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In situ, high-resolution evidence of metals at the sediment-water interface under ice cover in a seasonal freezing lake

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The ice cover in winter as a physical barrier and duration would profoundly impact on changes in endogenous metal loading, migration, and transformation. Although a gradual reduction in duration and occurrence of lake ice cover in boreal lake ecosystems has been confirmed, little attention to the ice-covered period is received compared to open water studies. In this study, novel-developed diffusive gradients in thin films (DGT, ZrO-Chelex) probes were deployed to obtain the *in-situ* and high-resolution information on metals (Cu, Zn, Pb, Mn, Cd, Cr, and As) at the sediment-water interface (SWI) in a seasonal ice-covered lake, Chagan Lake. In addition, "source-sink" characteristics of each metal related to their endogenous release were determined based on Fick's first law. Concentrations of labile metals at the SWI demonstrated significant spatial heterogeneity, peaking exactly below the SWI. Compared with other similar studies, concentrations of Pb (0.55 $\mu\text{g/L}$), Cr (0.58 $\mu\text{g/L}$), and As (2.4 $\mu\text{g/L}$) were a little higher even under-ice than that in other freshwater rivers and lakes, indicating potential pollution due to the agricultural intensification and petroleum extraction. The apparent diffusive fluxes suggested that sediments acted as a sink for Pb ($-0.01 \text{ mg m}^{-2} \text{ day}^{-1}$), Cr ($-2.37 \text{ mg m}^{-2} \text{ day}^{-1}$), and Cd ($-0.1 \text{ mg m}^{-2} \text{ day}^{-1}$), diffusing from the overlying water into the sediment, while Cu ($0.12 \text{ mg m}^{-2} \text{ day}^{-1}$), Zn ($0.75 \text{ mg m}^{-2} \text{ day}^{-1}$), Mn ($15.89 \text{ mg m}^{-2} \text{ day}^{-1}$), and As ($2.12 \text{ mg m}^{-2} \text{ day}^{-1}$) as a source from sediments into the overlying water. Dissolved oxygen was the principal factor (79.5%, $P = 0.032$), determining the variation of the available metals at the SWI. As the urgent need for research focused on under-ice ecosystem dynamics, this study addressed the previously unknown behavior

of the labile metals at the SWI and provided a unique perspective for the lake management during the ice-cover periods when external nutrient input was cut off.

KEYWORDS

Chagan Lake, *in-situ* high resolution, diffusive fluxes, winter, sediment-water interface

Introduction

More than half of the world's lakes (>50 million) are periodically frozen, and partially or fully covered with ice (Hampton et al., 2017). During the ice period, the ice cover significantly impacts the concentrations, migration, and transformation of metals due to the transportation differences between ice and water, and the elimination of wave action, which mixes the oxygen and contaminant (Ozersky et al., 2021). Besides, when the aqueous solutions are frozen, hydrophobic and hydrophilic compounds are known to become spontaneously segregated at grain boundaries of ice during the phase transition, leading to relatively higher concentrations of ions and metals in the water beneath the ice (Heger et al., 2006). Due to global warming, the duration and extent of lake ice cover in winter are predicted to decrease in many temperate lakes (Kamari et al., 2018). Therefore, it is vital to understand the biogeochemical dynamics of nutrients and contaminants underneath the ice (Hampton et al., 2017; Ozersky et al., 2021).

The accumulation of heavy metals in lake sediments poses a severe risk to benthic and aquatic biota and ecosystem function, ultimately, affecting human health through the food chain (Gall et al., 2015; Green and Planchart, 2018). The sediment-water interface (SWI) is one of the most important interfaces in the critical zone, and the micro-reactions and environmental changes of physical, chemical, and biological reactions dominate with a complex impact on the state and migration-transformation behavior of metals near the interface (Harper et al., 1998; Gall et al., 2015; Fan, 2019). Almost all the pollution and ecological problems are associated with aquatic environments at the SWI (Fan, 2019). Traditional sediment chemistry studies were mainly based on ex-situ measurements, which cannot reflect the actual information on heavy metals' physical and chemical characteristics (Ding et al., 2010; Ren et al., 2015). It has been verified that the diffusive gradients in thin films (DGT) is an ideal tool for the *in situ* evaluation of metal bioavailability in sediments (Menegario et al., 2017). Previous studies indicated that under anaerobic conditions, the concentrations of liable metals by DGT perform considerable apparent diffusion from sediment on the low dissolved oxygen (DO) condition (Ren et al., 2015; Yuan et al., 2020). Their surface binding characteristics with different solid phases (i.e., Fe/Mn oxides and organic matter) and metal binding

regulation are influenced by the pH, redox potentials, and pore water composition.

