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Pollution Characteristics and Risk Assessment of Volatile Organic Compounds in Songhua Lake, China

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Abstract
In order to assess the dangers to human health and the environment from Songhua Lake's volatile organic compounds (VOCs) pollution. A total of 18 VOCs were found in the water samples that were collected at 26 sampling locations in Songhua Lake utilizing the purge and trap technique and gas chromatography-mass spectrometry (GC-MS). Toluene and naphthalene had the highest detection rates among them, reaching 96.15%; trans-1,2-dichloroethylene, 1,2-dichloroethane, and isopropyl benzene had the lowest rates, only 3.85%. The maximum and average concentrations of 1,1-dichloroethane were 20.93 μg/L and 4.16 μg/L, respectively, the maximum concentration of isopropyl benzene was only 0.02 μg/L, and the average concentration was also the lowest. The spatial distribution of VOCs in Song Hua Lake was typically described as "high in the northwest and low in the southeast," with a concentration range of 0.00 to 23.21 μg/L. An examination of the current situation reveals that human activity-related ecological deterioration is the primary cause of the VOCs contamination in Songhua Lake. The results of the risk assessment revealed that there were only moderate ecological risks to aquatic organisms and that the non-carcinogenic and carcinogenic risk indices of Songhua Lake were within the safe range. Additionally, there were no non-carcinogenic or carcinogenic threats to the health of people as a whole.

Key words：volatile organic compounds (VOCs)；Songhua Lake；gas chromatography-mass spectrometry (GC-MS)；spatial distribution；risk assessment

Introduction

Volatile organic compounds (VOCs) are a type of organic compounds that are volatile at ambient temperature and have a boiling point between 50 °C and 260 °C[1]. VOCs can be released into the environment in a variety of ways due to their chemical and physical characteristics[2], and once there, they can be mobilized, dispersed, diluted, volatilized, adsorbed, and degraded[3]. The majority of VOCs are persistent in the environment and have carcinogenicity, teratogenicity, mutagenicity and bioconcentration[4–6]. When people consume drinking water that contains too many VOCs, it may lead to liver and kidney damage, respiratory system, immune system, neurological system and reproductive system disorders and even cancer[7,8]. In order to ensure water safety, attention should be paid to the environmental problems that VOCs may cause.

Songhua Lake, which spans Huadian City, Jiaohe City, and Fengman District of Jilin City, is situated at 126° 45′ -127° 38′ E and 43° 07′ -43° 50′ N in the center of Jilin Province. It is not only the largest man-made lake in Northeast China and also the third-largest artificial lake in all of China[9]. The Songhua

River, Huifa River, and Jiaohe River are the three main rivers that enter the lake[10]. Songhua lake has a long and narrow shape, with an average water depth of 30 to 40 m, and a total area of 554 km^2. Songhua Lake serves as a significant water source for Jilin Province and serves a variety of purposes, including power generation, water supply, flood control, irrigation, aquaculture, and navigation. Many unique wild creatures and hundreds of indigenous plants call their nature reserve home. The health of the local populace and the ecological security of wild animals and plants are both impacted by environmental quality[11].

The objective is to clarify the overall pollution status of VOCs in Songhua Lake by the detection of 54 target VOCs in the surface water of the lake and the qualitative and quantitative study of their concentrations and spatial distribution. The assessment of ecological and health risks will be done concurrently in order to offer crucial data for managing and guaranteeing the sustainability of the ecological environment and the safety of drinking water sources.

Materials and Methods

Study area and sample collection

Water samples were collected using a hand-held global positioning system (GPS) at 26 sampling points in Lake Songhua according to the principle of uniform sampling, and then mapped (Figure 1; Supporting Information Table S1). 40 mL ultra-clean brown glass sampling bottles were used to collect water samples, completely filled without headspace, and sealed with polytetrafluoroethylene (PTEE) gasket caps to avoid photolysis of the analytes; at the same time 50 μL of HCl solution (1:1, pH $\leqslant$ 2) was added to prevent biodegradation of the analytes. A parallel sample of each sample is backed up to prevent the original sample from breaking or being available for laboratory replication. Samples were stored away from light in a portable refrigerator at 4 °C and transported to the laboratory for analysis immediately after sampling.

Table S1: Geographical information on sampling sites in Songhua Lake.

Sampling points	**Latitude（N）**	**Longitude（E）**
SHH-1	43°14′50.100″	127°1′47.388″
SHH-2	43°14′8.448″	127°6′11.556″
SHH-3	43°17′2.004″	127°9′21.528″
SHH-4	43°18′39.456″	127°6′0.216″
SHH-5	43°21′18.720″	127°6′24.984″
SHH-6	43°23′21.408″	127°6′30.276″
SHH-7	43°25′40.872″	126°59′25.080″
SHH-8	43°30′55.368″	126°54′49.500″
SHH-9	43°35′7.584″	126°54′14.328″
SHH-10	43°35′42.432″	126°55′32.808″
SHH-11	43°37′33.060″	126°55′41.448″
SHH-12	43°38′50.064″	126°54′9.108″

