

## Article

# Distribution and Geochemical Processes of Arsenic in Lake Qinghai Basin, China

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**Abstract:** Lake Qinghai in the Qinghai-Tibet plateau is the largest lake in China, but the geochemical understanding of arsenic (As) in the lake is lacking. Water, sediment, and soil samples were collected from Lake Qinghai, rivers flowing into the lake, and lands around the lake. Water samples were analyzed for major ions and As, while sediment and soil samples were analyzed for major elements and As. The average As concentration ( $25.55 \mu\text{g L}^{-1}$ ) in the lake water was significantly higher than that ( $1.39 \mu\text{g L}^{-1}$ ) in the river water ( $p < 0.05$ ), due to the evaporative concentration of lake water. The average As concentration ( $107.8 \mu\text{g L}^{-1}$ ) in the pore water was significantly higher than that in the lake water, due to its secondary release from sediment solid phases in the reductive condition. The average As/Cl<sup>-</sup>, As/SO<sub>4</sub><sup>2-</sup> and As/Na molar ratios in the lake water were significantly lower than that in the river water, indicating As was partially transferred from dissolved phase to solid phase in the evaporative concentration process of the lake water. The average As/Ca molar ratio in the lake water was significantly higher than that in the river water, indicating more Ca than As precipitated in the lake water. Furthermore, the average As/Ca molar ratio in the lake water was significantly lower than that in the pore water, indicating more As than Ca was secondarily released from sediment solid phases. The average concentration of As(III) and As(V) were 0.35 and  $1.04 \mu\text{g L}^{-1}$  for the river water, respectively, and 6.99 and  $18.56 \mu\text{g L}^{-1}$  for the lake water, indicating As(V) was the predominant As form. The average As concentration was  $16.75 \text{ mg kg}^{-1}$  for the lake sediment and  $13.14 \text{ mg kg}^{-1}$  for the soil around the lake. Arsenic concentration was significantly negatively correlated with S and Ca concentration in the lake sediments, due to solid dilution effect induced by carbonate and sulfate precipitation. The average As/Sc molar ratio in the sediment (2.06) was significantly higher than that in the soil (1.32), indicating that relatively more As was enriched in the lake sediment.



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**Keywords:** arsenic; water; sediment; soil; Lake Qinghai

## 1. Introduction

Alpine lakes are among the least disturbed aquatic ecosystems [1]. Given their relative remoteness, no local impact masks the effects of large-scale changes, such as climatic and background diffuse contamination [2]. Therefore, alpine lakes can be viewed as sensors of regional and global environmental changes [2,3].

Lake Qinghai, the largest inland lake in China, is located in the arid/semi-arid zone, in the Qinghai-Tibet Plateau [4,5]. Due to its unique geographical location, it has attracted increasing attention worldwide [5–11]. Measurement of sediment grain-size fractions indicate that sedimentation in the north and southwest of Lake Qinghai is dominated by river input [8]. Elemental carbon and polycyclic aromatic compounds in the lake sediment have been investigated, demonstrating ubiquitous atmospheric deposition of soot and local river inputs of char [7]. Micro-plastics, mainly composed of polyethylene and polypropylene, are predominated in sheet and fiber shapes in the water of Lake Qinghai [11]. Major ion chemistry of the lake water was investigated, showing that the chemical composition of lake water can be mainly ascribed to evaporation and crystallization [5]. The mass balance

of major elements in the lake water was studied, indicating that atmospheric deposition might play a significant role in determining the distribution of major elements [4]. Trace elements are essential for biota growth and development, but toxic in higher concentration [12–15]. However, there have been few geochemical studies conducted on the trace elements in Lake Qinghai [9,10].

Arsenic (As) is considered as being one of the most toxic elements [16–20] and can cause cardiovascular diseases, skin lesions and cancer [21–25]. The As concentration range of 0.1–0.8  $\mu\text{g L}^{-1}$  in globe lake water and average of 1.5  $\mu\text{g L}^{-1}$  in world ocean water [12,26]. Due to the evaporative concentration, high As concentrations are also found in shallow groundwater (range: 0.1–96  $\text{mg L}^{-1}$ ) of the Owens Lake [27], surface water and groundwater (range: 100–259  $\mu\text{g L}^{-1}$ ) of the Poopo Lake Basin [28], agricultural evaporation ponds (range: 108–2099  $\mu\text{g L}^{-1}$ ) of San Joaquin Valley [29], and groundwater and alkaline lakes (range: 0.11–3680  $\mu\text{g L}^{-1}$ ) at the upper Paraguay basin [30]. With the evaporative concentration of water, the increase in As concentration was accompanied with increases in electrical conductivity [27],  $\text{Cl}^{-}$  [29] and Na [30] concentrations, and salinity [31]. High Na (average: 3310  $\text{mg L}^{-1}$ ) and  $\text{Cl}^{-}$  (average: 5772  $\text{mg L}^{-1}$ ) concentration in water of Lake Qinghai were observed in our previous studies, as a result of evaporative concentration [9,10]. Therefore, we deduced that As concentration in Lake Qinghai may be influenced by the evaporative concentration process.