The Chagan Lake (CL) is the representative lake in the cold regions of northeast China, which acts as an essential ecological barrier against desertification (Bu et al., 2009; Liu et al., 2021). Research suggests that aquacultural development has dynamically increased the metal concentrations in the CL (Xie, 2021). However, most studies on metals currently focus on open water season, while studies in the ice-covered period have often been neglected or assumed to be less important (Hampton et al., 2017; Kamari et al., 2018). There is still a significant research gap in the understanding and estimation of stocks and fluxes of metals under ice cover. In this study, the ZrO-Chelex DGT technique was employed for the first time to obtain accurate information regarding the spatial distributions of labile Cu, Zn, Pd, Mn, Cd, Cr, and As at the SWI of CL during the ice-covered period. Due to redox conditions under ice cover, we hypothesized that considerable concentrations and release of labile metal would be found at the SWI due to redox conditions under ice cover, even though the cold temperature would significantly affect water quality in the following spring. This study would provide a brand-new insight into the control of internal metal loading during ice-covered periods when external input was cut off.

Materials and methods

Study area and sampling collection

As the largest inland lake in Jilin Province, the CL is located west of Songnen Plain, Northeast China. It covers an area of 372 km², holding 5.98×10^8 m³ of water. The average and maximum depths of the CL are 1.52 and 6 m. The CL is located in a semi-arid and sub-humid region with a long-term annual average temperature of 5.5°C. The duration of the ice cover is approximately 4 months, from late November to next March. The CL plays a vital role in the regional economic and cultural heritage and is well-known for winter fishing. The CL receives the discharge from Daan and Qianguo irrigation districts. Therefore, a substantial amount of N, P, and heavy metals flow into the lake with irrigation discharge.

An ice drill was used to prepare holes with a diameter of 50 cm on the surface of the CL on December 20th, 2020, when the winds over the lake were light. Six cores (Table 1) with 20 cm overlying water were collected using a gravity corer ($\varphi 90 \text{ mm} \times 500 \text{ mm}$) and then covered with a rubber plug on both ends. Water temperature, DO, pH, conductivity, and *chlorophyll a* were measured by a portable multi-probe (YSI 650 MDS, United States). The concentrations of DOC were determined by Xpert-TOC/TN. Surface sediment samples were collected using a grab sampler and then placed in acid-washed plastic bags. Then the samples were transported carefully to the laboratory and stored at -18°C for further analysis.

Preparation of diffusive gradients in thin films devices

The sediment cores were stabilized for 12 h to ensure the equilibrium at the interface between the sediment and the water. The DGT device involves a device consisting of four components: a ZrO-Chelex binding gel, a diffusive gel, a membrane filter, and a fixed shell ($2.5 \text{ cm} \times 18 \text{ cm}$). The ZrO-Chelex binding gel was prepared using the method described by Xu D. et al. (2012). The diffusive gel was prepared from polyacrylamide using the method published by Zhang and Davison (2002). Specifically, the ZrO-Chelex binding gel is on the top, and the diffusive gel is sandwiched between a Whatman membrane filter with a pore size of $0.45 \mu\text{m}$, and the three layers were stacked on the base of the fixed shell. The assembled device was immersed in a 0.01 mol L^{-1} NaCl solution, to which N_2 was added continuously for 16 h before use.

Application of the diffusive gradients in thin films device

The ZrO-Chelex DGT devices would simultaneously measure multiple labile cations and oxyanions, and were

provided by EasySensor Ltd (Nanjing, China)¹. During the application, the ZrO-Chelex DGT device was slowly inserted into the sediment cores for 72 h. Water temperature was simultaneously measured three times at each site during the deployment. The SWI was marked after being withdrawn and then washed with deionized water to remove the sediment particles. A ceramic cutter was then used to cut the binding gel at 2 mm intervals. The gel samples were transferred to a 1.5 mL PE bottle with $1.8 \text{ mL } 1 \text{ mol L}^{-1} \text{ HNO}_3$ for 24 h. Quality control was ensured by analyzing duplicate samples with a precision of three replicates of 15% (relative standard deviation). All the concentrations of metals and solutions were analyzed using an Agilent 7700 inductively coupled plasma mass spectrometer.

Statistical analysis

Determination of labile metal concentrations

The concentrations of (C_{DGT}) of each metal ($\mu\text{g/L}$) are calculated using:

$$C_{DGT} = \frac{M \times \Delta g}{D \times A \times T} \quad (1)$$

where M is the amount of the target analyte accumulated in the DGT device (μg); Δg is the total thickness of the diffusive gel and the membrane filter (cm); D is the diffusion coefficient of the target metal in the diffusive gel ($\text{cm}^2 \text{ s}^{-1}$); A is the area of the window of the DGT device (cm^2); T is the time that the system was allowed to stand still (s).

Estimation of the diffusive fluxes at the sediment-water interface

The net exchange flux F of each metal at the SWI can be estimated based on Fick's first law:

$$F = F_s + F_w = \left(-\phi D_s \frac{\partial c_s}{\partial x_s} \right) + \left(-\phi D_w \frac{\partial c_w}{\partial x_w} \right), \quad (2)$$

1 <http://www.easysensor.net>

TABLE 1 Sampling site information.