SHH-13	43°39′33.156″	126°52′56.244″
SHH-14	43°40′45.660″	126°41′44.556″
SHH-15	43°42′2.520″	126°43′1.632″
SHH-16	43°42′26.964″	126°45′59.256″
SHH-17	43°44′40.308″	126°48′22.896″
SHH-18	43°45′2.088″	126°49′57.720″
SHH-19	43°45′29.628″	126°51′17.532″
SHH-20	43°43′57.540″	126°47′33.036″
SHH-21	43°39′50.256″	126°45′49.428″
SHH-22	43°37′26.616″	126°47′2.436″
SHH-23	43°38′33.360″	126°48′47.916″
SHH-24	43°39′28.188″	126°48′5.400″
SHH-25	43°37′15.816″	126°44′44.592″
SHH-26	43°35′53.952″	126°42′46.800″

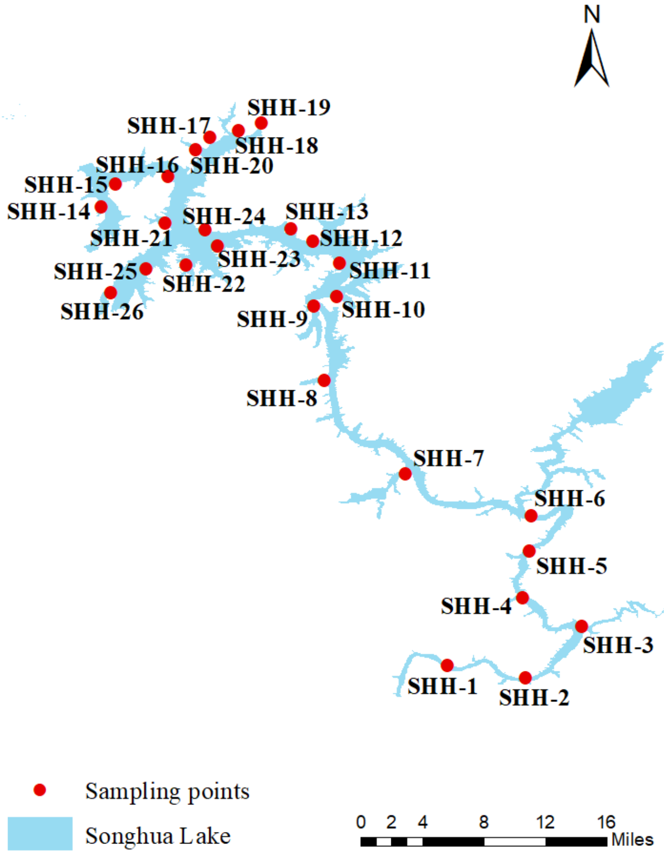

Figure 1: Schematic diagram of sampling points in Songhua Lake.

Chemicals and reagents

The VOCs mixed reference materials and pesticide residue grade methanol recommended by the United States Environmental Protection Agency (US EPA[12]) are purchased from AccuStandard. A total of 54 common VOCs were tested (Supporting Information Table S2). For analysis of the samples, the pesticide residue grade methanol was diluted stepwise to configure the standard series of solutions, and the internal standards were fluorobenzene and 1,4-dichlorobenzene-D4[13].

Table S2: Common VOCs.

1,1-dichloroethylene	Dichloromethane	Trans-1,2-dichloroethylene
1,1-dichloroethane	Cis-1,2-dichloroethylene	2,2-dichloropropane
Bromochloromethane	Chloroform	1,1,1-trichloroethane
1,1-dichloropropene	Carbon tetrachloride	1,2-dichloroethane
Benzene	Trichloroethylene	1,2-dichloropropane

Dibromomethane	Bromodichloromethane	Cis-1,3-dichloropropene
Toluene	Trans-1,3-dichloropropene	1,1,2-trichloroethane
1,3-dichloropropane	Tetrachloroethylene	Dibromochloromethane
1,2-dibromoethane	Chlorobenzene	1,1,1,2-tetrachloroethylene
Ethylbenzene	M-xylene	P-xylene
O-xylene	Styrene	Bromoform
Isopropylbenzene	1,1,2,2-tetrachloroethane	Bromobenzene
1,1,3-trichloropropane	N-propane	2-chlorotoluene
4-chlorotoluene	1,3,5-trimethylbenzene	Tert-butylbenzene
1,2,4-trimethylbenzene	Sec-butylbenzene	1,3-dichlorobenzene
1,4-dichlorobenzene	N-butyl benzene	1,2-dichlorobenzene
4-isopropyltoluene	1,2-dibromo-3-chloropropane	1,2,4-trichlorobenzene
Hexachlorobutadiene	1,2,3-trichlorobenzene	Naphthalene

Analytical methods

PT9800 & Aquatek100 and 25 mL purge tubes are used by the purging and trapping device. During use, the purging temperature was controlled at room temperature, the purging flow rate shall be 40 mL/min, purging time shall be 11 min, purging dry time shall be 1 min, the pre-desorption temperature shall be 190 °C, the desorption time shall be 2 min, the baking temperature shall be 200 °C, and the baking time shall be 6 min.

The chromatograph uses Agilent GC7890/MS5975 gas chromatograph-mass spectrometer with a DB-624 quartz capillary column (30 m×0.25 mm, 1.4 μm). Starting at 35 °C for 5 min, the column temperature was raised to 160 °C at a rate of 6 °C/min for 6 min, and then to 210 °C at a rate of 20 °C/min for 2 min. At a steady flow rate of 1.0 mL/min, helium gas (purity >99.99%) was loaded. The mass spectrometer was controlled at 200 °C for the EI ion source, 220 °C for the interface temperature, 70 eV for the ionization energy and 35.0-300.0 u for the scanning range[14,15].

