Effect of freeze–thaw cycles on soil physicochemical properties and fractions of Pb and Cr in the northeastern Qinghai–Tibet Plateau

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Abstract: Simulation experiments were conducted using soils in the northeastern Qinghai–Tibet Plateau to explore the effects of freeze–thaw cycles on soil physicochemical properties, Pb and Cr distribution, and fraction transformation. Soils were incubated at -15°C for 24 h and at 5°C for 24 h to complete a freeze–thaw cycle. The soil physicochemical properties and fractions of Pb and Cr were analyzed after serial freeze–thaw treatments. The results showed that different freeze–thaw cycles and water content affected soil physicochemical properties and fractions of Pb and Cr to some extent. The cation exchange capacity increased significantly in agricultural and pastoral soils after five freeze–thaw cycles. The sand proportion of soil in an urban area decreased at 60 cycles. Freeze–thaw cycles did not change the functional groups and mineral constituents of the soils. The infrared peaks of soils with different freeze–thaw conditions were very similar. The freeze–thaw treatment influenced the mobility, chemical fractions of Pb and ecological risk in most of the soils. The exchangeable Pb in agricultural and pastoral areas increased from 0.19 to 1.52/0.90% after 5/10 freeze–thaw cycles with 60% water content. The ecological values of Pb in urban soil were 8.32/7.38% higher at 10/15 freeze–thaw cycles compared with the control treatment. Hence, these findings provide useful information on physicochemical properties and fraction transformation of Pb and Cr in soils undergoing freeze–thaw cycles, and offer an additional insight on Pb and Cr behaviors in cold and freezing environments.

Keywords: freeze–thaw cycle; Pb and Cr; fractions; ecological risk; the northeastern Qinghai–Tibet Plateau

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Elevated concentrations of trace elements and emerging contaminant pollution have attracted wide attention (Lu *et al.* 2020a, b, 2021a, b; Wen *et al.* 2019; Wu *et al.* 2016, 2020). Human activities such as industry and mining, along with accelerated development of urbanization and agricultural production increase the ecological risk of pollutants (Chandraiah 2016; Li *et al.* 2018, 2020a; Lu *et al.* 2020c; Wu *et al.* 2018). The toxicity of trace elements depends not only on their total concentrations but also their bio-availability (Chen *et al.* 2018; Li *et al.* 2020b). Different chemical fractions, especially the exchangeable fractions, affect the toxicity of trace elements while the chemical fractions and ecological risk of trace elements are obviously influenced by soil components and properties (Xiao *et al.* 2016). The freeze–thaw cycle (FTC) is one of the important processes that affect the behavior of trace elements through changing physical structure, specific surface area, organic matter content, and other soil properties (Nagare *et al.* 2012; F. Wang *et al.* 2016; Q. Wang *et al.* 2020). Therefore, it is necessary to study the fraction transformation of trace elements after FTCs.

The FTC is a common climatic phenomenon in the high-latitude regions and NE of China (Ran *et al.* 2012), which gradually affects geochemical processes in soil (Lehrsch 1991; Oztas and Fayetorbay 2003; Hou *et al.* 2020). Significant effects of FTCs on soil components and properties have been widely investigated (Zhang *et al.* 2016; Liu *et al.* 2019). FTCs reduce the diameter of the soil

particles, destroy the soil structure and release dissolved organic matter that can re-mobilize soil trace elements (Dagesse 2011; Wei *et al.* 2019). FTCs change soil-water retention capacity and the soil pore structure significantly as well as increase the pore connectivity and total imaged porosity, leading to an irregular pore shape and a complex pore structure (Liu *et al.* 2021). FTCs can also have a considerable impact on the stability of minerals in soils, which in turn increases concentrations of trace elements in leachate (Sanchez *et al.* 2009; Wei *et al.* 2015). FTCs affect microbial activities, extractable N concentration and community structures in soil (Kværne and Øygarden 2006; Feng *et al.* 2007; Lu *et al.* 2019; Watanabe *et al.* 2019). Freeze–thaw treatment not only causes instability of P and N loss behavior but also gives rise to increased diversity among various soil samples (Cheng *et al.* 2021). Soil aggregate stability and density are also strongly altered by FTCs (Chamberlain and Gow 1979; Ghazavi and Roustaei 2013; Zhang *et al.* 2016). An increase in dissolved organic carbon (DOC) is a significant effect of FTCs in soil (Wang and Bettany 1993; Grogan *et al.* 2004; Han *et al.* 2018).