Sites	Latitude	Longitude	Air temperature $^\circ\text{C}$		Water temperature $^\circ\text{C}$		Wind speed m/s	Ice thickness mm	Water depth m
			Max	Min	Max	Min			
CG1	45.117667	124.270637	-10.3	-10.5	1.9	0.8	—	469.5	1.6
CG2	45.225368	124.104844	-11.8	-12.1	2.4	2.1	3.06	465.65	0.6
CG3	45.176735	124.167416	-10.1	-11	2	1.3	3.42	453.89	2
CG4	45.143761	124.214428	-9	-9.4	1.8	0.9	4.65	470.5	1.9
CG5	45.1158841	124.214273	-7.8	-8.8	1.5	1.1	5.36	503.8	2.45
CG6	45.108007	124.138007	0.5	0.4	-8.1	-8.4	5.36	557.87	3.2

where F is the diffusive flux at the SWI ($\text{mg m}^{-2} \text{ day}^{-1}$); F_s is the diffusive flux from the sediment; F_w is the diffusive flux from the overlying water; $\partial c_s/\partial x_s$ is the concentration gradient in the sediment; $\partial c_w/\partial x_w$ is the concentration gradient in the overlying water; x is the depth of the sediment (cm); c is the ion concentration (mg L^{-1}); D_s is the diffusion coefficient of each metal in the sediment, which can be calculated based on the molecular diffusion coefficient in water D_w and the surface sediment porosity ϕ .

Data processing and analysis

In this study, the diffusive flux patterns were produced using Microsoft Excel. SPSS Statistics 23.0 was used to analyze variance (ANOVA) and independent-samples t -tests. RStudio 6.5 was used to analyze correlation analysis. In addition, the RStudio 6.5 and Canoco 5 were used to perform redundancy analysis (RDA) to determine the factors influencing the metal profiles during the ice-covered period.

Results

Spatial profiles of labile metals during the ice-covered period

The DOC of the CL under ice in winter ranged from 10.29 to 27.42 mg/L (mean: 13.23 ± 7.06 mg/L); DO from 10.15 to 11.96 mg/L (mean: 11.41 ± 0.67 mg/L); ORP from 8.4 to 35.5 mV (mean: 27.55 ± 10.82 mV); Sal from 0.61 to 0.92 psu (mean: 0.70 ± 0.11 psu); TDS from 797 to 1,178 mg/L (mean: 910.17 ± 138.76 mg/L); Turbidity from 853.54 to 1,307.04 FNU (mean: $1,198.75 \pm 177$ FNU); and pH from 6.75 to 7.42 (mean: 6.96 ± 0.25). The mean values of DO and pH of CG2 were slightly lower than other sites (Table 2).

Concentrations of labile Cu ranged from 0.0005 to 1.99 $\mu\text{g/L}$ (mean: 0.18 $\mu\text{g/L}$); Zn from 4.43 to 18.81 $\mu\text{g/L}$ (mean: 8.06 $\mu\text{g/L}$); Pb from 0.28 to 23.61 $\mu\text{g/L}$ (mean: 0.55 $\mu\text{g/L}$); Cd from 0.06 to 0.29 $\mu\text{g/L}$ (mean: 0.09 $\mu\text{g/L}$); Cr from 0.11 to 16.18 $\mu\text{g/L}$ (mean: 0.58 $\mu\text{g/L}$); and As from 0.14 to 7.13 $\mu\text{g/L}$ (mean: 2.4 $\mu\text{g/L}$). The Mn

concentration ranged from 0.46 to 72.51 $\mu\text{g/L}$, the highest compared to the other metals (Figure 1). In the profile, the concentrations of all metals initially increased and then decreased with increasing depth peaking exactly below the water-sediment interface. The concentrations of Mn and Pb were considerably higher at site CG2 than at any other sampling site.

There were significant differences between different sampling sites in the concentrations of Mn ($P < 0.001$), Cu ($P < 0.001$), Zn ($P < 0.001$), and Pb ($P < 0.001$) by ANOVA analysis, as well as insignificant differences between the concentrations of Cd, Cr, and As at the SWI (from -20 mm to 20 mm) of CL during the ice-covered period.

Correlation analysis revealed that the C_{DGT} value for labile Cu was extremely significantly positively correlated with that of labile Zn ($R = 0.78$, $P < 0.001$) and Pb ($R = 0.75$, $P < 0.001$; Figure 2). The C_{DGT} value for Zn was significantly positively correlated with Pb ($R = 0.77$, $P < 0.001$). The C_{DGT} for Mn was significantly negatively correlated with Cu, Zn, and Pb values. There were no significant correlations between the C_{DGT} values for Cr and As and that of any other metals (Figure 2).