The main objectives of this study were to investigate the geochemical distribution and process of As in the water of Lake Qinghai and the enrichment of As in the sediment of Lake Qinghai and soil around the lake area.

## 2. Materials and Methods

### 2.1. Study Area

Lake Qinghai ( $36^{\circ}32'–37^{\circ}14' \text{ N}$ ,  $99^{\circ}37'–100^{\circ}45' \text{ E}$ ) is located in the northeastern Qinghai-Tibet Plateau, with an altitude of 3194 m, a surface area of 4260  $\text{km}^2$ , and depths of 21–29 m [4]. The lake is characterized by the Qinghai-Tibet Plateau continental climate, with an average precipitation of 336.6 mm (1951–2005) and evaporation of 925 mm (1959–2000) [32]. The lake is mainly fed by water discharge from the Buha River. The lake sediment is composed predominately of silts, clays, carbonates and illite/chlorite [4,5].

### 2.2. Sample Collection

Water, sediment, and soil samples were collected in September 2016 (Figure 1). Surface water samples (about 2 m depth) were collected along the Buha River ( $n = 12$ ) and at Lake Qinghai ( $n = 23$ ), respectively. In addition, water samples from different depths (from surface to bottom in 4 m intervals) were collected at eight sites at Lake Qinghai ( $n = 46$ ). The water samples were filtered immediately through 0.45- $\mu\text{m}$  Teflon filter and then were acidified using  $\text{HNO}_3$  to preserve As speciation. The water samples were transported to the laboratory and kept refrigerated ( $4^{\circ}\text{C}$ ) until their analysis.

Surface sediment and soil samples (about 0–20 cm) were collected at Lake Qinghai ( $n = 22$ ) and lands around the lake ( $n = 45$ ), respectively. Sediment pore water were extracted by centrifugation for 30 min at 2500 rpm. The supernatant pore water was filtered through 0.45  $\mu\text{m}$  Teflon filter.

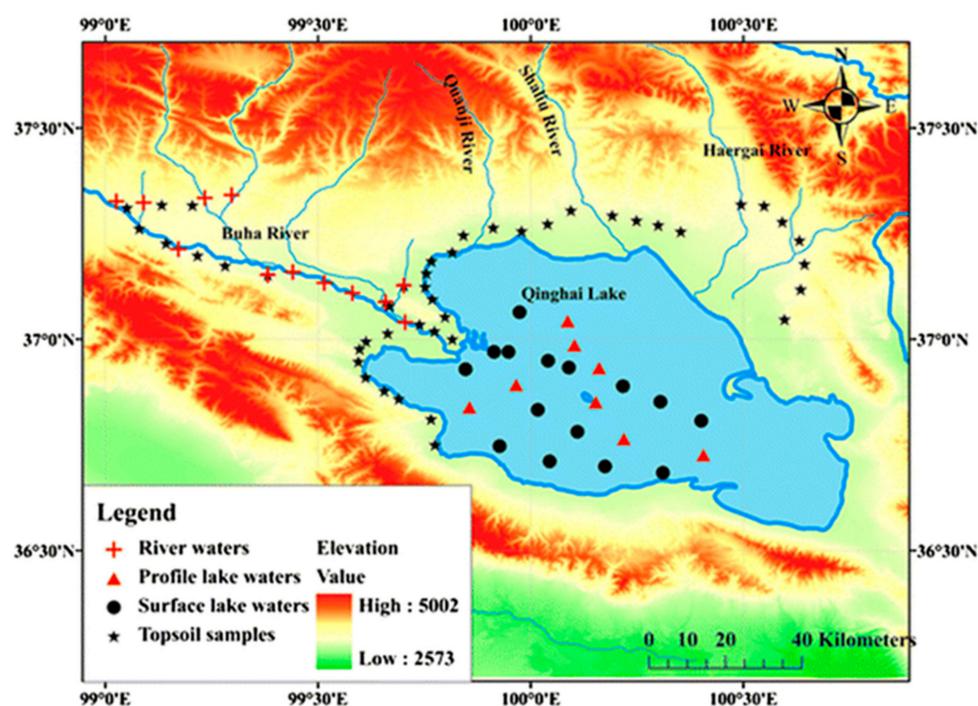


Figure 1. Locations of sampling sites in/around Lake Qinghai.