Water sample (20 mL) and 50 μL internal standard (mass concentration is 20 μg/L) were precisely added into the purge pipe using the manual sampler. The method showed good linearity in the range of 0.05~100.0 μg/L with the correlation coefficient greater than 0.99. The recovery rate of the 54 VOCs in the samples ranged from 75 % to 118 % with the RSDs of 2.66 %~13.13 % and the LODs of 0.01~0.25 μg/L.

Health risk assessment

The carcinogenic risk index (Risk), which is broken down into low-dose exposure risk and high-dose exposure risk, shows the incidence rate of cancer above the level of typical exposure to carcinogenic contaminants. Corresponding Equation (1) (2) [16,17]:

$$Risk = CDI \times SF,\ Risk < 0.01 \quad (1)$$

$$Risk = 1 - exp(-CDI \times SF)\text{，} Risk \gg 0.01 \quad (2)$$

Where CDI is the long-term daily intake dose, mg/(kg·d) and SF is the pollutant carcinogenicity slope factor, mg/(kg·d).

According to the non-carcinogenic risk index (HI), exposure levels above the reference dose value are likely to be dangerous, but exposure levels equal to or below the reference dose value are within the tolerable risk range. The reference dose value is typically expressed using HI, which is obtained using Equation (3):

$$HI = {}^{CDI}/_{RfD} \quad (3)$$

Where RfD is the non-carcinogenic reference dose of the pollutant, mg/(kg·d).

The two main routes of contaminant exposure to humans are direct ingestion and dermal contact.

Use the following Equation (4) to calculate the direct intake of the feeding route:

$$CDI = {}^{\rho \times U \times EF \times ED}/_{BW \times AT} \quad (4)$$

The intake dose through dermal contact was calculated using Equation (5) (6).

$$CDI = {}^{I \times A_{sd} \times EF \times FE \times ED}/_{BW \times AT \times f} \quad (5)$$

$$I = 2 \times 10^{-3} \times k \times \rho \times \sqrt{{}^{6 \times \tau \times TE}/_{\pi}} \quad (6)$$

The parameters used in the above formula are taken from the guidelines for exposure assessment of the US EPA, and were selected according to the national conditions of China[18] (Supporting Information Table S3).

Table S3: Related symbols, parameter names, units and values used in the formula.

Symbols	**Parameters**	**Value**	**Units**
ρ	Concentration of compounds in water	Measured	mg/L
U	Daily drinking water	2	L/d
EF	Exposure frequency	365	d/a
ED	Delayed carcinogenic exposure	70	a
ED	Delayed non-carcinogenic exposure	30	a
BW	Body weight	60	kg
AT	Average time of carcinogenic exposure	25550	d

AT	Average time of non-carcinogenic exposure	10950	d
I	Pollutant adsorption per unit surface area of a single bath	Calculated	Mg/（cm/times）
A_{sd}	Human surface area	16600	cm^2
FE	Bathing frequency	0.3	times/d
f	Intestinal absorption ratio	1	-
k	Skin absorption ratio	0.001	cm/h
τ	Delay time	1	h
TE	Bathing time	0.4	h
π	Circumference	3.14	-
TF	Retention ratio of VOCs after boiling	0.3	-

Ecological risk assessment

Ecological risk assessment is a typical method of estimating the likelihood that unfavorable ecological impacts would ensue from exposure to one or more pressure sources[16]. The risk of exposure of a given species to chemicals in the surrounding natural environment is quantified by introducing the risk quotient (RQ) model. The RQ value can be determined from the ratio between the measured environmental concentrations (MEC) and the predicted no-effect concentrations (PNEC) published by the European Medicines Evaluation Agency (EMEA). Equation (7):

$$RQ = {}^{MEC}/_{PNEC} \tag{7}$$

Where MEC and PNEC are the measured environmental concentrations of individual compounds (μg/L) and the predicted concentration of compounds with no effect on aquatic organisms (μg/L).

PNEC is determined by the ratio of chronic value (ChV) and evaluation factor (AF) as Equation (8):

$$PNEC = {}^{ChV}/_{AF} \tag{8}$$

Where ChV data were retrieved from the US EPA pollution prevention database PBT profilers (http://www.pbtprofiler.net/). Based on the chronic toxicity data, the value of AF was set to 100[19,20].

In order to assess the total ecological risk of Songhua Lake, the ecological risk of all detected VOCs was calculated by the following Equation (9):

$$RQ_{Total} = RQ_1 + RQ_2 + \cdots + RQ_n \tag{9}$$

Results and Discussion

Detection of VOCs in Songhua Lake

VOCs were detected in water samples collected from 26 sampling points of Songhua Lake, and a total of 18 species were detected. The detection results after deducting the laboratory blank value are shown in Table 1. Among the pollutants detected, benzene series are the most, followed by alkanes and alkenes, and other substances account for a small number. The detection rate of toluene and naphthalene in 18 VOCs is the highest, reaching 96.15%, that is, they are detected at all sampling points except SHH-3. The detection rate of benzene and 1,2-dichlorobenzene took the second place, 92.31%. Trans-1,2-dichloroethylene, 1,2-dichloroethane and isopropyl benzene had the lowest detection rate of 3.85%. The detection rates of the other pollutants ranged from 15.28% to 88.46%. Ma et al.[21] proposed that toluene may be the most prevalent VOCs pollutant in Chinese waters, which is consistent with the detection results of toluene in this study. Notably, naphthalene also had the highest detection rate and was also widely distributed. Some studies have proved that naphthalene has carcinogenic activity in rats and can cause kidney damage in rats and humans[22].