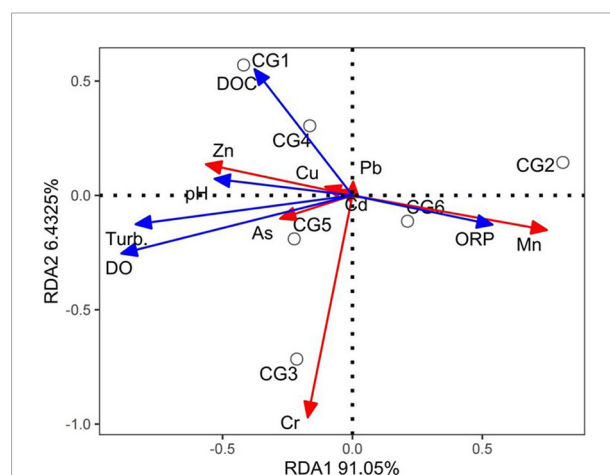
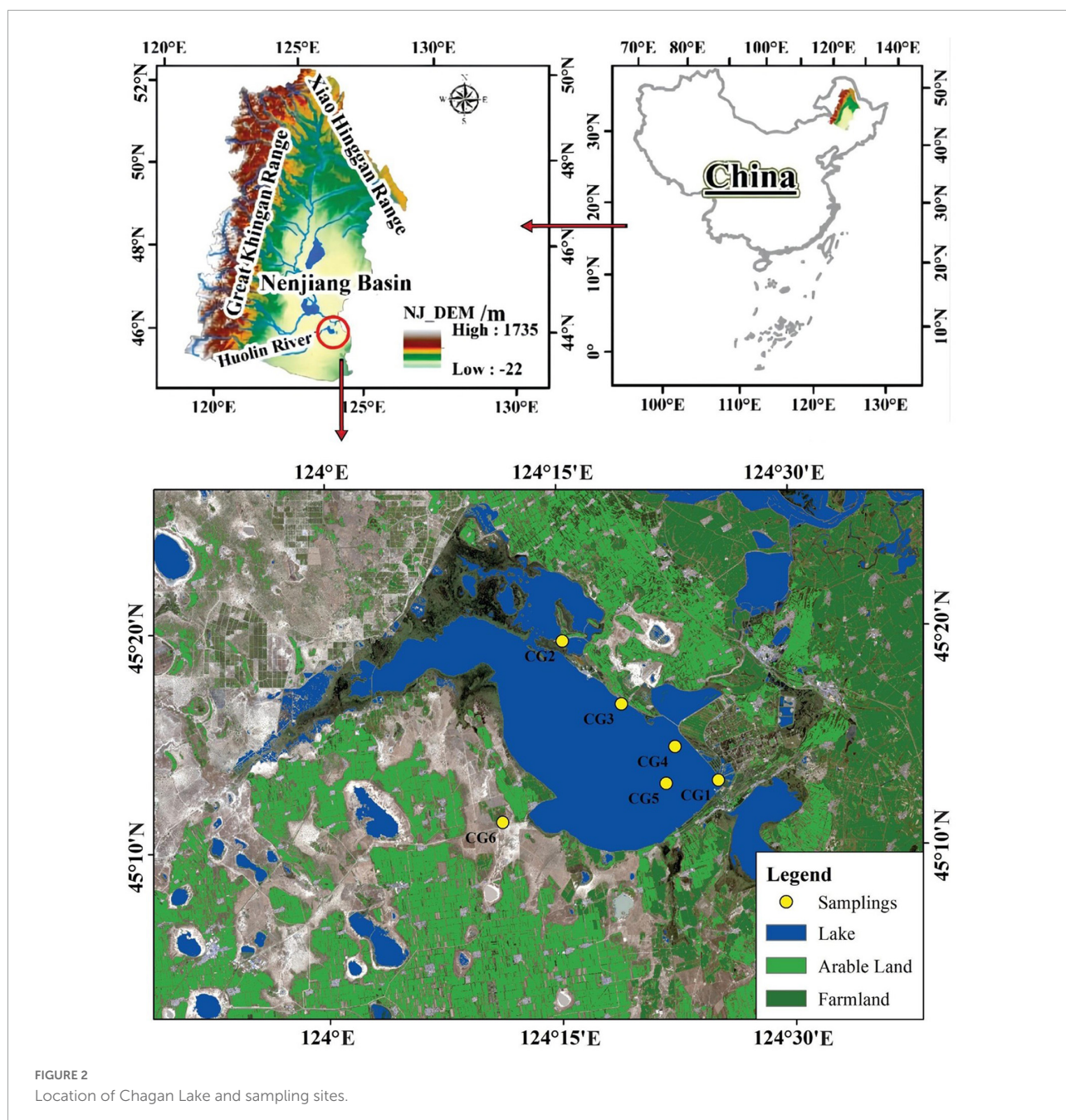


FIGURE 1 RDA analysis of influencing factors of metals during the ice-covered period.