It is generally regarded that FTCs can also decrease the adsorption and desorption capacities of trace elements compared to the unfrozen soil (Dang *et al.* 2012; Wang *et al.* 2017). With decreasing temperature and increasing frequency of FTCs, the absorption amounts of trace elements in soil also decrease. FTCs are

also important for the transport of trace elements from soil to aquatic environments (Quinton and Catt 2007; Wang *et al.* 2016). Previous research has demonstrated the great potential for increasing Pb immobilization and promoting the formation of both outer-sphere and inner-sphere complexes through successive FTCs (Du *et al.* 2020). Another study showed that long-term FTCs led to decreased pH and increased Pb concentration in the leachate (Yang *et al.* 2021). Some researchers concluded that the frequency of FTCs and soil–water content have a significant effect on the chemical fraction transformation of Cd in soil (McIntyre and Guéguen 2013); FTCs were observed to increase the labile Cd and Pb content (Hou *et al.* 2020). The results may have significant implications when considering ecological risk assessments of trace elements in climates experiencing seasonal FTCs (An *et al.* 2020). Based on the above research, FTCs might have an impact on the distribution of trace elements among various fractions in soil of the northeastern Qinghai–Tibet Plateau. In the case of intense changes in temperature between day and night, soil will continuously undergo FTCs during the storage period and alter the ecological risk of trace elements. However, available studies on trace elements under FTCs have mostly focused on the regions of the NE of China, while research on trace elements in the soil of the Qinghai–Tibet Plateau is rare. Hence, a deeper understanding of the effects of FTCs on trace elements is necessary.

In this study, soils from different areas in the northeastern Qinghai–Tibet Plateau were used to conduct laboratory simulation experiments to determine the effect of FTCs on the behavior of Pb and Cr in the samples. Under different freeze–thaw conditions, the fraction transformation and ecological risk from Pb and Cr in soils were explored. The purposes were (1) to investigate the changes in physicochemical properties, (2) to analyze the changes in Pb and Cr fractions and (3) to assess the ecological risks from Pb and Cr as affected by FTCs. The results may help us to better understand the behavior of Pb and Cr in soil.

Materials and methods

Site description and soil samples

The study area was located on the northeastern Qinghai–Tibet Plateau, China. FTCs widely occur in this region. The major soil type in the study area was sandy clay loam, with an alkaline pH (Wu *et al.* 2018). After consideration of the ranges of average lowest temperatures (-7.1°C), as well as average highest temperatures ($+8.0^{\circ}\text{C}$) during the freeze–thaw seasons in 1961–2017 (Yang *et al.* 2019), we chose -15°C and $+5^{\circ}\text{C}$ as the freezing and thawing temperatures in the lab-simulated experiments, respectively.

Table 1. Tessier sequential extraction scheme

Fraction (X-Pb or Cr)	Extraction procedures
Exchangeable fraction (EXCH-X)	MgCl ₂ 8 ml, pH 7, 1 h, continuous agitation, room temperature
Carbonates fraction (CARB-X)	NaOAc 8 ml, pH 5, 5 h, continuous agitation, room temperature
Fe-Mn oxides fraction (Fe/Mn-X)	0.04 M NH ₂ OH·HCl in 25% HOAc 20 ml, 6 h, agitation occasionally, $96 \pm 3^{\circ}\text{C}$
Organic matter fraction (ORG-X)	0.02 M HNO ₃ 3 ml + 30% H ₂ O ₂ 5 ml, pH 2, 2 h, agitation occasionally, $85 \pm 2^{\circ}\text{C}$. Add 30% H ₂ O ₂ 3 ml, repeat 3 h, cool and then add 3.2 M NH ₄ OAc in 20% HNO ₃ 5 ml, 0.5 h, continuous agitation, room temperature
Residual fraction (RES-X)	HClO ₄ : HNO ₃ : HF = 1 : 3 : 7, dryness, again HClO ₄ : HNO ₃ : HF 1 h, HCl 2 ml, dryness, 50% HNO ₃ 10 ml, make up to 50 ml with distilled water

Soils used in this study were collected in the summer of 2018. The sampling method referred to the Technical Specification for Soil Environmental Monitoring (HJ/T 166-2004). The soil sampling sites covered six kinds of zones including background area, urban area, industrial area, mining area, agricultural and pastoral area and salt-lake area. The topsoils (0–20 cm), which are sensitive to climate change, were collected in these six zones. Roots, stones and vegetation were removed, and the soils were air-dried, mixed and stored at 4°C in darkness until use.