Table 1: VOCs concentrations in the surface water of Songhua Lake.

VOCs	Detection rate (%)	Concentrations (μg/L)			Standard value (μg/L)
		Minimum	Maximum	Average	
Trans-1,2-dichloroethylene	3.85	ND	0.29	0.02	50.00
1,1-dichloroethane	23.08	ND	20.93	4.16	30.00
2,2-dichloropropane	30.77	ND	0.70	0.18	—
Carbon tetrachloride	38.46	ND	0.20	0.05	2.00
Benzene	92.31	ND	1.06	0.36	10.00
1,2-Dichloroethane	3.85	ND	0.63	0.05	30.00
Trichloroethylene	42.31	ND	0.25	0.04	8.00
1,2-Dichloropropane	15.38	ND	0.18	0.03	—
Bromodichloromethane	88.46	ND	3.04	0.43	60.00
Cis-1,3-dichloropropene	50.00	ND	0.11	0.02	—
Toluene	96.15	ND	0.67	0.27	700.00
Ethylbenzene	76.92	ND	1.10	0.27	300.00
M-/P-xylene	88.46	ND	2.35	0.54	500.00
O-xylene	80.77	ND	1.22	0.33	500.00
Styrene	50.00	ND	0.58	0.19	20.00
Isopropylbenzene	3.85	ND	0.02	0.00	250.00
1,2-Dichlorobenzene	92.31	ND	1.77	0.48	1000.00
Naphthalene	96.15	ND	0.41	0.24	—

The concentrations of detected VOCs ranged from ND (not detected) to 20.93 μg/L, with average concentrations ranging from 0.00 to 4.16 μg/L. The highest maximum and average concentrations were found for 1,1-dichloroethane. The maximum concentrations of bromodichloromethane and m-/p-xylene were 3.04 μg/L and 2.35 μg/L respectively, while the maximum concentrations of the remaining pollutants ranged from 0.02 to 1.77 μg/L, all much smaller than 1,1-dichloroethane; the average concentrations of all other pollutants did not exceed 0.54 μg/L. In comparison with Chinese national standards, the VOCs detection results of Songhua Lake did not exceed the Surface Water Quality Standard (GB 3838-2002) and the Sanitary Standard for Drinking Water (GB 5749-2022)[23,24], but the detection value of 1,1-dichloroethane was much greater than that of other pollutants, which deserves attention. 1,1-dichloroethane is mainly used as a solvent, a fumigant, a thermosensitive substance, and a fumigant. It is also used as a raw material for the production of polyvinyl chloride (PVC) and vinyl chloride monomer (VCM). It has a depressant effect on the central nervous system, irritates the stomach and intestines, and causes damage to the liver, kidneys and adrenal glands, may cause dermatitis on skin contact[25] and bioaccumulates in important human food chains, especially in aquatic organisms, thus posing a health and ecological hazard. It has been reported in the literature that 1,1-dichloroethane is a major component of the azeotropes produced by the distillation of vinyl chloride during PVC production[26], and studies have also shown that harmful monomers left in food packaging materials can migrate through the packaging materials to food, thus causing contamination of food[25]. In a study by Gao et al.[27], it was mentioned that the land use in the lakeside area of Songhua Lake is dominated by arable land (44.91%), which is influenced by arable land and human activities, with serious pollution from domestic and agricultural surface sources; and Songhua Lake is a scenic area with a high demand for tourism, which directly leads to the massive use of PVC-based products, thus increasing the risk of 1,1-dichloroethane residues in packaging materials to the water environment.

The concentrations of each VOC at each point were also analyzed (Figure 2) and it can be seen that the median values for all 18 VOCs were below 1.0 μg/L. Only three pollutants, 2,2-dichloropropane, styrene and naphthalene, did not show any abnormal values, which means that the concentrations of the remaining 15 VOCs were much higher at one or several sampling points than at other sampling points. This may be because the samples were collected during a period of high water abundance, and VOCs have the characteristics of easy degradation and volatilization, leading to generally low detection values. These points with abnormal values may have illegal emissions, this situation should be paid attention to.