TABLE 2 Physicochemical properties in Chagan Lake.

	DOC (mg/L)	DO (mg/L)	ORP (mV)	Sal (psu)	TDS (mg/L)	Turbidity (FNU)	pH
CG1	27.42	11.92	25	0.72	932	1,292	6.98
CG2	11.7	10.15	35.5	0.92	1,178	853.54	6.75
CG3	10.92	11.96	33.8	0.64	836	1,307.04	6.81
CG4	8.073	11.27	24.9	0.61	797	1,289.03	7.02
CG5	10.95	11.58	8.4	0.68	875	1,164.3	7.42
CG6	10.29	11.59	37.7	0.65	843	1,286.61	6.77
Mean \pm sd	13.23 ± 7.06	11.41 ± 0.67	27.55 ± 10.82	0.70 ± 0.11	910.1 ± 138.7	$1,198.7 \pm 177$	6.96 ± 0.25

DO, dissolved oxygen; DOC, dissolved organic carbon; ORP, oxidation-reduction potential; Sal, salinity; and TDS, total dissolved solids.



The apparent fluxes of metals across the sediment-water interface

The apparent diffusive fluxes of liable Cu ranged from -0.12 to $0.26 \text{ mg m}^{-2} \text{ day}^{-1}$ (mean: $0.12 \text{ mg m}^{-2} \text{ day}^{-1}$); Zn from -4.53 to $6.76 \text{ mg m}^{-2} \text{ day}^{-1}$ (mean: $0.51 \text{ mg m}^{-2} \text{ day}^{-1}$); Pb from -0.11 to $0.11 \text{ mg m}^{-2} \text{ day}^{-1}$ (mean: $-0.01 \text{ mg m}^{-2} \text{ day}^{-1}$); Cd from -0.34 to $0.02 \text{ mg m}^{-2} \text{ day}^{-1}$ (mean: $-0.10 \text{ mg m}^{-2} \text{ day}^{-1}$); Cr from -18.51 to $3.85 \text{ mg m}^{-2} \text{ day}^{-1}$ (mean: $-2.37 \text{ mg m}^{-2} \text{ day}^{-1}$) and As from -3.47 to 5.14 mg m^{-2}

day^{-1} (mean: $2.13 \text{ mg m}^{-2} \text{ day}^{-1}$; Figure 3). Concentrations of liable Mn ranged from 0.32 to $50.1 \text{ mg m}^{-2} \text{ day}^{-1}$, the highest among the other metals. Positive apparent diffusive fluxes were observed at most sampling sites for Cu, Mn, and As, indicating the upward movement from the sediment to the overlying water. Negative apparent diffusive fluxes were observed at most sampling sites for Zn, Pb, Cr, and Cd, with sediment as a sink.

The RDA analysis indicates that the DO explains 79.5% ($P = 0.032$) of the variation in the whole profile, and the RDA1 axis explains 91.05% of the variation in the SWI (Figure 4).