Freeze–thaw procedure

A total of 200 g of sieved soil were weighed and placed in a plastic bag. For the freeze–thaw time-simulated experiment, a soil sample containing 60% of field capacity was completely frozen at a temperature of -15°C for 24 h, followed by thawing at 5°C for another 24 h. The above-described procedure is referred to as one FTC. The calculation of field capacity is

$$\Phi = \left[\frac{M_2 - M_1}{M_1} \right] \times 100\%$$

where Φ is the field capacity, M_1 and M_2 are the weights of the dry and wet samples, respectively. In this study, each sample underwent a freeze–thaw frequency of 1, 5, 10, 15 or 60 times, designated as F1, F5, F10, F15 and F60, and an unfrozen treated soil considered as a control was marked as F0. For the water content of the freeze–thaw-simulated experiment, the water ratio of the field capacity was set as 40, 60, 80 and 100%, denoted as W40%, W60%, W80% and W100%. These soil samples underwent a fixed freeze–thaw frequency of 15 times. The same methods were used to determine pH value, cation exchange capacity (CEC), texture, morphology, functional groups and mineral constituents of the treated soils with different FTCs and water contents.

Physicochemical properties; Pb and Cr analysis

The pH was determined by measuring the supernatants with a solid–water ratio of 1:2.5 using a Myron L 6PII instrument (Myron L Company, Carlsbad, USA). The CEC of the soil was determined by the exchange method (Page *et al.* 1982), its texture was determined by the Bouyoucos hydrometer method (Shirazi and Boersma 1984). The soil types were determined using the taxonomy of the United States Department of Agriculture (Minasny and Mcbratney 2001). Scanning electron microscopy (SEM JSM-5610LV, JEOL, Japan) was used to investigate the surface morphology of all soil samples. Fourier transform infrared spectra of all samples were acquired by Nexus (Thermo Nicolet Corporation, USA). The mineral constituents were measured by X-ray diffraction (XRD) spectrometry (Axios, PANalytical, The Netherlands).

All experimental vessels were soaked for 24 h with HNO₃, cleaned with deionized water and dried before use. The total amounts of Pb and Cr were analyzed according to Li *et al.* (2018). The Pb and Cr were digested using concentrated HCl–HNO₃–HF–HClO₄, and their concentrations were determined by inductively coupled plasma–mass spectrometry (NexION2000B, PerkinElmer Inc., USA). The recovery rates of Pb and Cr ranged from 80 to 120%, and the relative standard deviation (RSD) of replicates was less than 5%. The Pb and Cr were divided into five types of fractions: exchangeable fraction (EXCH-X), carbonate fraction (CARB-X), Fe-Mn oxide fraction (Fe/Mn-X), organic matter fraction (ORG-X) and residual fraction (RES-X) according to the Tessier sequential extraction procedure (Tessier *et al.* 1979). The operating conditions used for each extraction and descriptions of the five fractions are given in Table 1. After each sequential extraction procedure, the supernatants were collected by centrifuging at 8000 rpm for 10 min and filtering through a 0.45 μm cellulose

Table 2. Site description and physicochemical properties of tested soil samples in the study area

Site area	Longitude	Latitude	pH	CEC	Texture		
					Clay	Silt	Sand
Urban area	101.75°E	36.63°N	7.30	12.97	24.40	19.52	56.08
Agricultural and pastoral area	100.85°E	36.98°N	7.94	18.12	17.48	19.98	62.54
Mining area	95.55°E	37.32°N	8.40	2.29	24.44	7.33	68.23
Industrial area	94.94°E	36.38°N	8.91	4.77	27.31	12.41	60.28
Salt-lake area	99.07°E	36.75°N	8.73	8.46	47.35	27.41	25.24
Background area	97.75°E	35.08°N	7.92	9.33	24.99	24.99	50.02

acetate syringe filter. The residue was washed with 10 ml Milli-Q water.