### 2.3. Sample Analysis

Concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in water samples were determined by an ion chromatography system (ICS, Dionex ICS-1100, Thermo Scientific, Waltham, MA, USA). Concentrations of K, Na, Ca, Mg, Fe, and Al in the water were measured using inductively coupled plasma mass spectroscopy (ICP-MS, X Series II, Thermo Electron, Waltham, MA, USA). Concentration of As in the water were determined using hydride generation-atomic fluorescence spectrometry (HG-AFS, Haiguang Instruments, Beijing, China) [33,34]. To determine the total As concentration, the water samples were pretreated with thiourea to reduce all As to As(III) prior to hydride generation. To determine the As(III) concentration, the samples were not pretreated with a reducing agent, but rather mixed with a sodium citrate buffer (0.4 M, pH 4.5).

Sediment and soil samples were freeze-dried, slightly crushed, and passed through a 2-mm sieve. The sediment and soil samples were digested with  $\text{HNO}_3$ -HF- $\text{HClO}_4$  [35]. The concentration of K, Na, Ca, Mg, Fe, Mn, Al, and S in the extracts were measured with inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II, Thermo Electron, Waltham, MA, USA). The Sc concentration in the extracts were determined by ICP-MS. The As concentration in the extracts were measured by HG-AFS.

The statistical analysis of the significant difference was performed by the Tukey-Kramer honest significant difference test at  $\alpha = 0.05$  level, using SAS JMP Statistical (JMP 12.0).

### 2.4. Quality Assurance and Control

Accuracy and precision were strictly controlled by using reagent blanks, duplicate samples, and reference materials GSS21 (National Institute of Metrology, Beijing, China). All samples were measured in triplicate and had relative errors less than 5% (Table 1).

**Table 1.** The detection limits, precision, and accuracy of various elements in the samples.

	K	Na	Ca	Mg	S	Cl	Al	Mn	Fe	Sc	As
Detection limits <sup>a</sup>	0.05	0.84	0.2	0.15	0.18	0.61	2.99	0.29	0.09	0.17	0.01
CV for the water (%) <sup>b</sup>	2.98	1.02	1.3	1.51	1.15	4.97					2.2
CV for soil/sediment (%) <sup>c</sup>	2.36	3.06	1.7	2.11	3.48		1.64	1.78	1.6	1.96	2.2
Relative errors (%) <sup>d</sup>	5.1	1.8	4.4	3.5	0.2		0.5	7.7	2.3	3.4	2.2

<sup>a</sup>:The detection limits for elements in water samples were calculated as 3\* standard deviation of blank determination ( $n = 5$ ). Potassium, Na, Ca, Mg and Cl were in  $\text{mg L}^{-1}$ , and Al, Mn, Fe, Sc and As were in  $\mu\text{g L}^{-1}$ . <sup>b</sup>:The average variance coefficients for the water were calculated by the replicate analyses of 14 water samples. <sup>c</sup>:The average variance coefficients (CV) for the sediment/soil were calculated by the replicate analyses of 10 sediment and soil samples. <sup>d</sup>: The average accuracy for soil and sediment analysis was assessed by the analyses of the elements in the certified reference materials GSS21 ( $n = 10$ ).

### 3. Results and Discussion

#### 3.1. Properties of the Water, Sediment, and Soil

The general physicochemical properties for the water, sediment and soil are shown in Table 2. The water, sediment and soil are generally characterized by an alkaline pH. The concentrations of dissolved K, Na, Mg, Cl and S in the lake water were much higher than those in the river water, which can be mainly ascribed to the evaporative concentration in Lake Qinghai [5]. Similarly, the high major element concentration was also observed in alpine lakes in Tibet, China (average elevation of higher than 4000 m) [36]. However, the dissolved Ca concentration was much higher in the river water than in the lake water. This indicated that Ca precipitates and accumulates in the bottom sediments of Lake Qinghai [4,5]. In addition, the major element concentration was generally higher in the pore water than that in the lake water. This can be linked to the secondary release from sediment solid phase in the reductive condition [37].