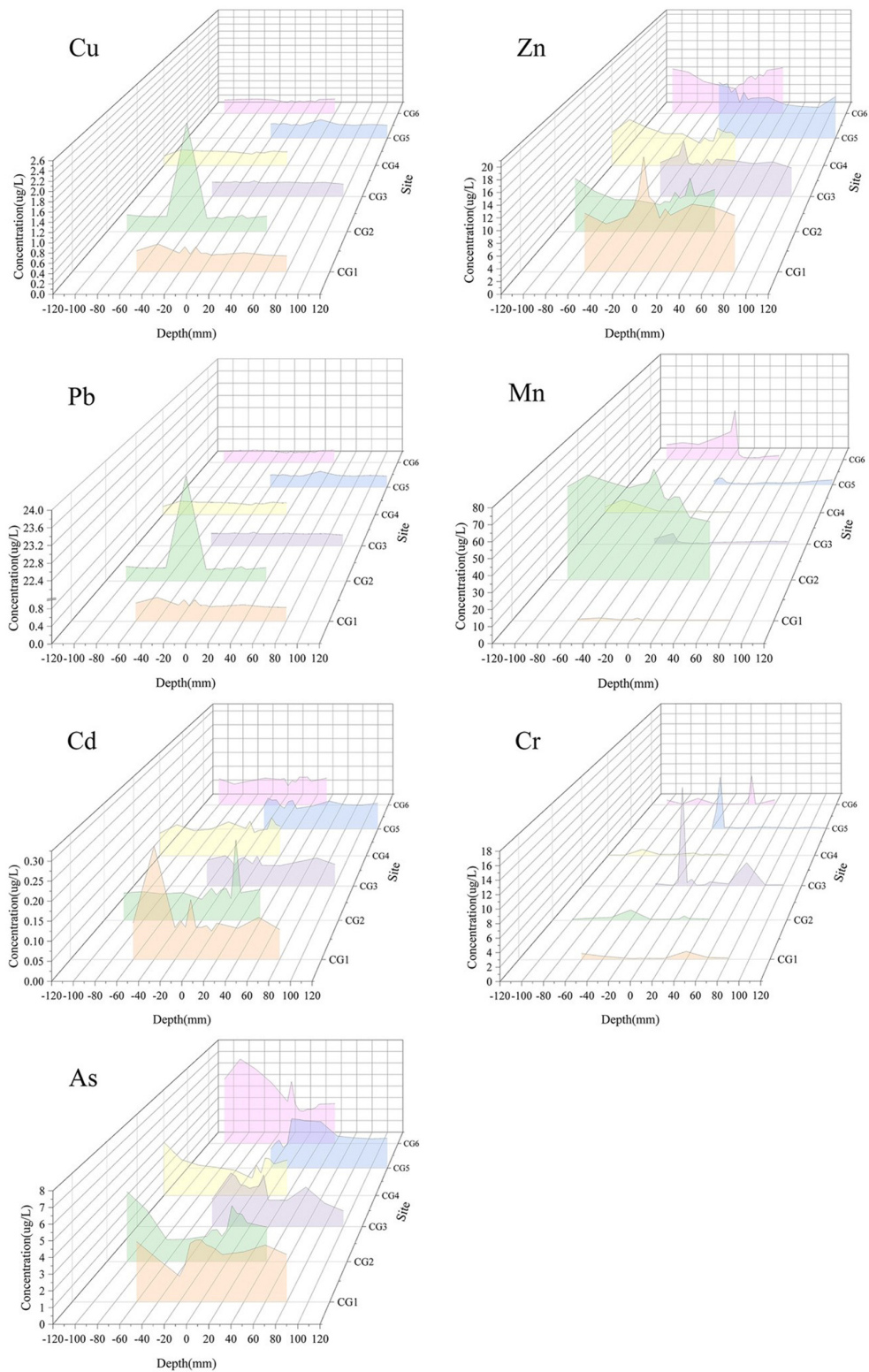
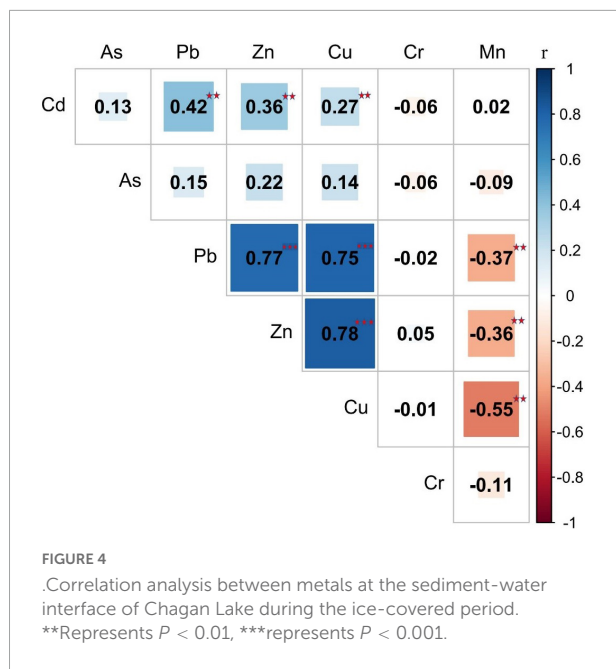


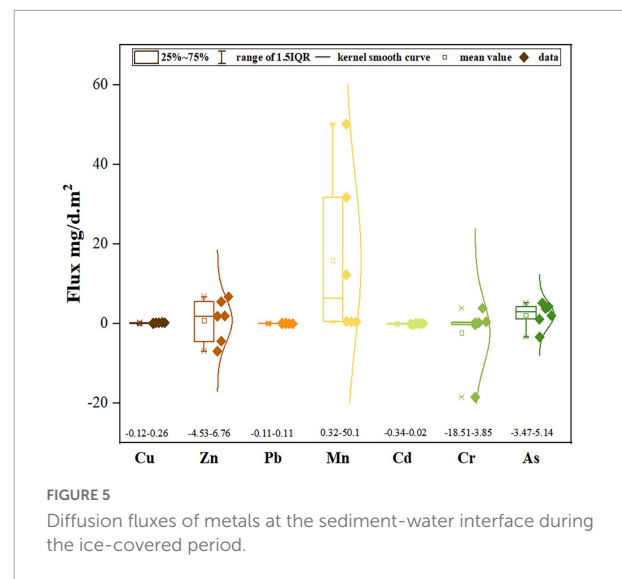
FIGURE 3
The vertical distributions of labile Cu, Zn, Pb, Mn, Cd, Cr, and As at the sediment-water interface during the ice-covered period of Chagan Lake.