Ecological risk assessment

A risk assessment code (RAC) was used to determine the ecological risks of Pb and Cr in soils. The RAC was calculated as the percentage sum of EXCH-X and CARB-X (Xiao *et al.* 2016), and was classified into five levels including safe (<1%), low risk (1–10%), medium risk (11–30%), high risk (31–50%), and very high risk (>50%) according to previous studies (Chen *et al.* 2018; Li *et al.* 2020b).

Results and discussion

Change in soil physicochemical properties affected by FTCs

The pH values of soils in the urban area, the agricultural and pastoral area, the mining area, the industrial area, the salt-lake area, and the background area reached 7.30, 7.94, 8.40, 8.91, 8.73 and 7.92, respectively (Table 2). It is worth noting that during freeze–thaw ageing, the pH value in soil of the urban area showed a definite

increasing trend (Fig. 1a). Compared to the control treatment, the pH of the urban soil at 60 FTCs was 12.5% higher. Interestingly, the pH of the soil in the agricultural and pastoral area at 10 FTCs was the highest, while the value in the mining area at 10 FTCs was the lowest. The pH in the salt-lake and background areas under different freezing treatments showed the same trends, while that in the industrial area changed slightly at different FTCs. In addition, with an increase of freezing water content, the pH values of the urban soil gradually increased. The values in the mining and salt-lake areas with different water content showed the same trends (Fig. 1d).

CEC refers to the amount of readily exchangeable cations existing in a diffuse layer (Liu *et al.* 2019). Table 2 shows that soils in the urban and agricultural and pastoral areas had the largest CEC, reaching *c.* 12.97 and 18.12 cmol kg^{-1} , respectively. Figures 1b and e show the variation in CEC of soils in six areas with different FTCs and water content. With an increase in the number of FTCs, the CEC in the different areas showed considerable irregular fluctuation. It increased significantly in the urban soil with 1 and 60 FTCs, as it did also in the agricultural and pastoral soils with an increase to 5 FTCs. CECs in the mining, industrial, salt-lake and background areas had small ranges of fluctuation with different FTCs. With an increase in the water content of freeze–thaw, the CEC different areas showed roughly the same regular fluctuation with different FTCs. It

Fig. 1. Variation in pH and cation exchange capacity for different freeze–thaw cycles (FTCs) and water content; UA, APA, MA, IA, SLA and BA refer to the urban, agricultural and pastoral, mining, industrial, salt-lake and background areas, respectively. F0, F1, F5, F10, F15 and F60 refer to the number of freeze–thaw cycles (0, 1, 5, 10, 15, 60 cycles), and W40%, W60%, W80% and W100% refer to water ratio of field capacity (40, 60, 80 and 100% water ratio).

Fig. 2. Morphologies of soils in different areas for different FTCs and water content. For an explanation of the symbols see Figure 1.

increased significantly in the agricultural and pastoral area with 40% water content, and slightly with up to 100% water content. Soils in the mining, industrial, salt-lake and background areas had small ranges of fluctuation with different water content.

The target soils in the urban, agricultural and pastoral, industrial and background areas treated by freeze–thaw for different cycling times and water content changed significantly, unlike those in the mining and salt-lake areas (Figs 1c and f). The texture of soil in the urban area was significantly affected by 60 FTCs compared to the control and other freeze–thaw treatments. The sand proportion of soil in the urban area decreased at 60 FTCs, while the silt proportion increased significantly. The sand proportions in the agricultural and pastoral, industrial and background areas decreased with freeze–thaw at different cycling times and water content, while the silt proportions in these areas increased, and the clay proportions changed only slightly. FTCs did not remarkably change the sand, silt and clay proportions of soils in the mining and salt-lake areas. Combined with the morphology of soils at different FTCs and water content, the micro-morphology of most soils under different freeze–thaw conditions changed dramatically as a result of the FTCs (Fig. 2).