**Table 2.** Statistical values of physicochemical parameters for the water, sediment, and soil.

		Unit	Mean	Median	SD	CV%	Max	Min	<i>n</i>
River water	pH		8.04	8.08	0.27	3.3	8.38	7.45	12
	Alkalinity	$\text{mmol L}^{-1}$	2.72	2.86	0.48	17.8	3.55	1.86	12
	K	$\text{mg L}^{-1}$	2.00	1.81	1.00	50.0	3.93	0.69	12
	Na	$\text{mg L}^{-1}$	14.28	13.98	8.95	62.7	28.97	2.60	12
	Ca	$\text{mg L}^{-1}$	65.15	62.51	23.92	36.7	106.24	32.63	12
	Mg	$\text{mg L}^{-1}$	13.56	13.39	4.78	35.3	19.55	6.74	12
	Cl <sup>-</sup>	$\text{mg L}^{-1}$	12.42	12.53	7.29	58.7	25.49	2.03	12
	SO <sub>4</sub> <sup>2-</sup>	$\text{mg L}^{-1}$	24.63	23.95	6.95	28.2	35.70	11.27	12
	As	$\mu\text{g L}^{-1}$	1.39	1.36	0.17	12.0	1.74	1.17	12
	As <sup>+5</sup>	$\mu\text{g L}^{-1}$	1.04	1.05	0.07	7.1	1.13	0.84	12
As <sup>+3</sup>	$\mu\text{g L}^{-1}$	0.35	0.33	0.16	45.2	0.69	0.13	12	
Lake water	pH		9.23	9.22	0.08	0.9	9.44	9.12	69
	Alkalinity	$\text{mmol L}^{-1}$	22.87	22.50	3.02	13.2	29.69	15.23	69
	K	$\text{mg L}^{-1}$	162.29	159.95	60.96	37.6	297.90	42.57	69
	Na	$\text{mg L}^{-1}$	3310.80	3327.70	1330.22	40.2	6182.55	707.20	69
	Ca	$\text{mg L}^{-1}$	8.97	8.43	3.29	36.7	18.44	1.57	69
	Mg	$\text{mg L}^{-1}$	831.21	790.07	321.14	38.6	1637.94	109.34	69
	Cl <sup>-</sup>	$\text{mg L}^{-1}$	5772.26	5610.97	2358.29	40.9	11,030.03	1236.86	69
	SO <sub>4</sub> <sup>2-</sup>	$\text{mg L}^{-1}$	1661.17	1560.45	638.60	38.4	3196.95	354.71	69
	As	$\mu\text{g L}^{-1}$	25.55	25.69	8.67	33.9	41.76	8.86	69
	As <sup>+5</sup>	$\mu\text{g L}^{-1}$	18.56	17.98	7.18	38.7	31.43	5.70	69
As <sup>+3</sup>	$\mu\text{g L}^{-1}$	6.99	6.99	2.48	35.5	12.81	2.06	69	
Pore water	K	$\text{mg L}^{-1}$	321.47	347.47	65.06	20.2	432.54	206.16	20
	Na	$\text{mg L}^{-1}$	5225.45	5800.23	878.68	16.8	6034.66	3429.23	20
	Ca	$\text{mg L}^{-1}$	34.34	29.13	19.19	55.9	90.38	11.90	20
	Mg	$\text{mg L}^{-1}$	1669.14	1778.50	291.42	17.5	2161.22	1137.85	20

Table 2. Cont.

		Unit	Mean	Median	SD	CV%	Max	Min	n
	Cl <sup>-</sup>	mg L <sup>-1</sup>	10,050.58	11,067.97	1673.77	16.7	11,522.44	6658.39	20
	SO <sub>4</sub> <sup>2-</sup>	mg L <sup>-1</sup>	3556.06	3698.14	731.15	20.6	5022.34	2251.91	20
	As	µg L <sup>-1</sup>	107.80	96.63	35.33	32.8	197.50	58.50	20
Sediment	pH		9.39	9.42	0.4	4.2	10.03	8.86	22
	OM	%	10.25	10.16	2.39	23.3	15.59	3.03	22
	Carbonate	%	33.76	34.15	6.67	19.8	49.88	16.37	22
	Mn	mg kg <sup>-1</sup>	490.03	509.45	69.38	14.2	589.27	253.49	22
	Al <sub>2</sub> O <sub>3</sub>	%	8.96	9.03	1.04	11.6	11.29	5.67	22
	Fe <sub>2</sub> O <sub>3</sub>	%	3.25	3.37	0.56	17.2	4.19	1.43	22
	MgO	%	4.56	3.61	2.57	56.4	14.59	2.66	22
	CaO	%	18.27	18.41	2.90	15.9	22.86	11.65	22
	Na <sub>2</sub> O	%	1.64	1.61	0.24	14.4	2.52	1.36	22
	K <sub>2</sub> O	%	1.91	1.93	0.25	13.1	2.42	1.23	22
	As	mg kg <sup>-1</sup>	16.75	16.20	2.76	16.5	21.93	12.40	22
Soil	pH		8.83	8.76	0.55	6.3	10.39	7.95	45
	OM	%	7.48	7.97	3.33	44.5	13.24	1.21	45
	Mn	mg kg <sup>-1</sup>	584.09	596.68	87.77	15.0	752.97	394.15	45
	Al <sub>2</sub> O <sub>3</sub>	%	10.90	10.89	1.25	11.5	13.51	7.77	45
	Fe <sub>2</sub> O <sub>3</sub>	%	4.20	4.28	0.60	14.3	5.32	2.86	45
	MgO	%	2.21	2.12	0.52	23.7	4.76	1.50	45
	CaO	%	8.26	8.32	2.74	33.2	13.55	2.15	45
	Na <sub>2</sub> O	%	1.74	1.73	0.15	8.5	2.08	1.42	45
	K <sub>2</sub> O	%	2.15	2.13	0.20	9.4	2.54	1.61	45
	As	mg kg <sup>-1</sup>	13.14	13.65	2.41	18.3	17.19	7.25	45