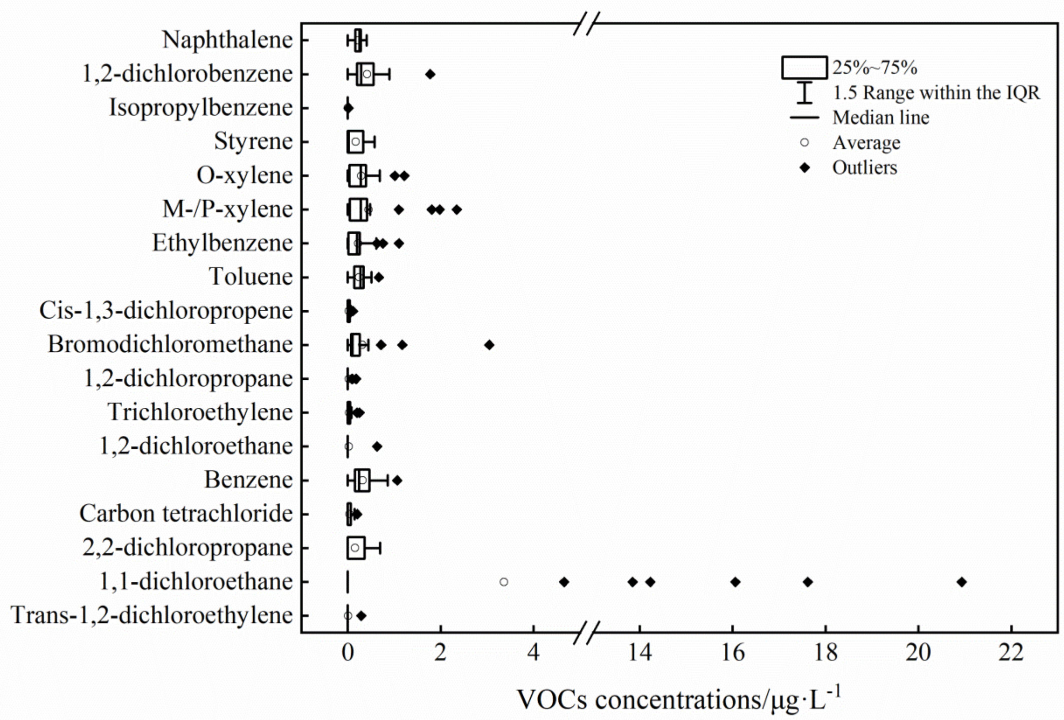

Figure 2: Boxplot of VOCs concentrations in Songhua Lake.

Compared with Chen et al.[28] study on the concentrations of VOCs in typical drinking water sources in five major watersheds in China, it was found that 7 of the 10 VOCs with the highest detection rate in five major watersheds (toluene, m-/p-xylene, o-xylene, naphthalene, 1,2-dichloropropane and ethylbenzene) were detected in Songhua Lake, with 1,2-dichloropropane having the lowest detection rate of 13.79%. The concentration range of conventional VOCs detected in five major watersheds is 0~9.81 μg/L, only the detectable concentration of 1,1-dichloroethane in Songhua Lake exceeds this range. Therefore, the detection of VOCs in Songhua Lake is roughly consistent with the detection of VOCs in the five major river watersheds in China.

Spatial distribution of VOCs in Songhua Lake

The concentration distribution of 18 VOCs detected in Songhua Lake is shown in Figure 3, and the total concentration of 18 VOCs (ΣVOCs) is from 0.00 to 23.21μg/L. The highest ΣVOCs were found at point SHH-25, followed by point SHH-5. ΣVOCs at point SHH-3 was zero, which means that no VOCs were detected at this point. Both SHH-19 and SHH-23 had low ΣVOCs of 0.95 and 0.97 μg/L respectively. The average concentration of the 26 sampling points was 6.30 μg/L, there are 8 sampling points with ΣVOCs above the average value.

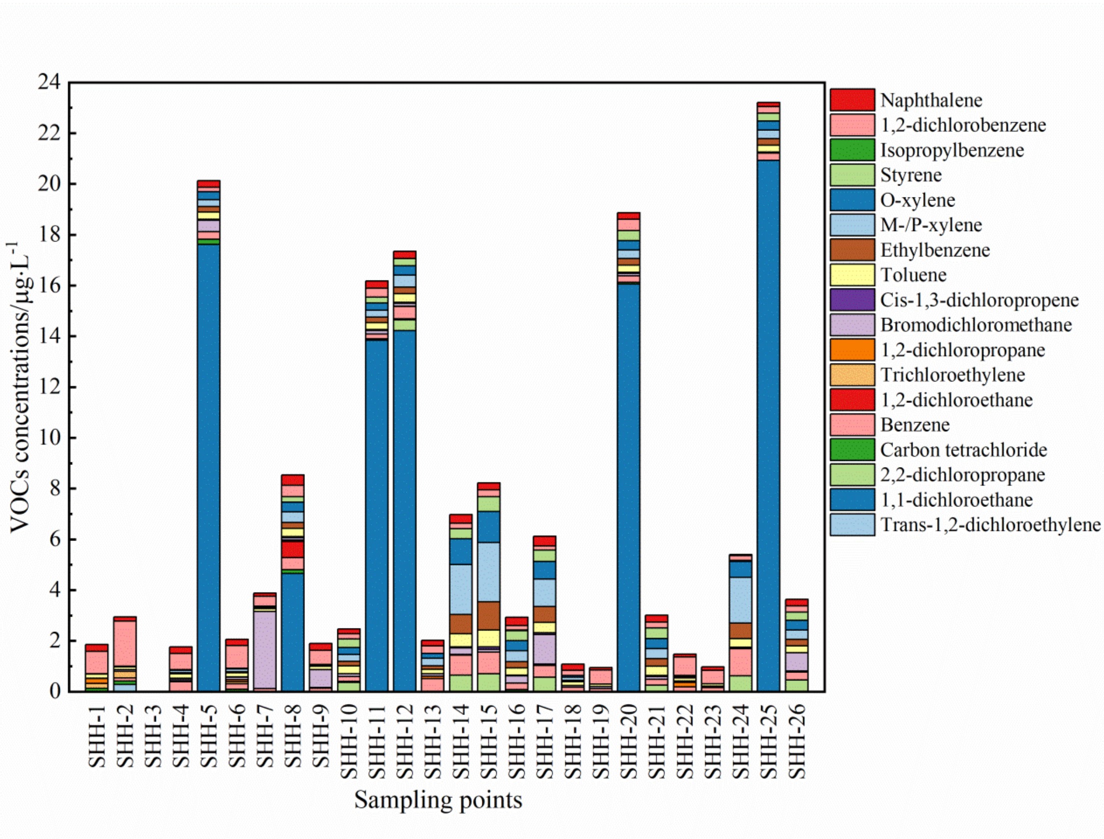

Figure 3: Concentration distribution of VOCs concentrations in Songhua Lake.