The infrared spectra and XRD patterns of soils in the six areas treated by freeze–thaw with different FTCs and water content are illustrated in Figure 3. Slight differences exist in the infrared spectra of the soils at different cycling times and water content (Fig. 3(a1–a6)). Bands were identified at $3650\text{--}3350\text{ cm}^{-1}$, which represent the N–H/O–H stretching vibration due to the presence of cellulose (Venkateswarlu *et al.* 2013). The bands around 2930 cm^{-1} reveal the asymmetric C–H stretching vibration, representing aliphatic groups (An *et al.* 2020). The bands of soils with peaks at $1630\text{--}1410\text{ cm}^{-1}$ are attributed to the presence of –COOH, while those around 1100 cm^{-1} are ascribed to amine and alcohol groups (Rafiq *et al.* 2017). The peaks near 778 cm^{-1} are explained by the presence of Si–O–Si. The infrared peaks of the soils with different freeze–thaw conditions were very similar, indicating that all the soils had similar functional groups. However, the relative intensity of the groups was affected by FTCs, indicating that repeated freeze–thawing increased or diminished the abundances of functional groups in the soils. XRD patterns showed that soils treated by freeze–thaw with different cycling times and water content were

mainly composed of quartz, calcite, muscovite, albite and dolomite (Fig. 3(b1–b6)). The XRD patterns of all soils with different treatments were very similar, indicating that the freeze–thaw treatment did not affect the mineral constituency of soils in the study area.

Changes in Pb and Cr fractions under FTC

The bio-availability and mobility of Pb and Cr are related to their distribution among various fractions in the soil. To investigate how the transformations of Pb and Cr were affected by FTCs in soil, the amount of Pb and Cr fractions under different freeze–thaw conditions were measured throughout the experiment as shown in Figure 4. The statistical results showed that the concentrations were affected by the FTCs.

The variations in Pb concentration demonstrated that transformations among Pb fractions occurred during different FTCs and water content (Fig. 4(a1–a6)). The concentrations of EXCH-Pb and Fe/Mn-Pb in urban soil were very low, accounting for less 0.1%. After different FTCs, these concentrations changed slightly, while those of CARB-Pb and ORG-Pb mostly increased significantly, and that of RES-Pb decreased significantly. After 5 and 10 FTCs at 60% water content, EXCH-Pb in soils from the agricultural and pastoral area increased from 0.19 to 1.52 and 0.90%, respectively. Compared to the soil of the control treatment in the agricultural and pastoral area, CARB-Pb increased slightly during the freeze–thaw process, while Fe/Mn-Pb and RES-Pb changed slightly. The percentage of ORG-Pb increased sharply during one FTC at 60% water content. The Pb in the soil of the mining area existed mostly bound to the Fe–Mn oxide; the ORG-Pb decreased during most freeze–thaw conditions, for instance, 5, 10, 15 and 60 at 60% water content. EXCH-Pb changed slightly during different freeze–thaw treatments. With increasing water content, CARB-Pb tended to increase gradually, while it increased to some extent at most FTCs at 60% water content, except 10 FTCs. The percentages of ORG-Pb and RES-Pb with different treatments and water content changed little. The percentages of EXCH-Pb in the industrial area increased by 1.21 and 1.91% during 1 and 5 FTCs at 60% water content relative to the control treatment, while CARB-Pb increased by 2.58% during 5 FTCs at 60% water content only. The percentage of Fe/Mn-Pb

Fig. 3. Infrared spectra and X-ray diffraction spectra of soils in different areas for different FTCs and water content. For an explanation of the symbols see Figure 1.

increased during different FTCs and water content except for 1 FTC at 60% water content; conversely, the percentages of ORG-Pb and RES-Pb mostly decreased compared to the control treatment. Different freeze-thaw treatments did not significantly affect the distribution of Pb in different fractions of the soil of the salt-lake area. The percentage of EXCH-Pb increased by 0.67 and 0.94% during 5 and 60 FTCs at 60% water content, while that of CARB-Pb increased by 0.59 and 0.56% during 60 FTCs at 60% water content and 15 FTCs at 80% water content, respectively. The percentage of Fe/Mn-Pb decreased compared to the control, except for 1 FTC at 60% water content. Conversely, the percentage of ORG-Pb increased slightly while that of RES-Pb changed little. The results

indicate that FTCs could promote the mobility and bio-availability of Pb in soils in the urban, agricultural and pastoral, mining, industrial and background areas, the exception being the salt-lake area.