The average organic matter content was 10.25% for the sediment and 7.48% for the soil. The concentrations of Al, Fe, Mg, Na, and K in the sediments were similar to those in the upper crust [38], but the Ca concentration were higher in the sediment (average 18.27%) than that in the upper crust (average 3.85%). This result further demonstrated the Ca precipitation in the lake. In the soil around the Lake Qinghai, the major element concentrations were similar to those reported by previous studies [4,37,39,40].

### 3.2. Concentration of As in the Water, Sediment, and Soil

Dissolved As concentration in the water of Lake Qinghai ranged from 8.86 to 41.76 µg L<sup>-1</sup> (Table 2). The average As concentration (25.55 µg L<sup>-1</sup>) in water of Lake Qinghai is similar to that in other alpine lakes (27.5 µg L<sup>-1</sup>) in Qinghai-Tibet Plateau, China [36], but higher than that in Lake Taihu (2.5 µg L<sup>-1</sup>) [41] and Lake Dongping (7.3 µg L<sup>-1</sup>) [42]. For surface water in the agricultural evaporation ponds, evaporative concentration led to a major increase in As concentration from 108 to 2099 µg L<sup>-1</sup>, accompanied with high Cl<sup>-</sup> and electric conductivity [29]. With the evaporative concentration, similarly, the high As concentration is also observed in surface water from Rio Loa basin (average: 1400 µg L<sup>-1</sup>) [43] and the upper Paraguay basin (average: 1108.5 µg L<sup>-1</sup>) [30] and in shallow ground water beneath the southern Carson Desert (average: 160 µg L<sup>-1</sup>) [44]. Therefore, the evaporative concentration for the water of Lake Qinghai might be one of the reasons for its higher As concentration relative to its catchment rivers.

In the water of Buha River, dissolved As concentration ranged from 1.17 to 1.74 µg L<sup>-1</sup> (Table 2). The average As concentration (1.39 µg L<sup>-1</sup>) in the water of Buha River is one order of magnitude lower than that for rivers in Qinghai-Tibet Plateau (22.1 µg L<sup>-1</sup>, n = 104) [36].

In the sediment pore water of Lake Qinghai, dissolved As concentration ranged from 58.5 to 197.5 µg L<sup>-1</sup>, with an average of 107.8 µg L<sup>-1</sup> (Table 2). Statistical tests indicated that dissolved As concentration in the pore water was significantly ( $p < 0.05$ ) higher than that in the water of Lake Qinghai and Buha River (Figure 2). Similarly, As concentration in pore water is 10~60 times higher than that in bottom water in Lake Washington [45].

The high As concentration in pore water may be caused by the released of As from the sediment under reductive conditions [44,46–48]. The sediment of Lake Qinghai is usually characterized by reductive condition with negative Eh values [37]. Therefore, this reductive condition may lead to the release of As from sediment solid phases into the pore water of Lake Qinghai.

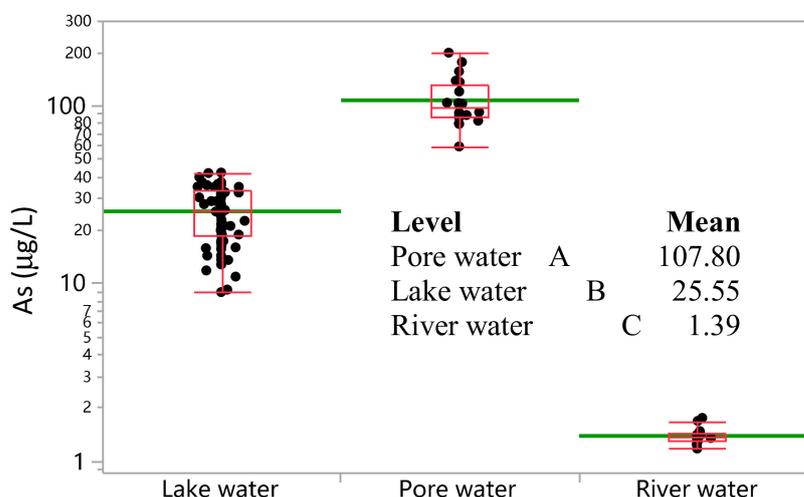


Figure 2. Comparisons of As levels in the lake water, river water and pore water.