ArcGIS 10.2 software was used to analyze the total concentration of VOCs at 26 sampling points in Songhua Lake. As shown in Figure 4, the spatial distribution of VOCs pollution in Songhua Lake is generally "high in the northwest and low in the southeast", that is most of the sampling points with higher ΣVOCs are located in the northwest of the lake in Fengman District and Jiaohe City of Jilin, while the southeast of the lake in Huadian City and Jiaohe City generally had low ΣVOCs, with the exception of SHH-5.

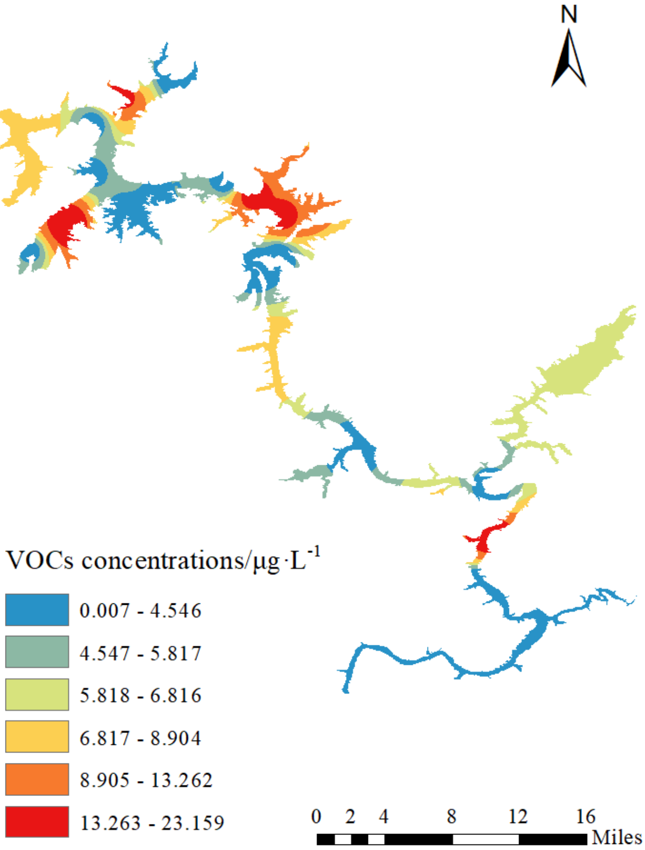

Figure 4: Spatial distribution of VOCs concentrations in Songhua Lake.

Combined with the existing map information analysis, ΣVOCs higher sampling points are mostly located near the dock or holiday resorts in more concentrated areas, such as the most serious pollution near point SHH-25 is Wuhu Island scenic spot, and there are cruise ship docks, Songhua Lake sightseeing tower, large amusement parks, leisure hotels, etc. on the island. There are more than ten tourist resorts near SHH-20, where the pollution is relatively serious, fishing grounds and resorts are also distributed in upstream. There are also fishing grounds and resorts in the vicinity of SHH-11 and SHH-12, the Qingling Marina, the Golden Toad Island Scenic Area and the Fenglin Resort. SHH-14 and SHH-15 with light pollution have a number of marinas in the vicinity, and upstreams are the Zhuqueshan National Forest Park, the Wujiashan Forest Park and residential communities. However, SHH-5, which is located at the southeast end of the lake and is heavily polluted, is mostly surrounded by villages. Because of its surrounding natural scenery and pleasant scenery, it attracts many tourists to come here to camp, play in the water and have a picnic. Due to its undeveloped facilities and lack of supervision, the environmental pollution problem needs to be solved urgently, and such problems may also exist near the less polluted point SHH-8.

According to the Master Plan of Songhua Lake Scenic Spot (2011-2030), the sewage discharged by shipping ships into Songhua Lake has been controlled to a certain extent, which may also be one of the reasons for the generally low VOCs detection value. Combined with the study by Gao.[29], which showed that the northwestern part of Songhua Lake has scattered residents who grow crops such as maize and a large number of fishery farms with more serious bon-point source pollution, and the higher ΣVOCs in the northwestern part are mainly attributed to the ecological damage caused by human activities, such as the extinction of the original vegetation (trees, shrubs, herbs, etc.) by artificially grown crops, garbage stacking and domestic sewage and industrial sewage discharged into Songhua Lake through the Songhua River. The southeastern part of Songhua Lake is basically a natural ecological environment and landscape pattern with good water quality. Still, it is also under threat from the impact of human activities and regional environmental pollution.

Health risk assessment results

Since the toxicity data of all VOCs compounds cannot be obtained, health risks were assessed only for those VOCs compounds that were at risk, and detailed evaluation parameters are presented in Supporting Information Table S4. The Risk of VOCs in Songhua Lake was calculated according to the risk assessment formula of MEPAS (Figure 5). It has been demonstrated that direct ingestion of water with VOCs residues results in a carcinogenic risk that is generally one order of magnitude higher than dermal contact[16], so only the health risk from the drinking water route is calculated here.

Table S4: Chemical and toxicological characteristics of VOCs.