Discussion

Spatial profiles of labile metals during the ice-covered period

The SWI is the boundary between the overlying water column and sediments, and this zone is easily affected by physical disturbance (e.g., temperature, currents caused by resuspension), biological processes (e.g., bioturbation generating mounds and trenches), and chemical process (Wu et al., 2014, 2016; Fan, 2019). These processes affect the migration and transformation of metals around the SWI in complex ways (e.g., oxidation, reduction, adsorption, desorption, and degradation; Voermans et al., 2017; Fan, 2019). In this study, peak concentrations of labile metals also appeared just below the SWI during the ice-covered period (Figure 5). The vertical variation of labile metals on the sediment profiles generally shows a decreasing trend with depth. Most metals in the surface sediment were reported in an active or incompletely degraded state, therefore they have a high tendency to participate in the biogeochemical process at the SWI (Ren et al., 2015; Wu et al., 2015; Liu et al., 2016). The behavior of labile metals near the SWI is significant because the dynamic chemical and biochemical processes occurring in surface sediment cause major transformations in the speciation/mobility of metals due to remobilization or sequestration from minerals/organisms (Wu et al., 2014). These processes can result in an increase in the CDGT values of the metals at the SWI. Moreover, the biological and physical disturbances increase the sediment's porosity and resuspended sediment particles, consequently inducing the release of contaminations from the sediment to



the pore water. This results in increases in the concentrations of labile metals in the pore water at the SWI (Song et al., 2005; Fan, 2019). A substantially higher average concentration was found at sampling site CG2 than at any other site ($P < 0.001$), indicating notable spatial heterogeneity (Figure 5).

Few studies were reported on labile metals by DGT technique during the ice-covered period in lakes in China, and it is only possible to compare our findings with the former research in Lake Xingkai (In press). Compared with the Lake Xingkai Basin, the CL had a considerably higher concentration of labile Cr (0.58 vs 0.06 $\mu\text{g/L}$), Pb (0.55 vs 0.26 $\mu\text{g/L}$), Cd (0.09 vs 0.04 $\mu\text{g/L}$), and As (2.4 vs 1.06 $\mu\text{g/L}$; Table 3). Different from Lake Xingkai Basin, located far away in the border area, the CL was extensively affected by human activity, such as petroleum extraction, the use of pesticides and fertilizers, and famous winter fishing, contributing to the accumulation of heavy metals (Zhang et al., 2008; Xie et al., 2010). Besides, there were fewer inflow rivers to the CL, thus intensifying the accumulation of metals with low flow. A much lower concentration of labile Mn (12.5 vs 366.27 $\mu\text{g/L}$) was found compared to the Lake Xingkai basin but similar to the background value of soil in Jilin Province (452.65 ppm), which might be caused by the diagenetic process (Zhao et al., 1987). Compared with world average freshwater, concentrations of most metals in CL were a little higher even in a cold season, while much lower than in the developed warm area (Lake Xuanwu), indicating potential pollution in the CL.

Similar to previous studies (Yuan et al., 2011, 2014), strong correlations were found between Cu, Zn, and Pb concentrations, while there was a significantly negative correlation between Mn and Cu, Zn and Pb (Figure 2). This might be caused by Mn oxides in sediments mainly origin from natural geochemical processes (Yuan et al., 2014; Maina et al., 2019). Besides, Mn/Fe oxides have a strong capacity to adsorb metals due to the large specific surface areas and regular porous structures (Xu L. et al., 2012;

TABLE 3 The Cdgt of labile metals ($\mu\text{g/L}$) in Chagan Lake and other areas.

	Cu	Zn	Pb	Mn	Cd	Cr	As	References
Chagan Lake	0.18	8.06	0.55	12.5	0.09	0.58	2.4	This study
Lake Xiaoxingkai	0.05	8.91	0.26	366.27	0.04	0.04	1.64	Unpublished data
Lake Xingkai	0.11	10.83	0.26	302.9	0.04	0.06	1.06	Unpublished data
Sava River, Croatia	0.166	1.86	0.02	8.24	0.0016	0.033		Dragun et al., 2008
Xizhi River	2.03	31.12	1.55					Gao et al., 2021
Lake Xuanwu	1.32	4.43	1.47	0.68	0.3	5.87	5.85	Wang, 2018
Aha Lake	0.54	2.17	0.06	28.34	0.02	0.11	0.71	Fei et al., 2021
World average freshwater	2	10	0.2	5	0.07	0.5	2	Foerstner and Wittmann, 1980

Xia et al., 2020). Therefore, the reductive dissolution of iron and manganese oxides would release labile metals (e.g., Cu, Zn, and Pb), resulting in higher concentrations (Yuan et al., 2011). Moreover, previous research has shown that Mn oxides in sediment are essential oxidants for the degradation of OM (Luo et al., 2000). The notable release of dissolved Mn at the SWI of Aha Lake was a result of the participation of MnO_2 in OM degradation as an oxidant (Liu, 2019). The flux estimates obtained in this study similarly revealed a marked release of dissolved Mn at the SWI of CL. This may be an essential factor leading to the significant negative correlations between the concentration of Mn and Cu, Zn and Pb.