The average concentration of As(III) and As(V) were  $0.35 \mu\text{g L}^{-1}$  and  $1.04 \mu\text{g L}^{-1}$  for the river water, respectively, and  $6.99 \mu\text{g L}^{-1}$  and  $18.56 \mu\text{g L}^{-1}$  for the lake water (Table 2). This result indicated that As(V) was the predominant As form both in the lake and river water. In general, As(V) is the most prevalent dissolved form of As in an aerobic freshwater and saltwater environment [26]. The average concentration ratio of As(III) to As(V) was 0.34 for the river water and 0.42 for the lake water. In addition, As(III) concentration was more correlated to the total As concentration in the river water, while in the lake water As(V) concentration was more correlated with the total As concentration (Figure 3). Therefore, after the inflow of Buha river into Lake Qinghai, transformation of As speciation between As(III) and As(V) may be occurring in the water. Redox potential (Eh) and pH are the two most important factors controlling As speciation [26]. In addition, arsenic speciation is also influenced by salinity [49], microbial activity [50], and the characters of local phytoplankton and zooplankton communities [51].

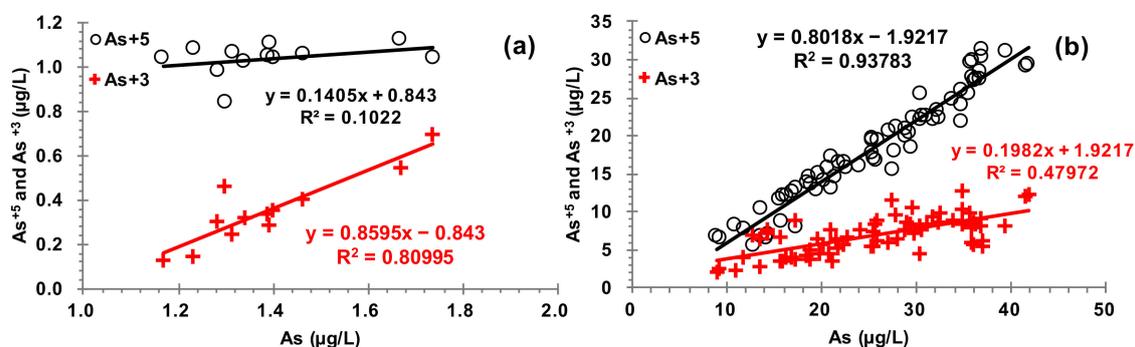
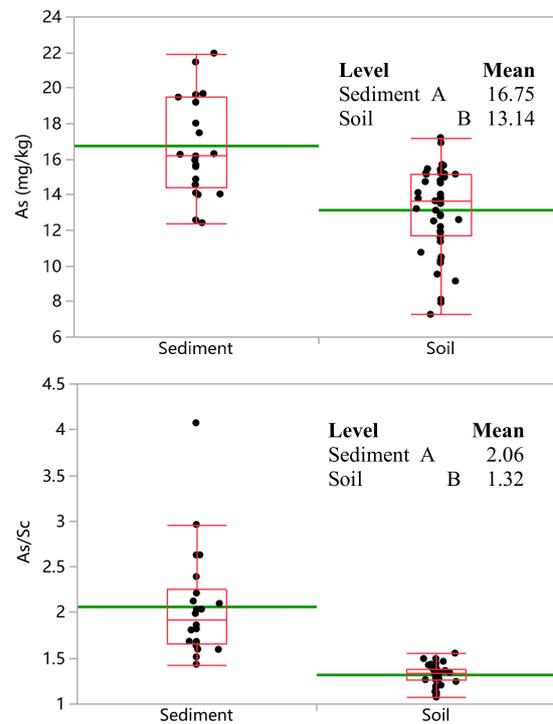


Figure 3. Relationships between As(III/V) and As concentrations in the water of Buha river (a) and Lake Qinghai (b).

In the sediment of Lake Qinghai, arsenic concentration ranged from  $12.4$  to  $21.93 \text{ mg kg}^{-1}$  (Table 2). The average concentration of As ( $16.75 \text{ mg kg}^{-1}$ ) in the sediment of Lake Qinghai is similar to that in the Yangtze's source area ( $18.06 \text{ mg kg}^{-1}$ ) [52], the Yungui Plateau Lake Ecoregion ( $14.16 \text{ mg kg}^{-1}$ ) [53] and the 275 alpine/arctic lakes across Europe ( $12 \text{ mg kg}^{-1}$ ) [2]. As shown in Figure 4, the average As concentration in the sediment of

Lake Qinghai was significantly higher than that in the soils ( $13.14 \text{ mg kg}^{-1}$ ) around the lake ( $p < 0.05$ ).