VOCs	***SF* [mg/(kg/d)]**	***RfD* [mg/(kg/d)]**
Trans-1,2-dichloroethylene	—	0.02
1,1-dichloroethane	0.0057	0.2
2,2-dichloropropane	—	—
Carbon tetrachloride	0.07	0.004
Benzene	0.055	0.004
1,2-dichloroethane	0.091	0.006
Trichloroethylene	0.046	0.00048
1,2-dichloropropane	0.0033	0.078
Bromodichloromethane	0.062	0.02
Cis-1,3-dichloropropene	0.1	0.03
Toluene	0.004	0.08
Ethylbenzene	0.011	0.01
M-/P-xylene	—	0.2
O-xylene	—	0.2
Styrene	—	0.2

Isopropylbenzene	—	—
1,2-dichlorobenzene	—	0.09
Naphthalene	0.02	—

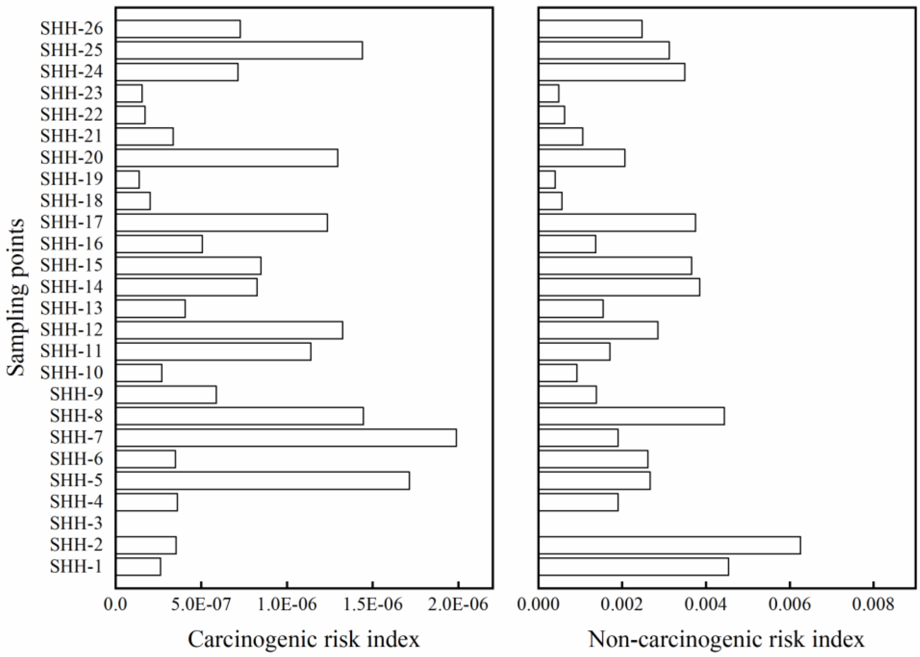

Figure 5: Carcinogenic/Non-carcinogenic risk index of VOCs in Songhua Lake.

US EPA uses 10^{-4} and 10^{-6} as criteria for carcinogenic risk identification. When the calculated Risk is less than 10^{-6}, the carcinogenic risk is considered to be negligible. The Risk is in the range of 10^{-6}~10^{-4}, which may pose some degree of risk to weaker people, but are acceptable. Risk exceeding 10^{-4}, is considered to be a serious cancer risk[16]. In Figure 5, the Risk of 8 points in Songhua Lake is at 1×10^{-6}~2×10^{-6}, which means there is a certain threat to residents living nearby. The Risk of most sampling points is far below the risk threshold (10^{-6}), indicating that the potential risk of Songhua Lake to human health is at a low to medium level and in an acceptable range. The carcinogenic risk range of 12 sampling points in groundwater drinking water sources in Klulun River Basin is 5.33×10^{-6}~1.96×10^{-5}[30], all of which exceeded the risk threshold, compared to which the cancer risk is lower and safer in Songhua Lake. However, the points that exceeded the risk threshold need to pay continuous attention to the impact of regional VOCs on nearby residents and tourists.

According to the relevant definition of non-carcinogenic risk in US EPA, a pollutant is considered to be hazardous to human health when its risk index exceeds 1. From Figure 5, it can be seen that the HI of Lake Songhua ranges from 0 to 6.3×10^{-3}, which is far less than 1, indicating that the non-carcinogenic impact of Lake Songhua on human beings can be completely negligible. Comparing the non-carcinogenic index values of VOCs in the groundwater of the Lower Liaohe River Plain (0~0.3224)[31], the HI of Songhua Lake is lower. This difference arises probably because the groundwater of the Lower Liaohe River Plain is seriously polluted by industrial wastewater. Based on the above information analysis, the next step of VOCs risk management and control in Songhua Lake should focus on several points with high health risk value. It is necessary to strengthen the supervision of the fishery and the protection of the primitive vegetation, as well as the timely transfer and treatment of domestic sewage.

Ecological risk assessment results

The risk quotient values of the lowest and highest concentrations of single VOCs detected in Songhua Lake for fish are listed in table S5. When the RQ value is greater than 1.00, this area is considered to be a high-risk area. When the RQ value is between 0.10 and 1.00, this area is considered to be of moderate risk. When the RQ value ranges from 0.01 to 0.10, it is a low-risk area[6]. From Table S5, there are no high-risk points in Songhua Lake, and the RQ values of most sampling points are between 0.10 and 0.64, which are of moderate ecological risk to fish.