Source-sink characteristic of internal metal loading under the ice

Lake sediment can function either as an internal metal load or sink. Therefore, studies on the source-sink characteristics at the SWI are becoming a hotspot (Templeton et al., 2000; Wang et al., 2015). It is found that the diffusive fluxes of Zn, Pb, Cr, and Cd were negative, suggesting that the sediment acted as a sink for these metals. In contrast, the diffusive fluxes of Cu, Mn, and As were positive, indicating sediments as a source. During the initial stage of the ice-covered period in winter, the DO concentration in the CLs water was still relatively high, and the SWI might still be in a continuously oxidative environment. Under these conditions, as micro- and nanoparticles, Fe/Mn oxides known for their high activity and large surface areas were important geological adsorbents for metals such as Zn, Pb, Cr, and Cd (Banks et al., 2012; Wang, 2018; Liu, 2019). The OM-bound metals are another major form of these metals in sediment (Zoumis et al., 2001; Fan et al., 2002, 2019). The OM bound with metal degradation was to be reported released into the overlying water. In lake sediment, sulfides, after sulfate reduction, also have a strong ability to bind to metal ions. This produces insoluble metal sulfides, one of the major forms of metals in sediment (Burdige, 1993; Toro et al., 2002).

Biological disturbances resuspend sediment particles and metal sulfides were exposed to water containing active aerobic

organisms (Caille et al., 2003). In the presence of sulfur-oxidizing bacteria, metal sulfides were oxidized into sulfates, releasing metals bound to the sulfides (Vera et al., 2013). The oxidation of sulfides produces H^+ and therefore reduces the pH at the SWI (Miao et al., 2006). The relatively high DO content and the low water pH of 6.75 during the ice-covered period indicated a weak release of Cu and As.

Mechanisms behind the metal distributions

DO was found as the primary factor (79.5%, $P = 0.032$) affecting the vertical distribution of the labile metals at the SWI. In sediments, metals combine with Fe/Mn oxides and sulfides, forming insoluble oxidizable states. As the DO concentration increased, the Fe (II) and Mn (II) released due to oxidation rapidly form colloidal Fe and Mn oxides or hydroxides, which have a strong ability to adsorb metal ions and are highly susceptible to co-precipitating with metals. During the freezing period, ice cover and continuous mineralization of organic aggregates would lead to conditions of hypoxia and anoxia at the SWI. This created favorable conditions for endogenous metal release from bounded to Fe/Mn/S oxides into the pore water (Toro et al., 2002; Shao et al., 2012; Xia et al., 2020). Therefore, changes in DO concentration control the release and precipitation of metals. Moreover, metals bound to OM were a major form in sediments (Zoumis et al., 2001; Fan et al., 2002). When OM bound to metals was degraded by microorganisms, these metals were released into the water. As a principal factor affecting microorganism-induced degradation (Canfield et al., 1993), DO also substantially impacts the concentrations of metals in the water. DO dynamics with a high spatiotemporal resolution by planar optode should be obtained in further study.

Conclusion

Diffusive gradients in thin films technique was firstly employed to acquire high-resolution millimeter-scale *in situ*

information regarding the labile Cu, Zn, Pb, Mn, Cd, Cr, and As at the SWI in the CL during the ice-covered period. The labile metals at the SWI of CL displayed markedly different spatial and vertical distribution patterns. Specifically, the concentration of each metal peaked exactly below the interface. Based on Fick's first law, the diffusive fluxes revealed that the sediment acted as a sink for Zn, Pb, Cr, and Cd, while a source for Cu, Mn, and As in winter. Compared with other studies, Pb, Cr, and As concentrations under-ice were even slightly higher, indicating potentially ecological risk. *In situ* passive sampling techniques could help inform potential ecological or human health risks associated with metal contamination without disturbing aquatic biota. DO was identified as the primary factor affecting the vertical distribution of the labile metals at the SWI. It may be worth considering actions to take into account redox processes and control the O₂ dynamics when management decision-making during remediation planning. Our results quantified the endogenous metal concentrations and diffusion fluxes across the SWI during the ice-cover period, giving insight into lake water quality management in temperate seasonal frozen lakes.

Data availability statement

The original contributions presented in this study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

XZ and YY proposed and structured the study. QW, ZW, YzZ, QY, and SL were involved in the experiments. XZ, QW, XD, and ZW wrote the manuscript. QW, XD, and YjZ made the figure. XZ, QW, and YY reviewed and improved the English of the manuscript and made a funding acquisition. All authors participated in discussion of the research.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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