**Figure 4.** Comparisons of As levels and As/Sc ratio in the lake sediment and soil around the lake.

### 3.3. Relationships between As and Other Elements in the Water, Sediment, and Soil

The results of correlation analysis between As and other elements in the water, sediment, and soil are shown in Table 3. The significantly positive correlation between As and B concentrations was observed in the river water ( $p < 0.01$ ), lake water ( $p < 0.01$ ), and pore water ( $p < 0.05$ ). Our previous study reported that the geochemical process of B in Lake Qinghai was characterized by evaporative concentration and reductive release [10], which was similar to that of As in the present study. Arsenic concentration was significantly ( $p < 0.01$ ) positively correlated with concentrations of V, Sc, P, S, Cl, Mn, Fe, Mg, and Ca in the lake water rather than in the river water and pore water. This might be caused by evaporative concentration. Sodium and Cl are the conservative elements and can be used to indicate the level of evaporative concentration [29,30]. The high concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  in the lake water (Table 2) and their significantly positive correlation with As concentration (Table 3), therefore, further demonstrated that the higher As concentration in the lake water was related with the evaporative concentration process.

**Table 3.** Correlation coefficients of As with other elements in the water, sediment, and soil.

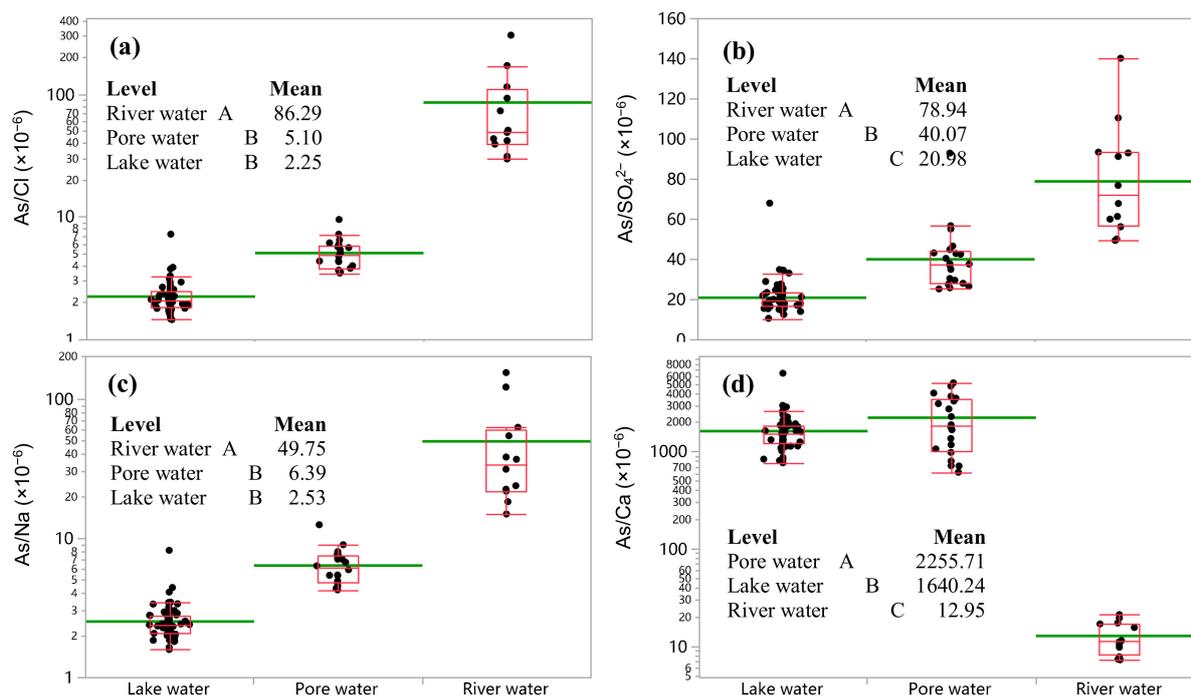
	As									
	River Water, <i>n</i> = 12		Lake Water, <i>n</i> = 69		Pore Water, <i>n</i> = 20		Sediment, <i>n</i> = 22		Soil, <i>n</i> = 45	
	R <sup>2</sup>	<i>p</i>	R <sup>2</sup>	<i>p</i>	R <sup>2</sup>	<i>p</i>	R <sup>2</sup>	<i>p</i>	R <sup>2</sup>	<i>p</i>
V	0.15	0.63	0.96	<0.0001	0.23	0.37	−0.02	0.94	0.87	<0.0001
Sc	−0.23	0.47	0.61	<0.0001	−0.30	0.22	0.04	0.86	0.89	<0.0001
B	0.77	0.00	0.93	<0.0001	0.58	0.01	0.27	0.22	0.31	0.04
P	0.39	0.21	0.84	<0.0001	−0.14	0.57	−0.32	0.14	0.49	0.00
S	−0.05	0.88	0.81	<0.0001	0.16	0.52	−0.66	0.00	0.29	0.05
Cl	0.52	0.08	0.87	<0.0001	0.41	0.09				
Mn	0.50	0.10	0.53	<0.0001	−0.04	0.88	0.09	0.68	0.81	<0.0001
Al	−0.45	0.14	−0.13	0.29	0.24	0.36	0.26	0.24	0.87	<0.0001
Fe	0.46	0.13	0.59	<0.0001	0.10	0.69	0.03	0.88	0.87	<0.0001
Mg	0.44	0.15	0.74	<0.0001	0.46	0.06	0.26	0.25	0.46	0.00
Ca	0.16	0.62	0.68	<0.0001	−0.37	0.17	−0.58	0.00	0.07	0.65
Na	0.59	0.05	0.88	<0.0001	0.35	0.15	0.21	0.36	−0.45	0.00
K	0.60	0.04	0.85	<0.0001	0.45	0.06	0.07	0.75	0.80	<0.0001

