last several decades has led to the release of VOCs into the environment, including groundwater sources of drinking water, which are especially vulnerable to the impacts of soluble chemical contamination [37]. It is known that human activities emit the majority of chlorine-containing chemicals and benzenes [38], which tend to accumulate in the environment as shown in this paper. Tables S2–S4 detail the original data of the 25 VOCs in the water and sediment samples during the three seasons.

3.4. Impact of Environmental Factors on VOCs

Table S5 includes the original data of the water quality from the different sampling sites. PCA was used to comprehensively evaluate the environmental factors on the TVOCs. As shown in Figure 4A,C, the TVOCs were related to the TOC in spring and winter. The two axes explained 77.93% and 82.13%, respectively. In the summer, the TOC and NO_2^--N had positive correlations with the TVOCs (Figure 4B), and the two axes explained 81.97%. The TOC is a direct and reliable indicator that has been widely used to characterize organic pollution in water bodies and sediments [38] because of its potential hazards to humans [39], which means the VOCs are related to the river pollution in the Huangshui River. TOC can come from food waste [40] and released oils [41] and metals, such as Cu, Cr, Al, and Ni [42,43], which are related to pollution by humans. In addition, NO_2^--N is often produced by sewage discharge, including vast amounts of agriculture and the breeding of cattle and sheep [44]. We also found that NO_2^--N was detected in urban and industrial wastewater [44,45], providing further evidence of human activities. Nitrogen often promotes excessive growth of cyanobacteria [46,47], and several cyanobacteria species can produce VOCs, which have negative impacts on the atmosphere and human health [48,49]. For example, in Lake Taihu in 2019, bloom aggravated the secretion of VOCs and caused serious odors [50]. This was yet another piece of evidence that plankton in water bodies, such as algae, play a substantial role in the concentrations and species of VOCs, which indicates that nitrogen in the urban rivers on the Tibetan plateau is environmental pollution that should be taken seriously. The TN, TP, NO_3^--N, and NH_4^+-N in our study had no significant correlations with VOCs.

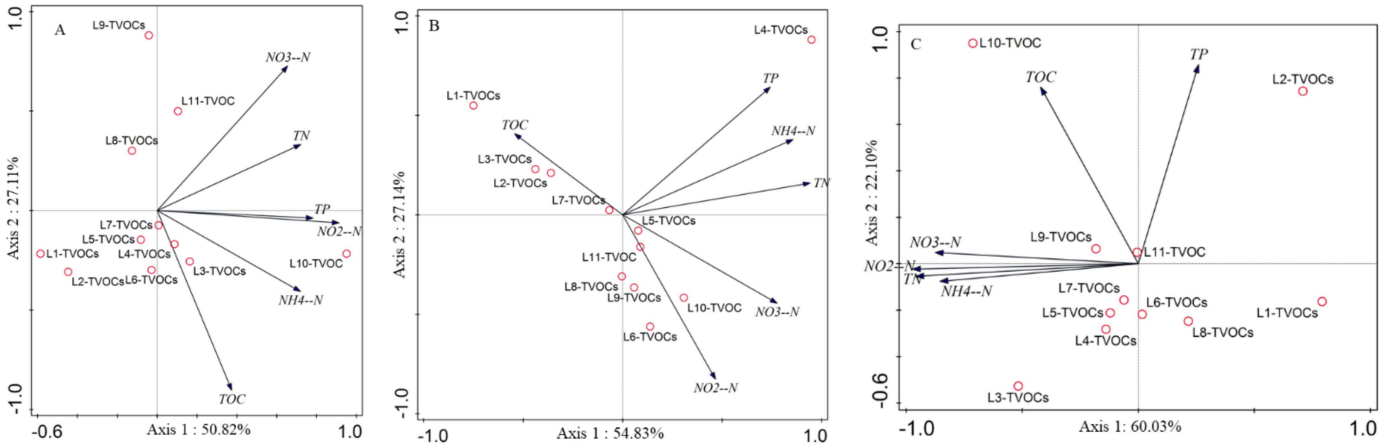

Figure 4. PCA biplot based on the TVOCs and environmental variables of spring (**A**), summer (**B**), and winter (**C**). L1–L11: 11 monitoring locations.

4. Conclusions

A total of 25 VOCs were collected from 11 monitoring locations and classified into three groups: eight alkenes, six alkanes, and eleven aromatics. The results showed that the concentrations of alkenes, alkanes, and aromatics in the sediment were significantly higher than in the water for all seasons ($p < 0.001$). Comparing the alkene, alkane, and aromatic concentrations in different seasons, it was shown that they were higher in summer than in spring and winter ($p < 0.01$). We presume that this was associated with the low temperature due to the high altitude of Tibetan plateau and the anthropogenic impact of the large numbers of visitors in summer. Chloroform, 1,4-DCB, o-Xylene, methylene chloride, vinyl chloride, and bromoform were the main VOCs found in our study, and several VOCs surpassed the national standard, which could lead to carcinogenic potential and human carcinogenic effects. Principal component analysis suggested that the TOC was responsible for the presence of the TVOCs in the river, accounting for 77.93%, 81.97%, and 82.13% of the total variance in the dataset in spring, summer, and winter, respectively. In addition, NO_2^--N was another important factor for the river's pollution status, and TN, TP, NO_3^--N, and NH_4^+-N had no significant correlations with the VOCs.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/su141911983/s1, Table S1: Sampling sites information, Table S2: Statistical summary of the VOCs in the samples from spring, Table S3: Statistical summary of the VOCs in the samples from summer, Table S4: Statistical summary of the VOCs in the samples from winter, Table S5: Water quality in the different sampling sites of the Huangshui River.

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