In order to intuitively understand the ecological risk of Songhua Lake, the contribution analysis of RQ values at all sampling points (Figure 6) showed that m-/p-xylene has the largest contribution to the ecological risk quotient of Songhua Lake, followed by 1,2-dichlorobenzene and o-xylene. These three VOCs in Songhua Lake are not the pollutions with the highest concentration or the highest detection rate. From this, we can learn that in order to establish a complete and effective VOCs pollution control strategy for important drinking water sources, it is not simply determined by factors such as concentrations and detection rates, but by the comprehensive consideration of the ecological risk assessment of single compounds and composite pollutants. This is because, in the actual ecological environment, compounds do not exist alone, and organisms are exposed to a complex environment containing multiple pollutants[6].

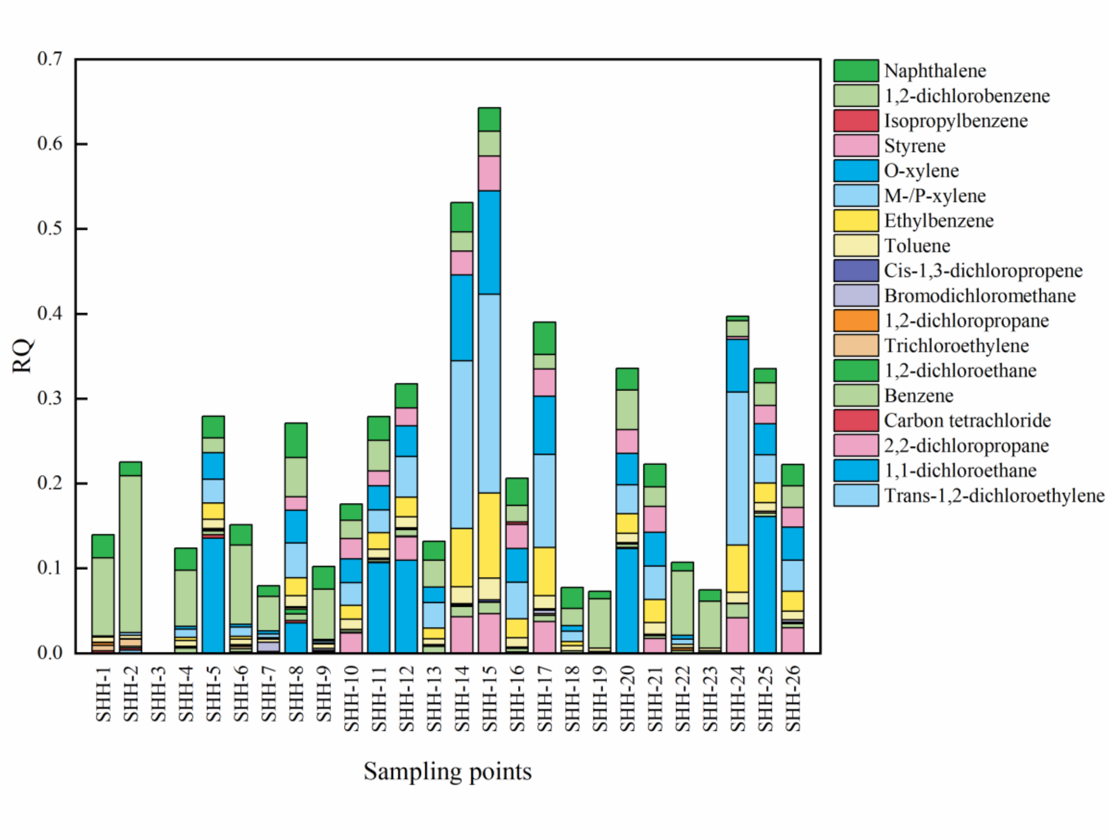

Figure 6: Ecological risk quotients of Songhua Lake.

Conclusions

This study evaluated the VOCs concentrations in the surface water of Songhua Lake in northeastern China. In 26 sampling stations, a total of 18 VOCs were found, and 4 of those had detection rates that were 90% or above. VOCs were found in concentrations ranging from ND to 2.93 μg/L, with an average concentration of 0.00 to 4.16 μg/L. The existence of large PVC-based product manufacture, usage, and recycling in the area may be indicated by the concentration of 1,1-dichloroethane at the detection stations being much greater than other VOCs. However, overall, the concentration of VOCs in Songhua Lake is below the national standard limits.

Furthermore, the spatial distribution of the VOCs concentrations in Songhua Lake's surface water was created. The findings indicate that VOCs pollution is typically "high in the northwest and low in the southeast," and that human activity has a significant impact at sampling points with higher ΣVOCs levels, which are typically found close to wharves or in areas where resorts are concentrated.

In Songhua Lake, HI and Risk of VOCs are within the safe range as determined by the cancer risk study of personal exposure. Notwithstanding the fact that some sampling points' risks surpass the risk threshold (10^{-6}), overall human health will not be substantially threatened. According to the findings of the ecological risk assessment, the principal environmental hazards at Songhua Lake include m-/p-xylene, 1,2-dichlorobenzene, and o-xylene. The concentration and rate of VOCs detection are not always correlated with RQ.

According to the study's findings, Songhua Lake's VOCs quality requirement can guarantee the safety of the water for the local residents and related sectors, but there is a risk to fish in the ecosystem and subsequently to humans through the food chain. Thus, it is still important to keep an eye on Songhua Lake's water quality and to tighten up the control over the discharge of domestic and industrial wastewater nearby

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