In the sediments of Lake Qinghai, As concentration was significantly negatively correlated with S and Ca concentrations ( $p < 0.01$ ). This might be due to a solid dilution effect caused by carbonate and sulfate precipitation. Abundant calcium carbonate precipitates as well as sulfate occurred in Lake Qinghai [4,5]. Arsenic is often rich in argillaceous sediments, while it is often poor in sandstone and calcareous sediments [12]. In addition, arsenic electrostatic attraction with positively charged mineral surface such as Fe/Mn oxides is a major force responsible for As sorption, other anions (e.g.,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$ ) with similar or higher charge densities may compete for the same sorption sites on the mineral surface and caused reduced As adsorption and even desorption [47].

In the soil around Lake Qinghai, As concentration was significantly ( $p < 0.01$ ) positive correlated with V, Sc, Mn, Al, Fe and K concentrations (Table 3). The Fe, Mn and Al (hydr)oxides generally play an important role in controlling the concentration of As in soils [47]. Scandium is a conservative metal with no significant anthropogenic source [54]. The significantly positive correlation between As and Sc concentrations indicated that the effect of anthropogenic activity on concentration of As in the soil around Lake Qinghai might be insignificant.

### 3.4. Ratio of As to Major or Reference Elements

As shown in Figure 5, the average  $\text{As}/\text{Cl}^-$ ,  $\text{As}/\text{SO}_4^{2-}$  and  $\text{As}/\text{Na}$  molar ratios were  $86.29 \times 10^{-6}$ ,  $78.94 \times 10^{-6}$ , and  $49.75 \times 10^{-6}$  in the water of Buha River, respectively, which were significantly ( $p < 0.05$ ) higher than those in the water and sediment pore water of Lake Qinghai. This indicated that partially As was transferred from dissolved phase to solid phase in the evaporative concentration process of lake water. However, the average  $\text{As}/\text{Ca}$  molar ratios in the river water were significantly lower than that in the water and sediment pore water of Lake Qinghai ( $p < 0.05$ ). This indicated that more Ca than As precipitated in the evaporative concentration process of lake water. In addition,  $\text{As}/\text{Ca}$  molar ratios in the sediment pore water were significantly higher than those in the lake water ( $p < 0.05$ ). This indicated that more As than Ca was secondarily released from sediment solid phases in the reductive condition.



**Figure 5.** Ratio of As to major or reference elements ((a): Cl, (b):  $\text{SO}_4^{2-}$ , (c): Na, (d): Ca) in the river water, lake water and pore water.

In the sediment of Lake Qinghai, the average As/Sc ratio was 2.06 (Figure 4), which was significantly ( $p < 0.05$ ) higher than that in the soil around the Lake Qinghai. The metal/Sc ratios have been often used to identify natural and anthropogenic sources of metals in sediments and soils [54]. The relatively high As/Sc ratio may indicate that relatively more As was enriched in the lake sediments.

#### 4. Conclusions

The average concentration of dissolved As was  $25.55 \mu\text{g L}^{-1}$  in the water of Lake Qinghai, which was higher than that in world fresh water and open sea. This is related to the evaporative concentration process of lake water. The average concentration of dissolved As was  $107.8 \mu\text{g L}^{-1}$  in the sediment pore water, which was much higher than that in the lake and river water. This can be ascribed to the secondarily release from the sediment's solid phase in the reductive condition. The average concentration of As in the lake sediment was  $16.75 \text{ mg kg}^{-1}$ , which was significantly higher than that ( $13.14 \text{ mg kg}^{-1}$ ) in the soil around the lake ( $p < 0.05$ ). The enrichment of As in the lake sediment was significantly higher than that in the soil around the lake. The concentration of As in multiple media could be used as a baseline to assess the influence of anthropogenic activities on As distribution in the Lake Qinghai basin.

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