The percentage distribution of Cr in different fractions during different FTCs and soil water content are shown in Figure 4(b1–b6). The percentage of EXCH-Cr increased significantly only during 15 FTCs at 80% water content. After 10, 15 and 60 FTCs at 60% water content, the percentage of CARB-Cr in urban area increased from 0.14 to 0.49, 0.39 and 0.45%, respectively. The percentage of Fe/Mn-Cr decreased slightly except at 1 FTC at 60% water content. The percentages of ORG-Cr and RES-Cr fluctuated

Fig. 4. Chemical fractions of Pb and Cr in different areas for different FTCs and water content. For an explanation of the symbols see Figure 1.

during different numbers of FTCs and soil water content. The percentages of Cr fractions in soils of the agricultural and pastoral, salt-lake and background areas changed little, indicating that the impact of different FTCs on fractions of Cr is more obvious than for Pb. EXCH-Cr in the mining area decreased with increasing number of FTCs and soil water content; conversely, Fe/Mn-Cr in soil increased slightly except for 60 FTCs at 60% water content. EXCH-Cr in the industrial area reached a maximum value of 6.52% after 1 FTC at 60% water content, and Fe/Mn-Cr and ORG-Cr decreased accordingly. Overall, the transformation between chemical fractions of Cr in soils was less than for Pb, indicating that Cr was less mobile.

Tables 3 and 4 demonstrate the correlation among various Pb and Cr fractions under different FTCs and water content, respectively. There are positive correlations between FTCs and percentage of CARB-Pb in the urban area ($R^2 = 0.786$, $P < 0.05$). The percentage of Fe/Mn-Cr is positively related to FTCs in the salt-lake area. There were significant correlations between FTCs and ORG-Cr and RES-Cr in the agricultural and pastoral area. The percentage of EXCH-Cr decreased with increasing water content in the industrial area, while that of Fe/Mn-Cr behaved similarly in the background area. The percentage of CARB-Pb positively related to water content in the mining area. There were significant negative correlations between water content and ORG-Cr and RES-Cr in the urban area. The

Table 3. Fitting equation and correlation between FTCs and fractions of Pb or Cr

Fractions	Area	Pb or Cr	Fitting equation	R^2	P
Carbonate	Urban area	Pb	$Y = 0.1602X - 0.104$	0.786	0.045
Fe–Mn oxide	Salt-lake area	Cr	$Y = 0.0423X + 1.194$	0.816	0.036
Organic	Agricultural and pastoral area	Cr	$Y = -0.0661X + 4.9$	0.843	0.028
Residual	Agricultural and pastoral area	Cr	$Y = 0.0854X + 38.541$	0.832	0.031

Note: R^2 and P indicate coefficient of determination and significant value, respectively.

Table 4. Fitting equation and correlation between water content of freeze–thaw and fractions of Pb or Cr

Fractions	Area	Pb or Cr	Fitting equation	R^2	P
Exchangeable	Industrial area	Cr	$Y = -0.010X + 0.015$	0.916	0.043
Carbonate	Mining area	Pb	$Y = 22.1314X - 8.758$	0.944	0.028
Fe–Mn oxide	Background area	Cr	$Y = -1.2191X + 1.540$	0.959	0.021
Organic	Urban area	Cr	$Y = -13.4115X + 16.233$	0.912	0.045
Residual	Urban area	Cr	$Y = -13.0984X + 48.415$	0.950	0.025

Note: R^2 and P indicate coefficient of determination and significant value, respectively.

Fig. 5. Risk assessment code of Pb and Cr in soils of different areas for different FTCs and water content. For an explanation of the symbols see Figure 1.

results indicate that FTCs can promote the mobility of Pb and Cr in soils of the northeastern Qinghai–Tibet Plateau.

Effect of FTCs on the ecological risks from Pb and Cr

To elucidate the impact of freeze–thaw frequency and soil-water content on the ecological risk from Pb and Cr, soil samples in the six areas with different FTCs and soil water content were analyzed (Fig. 5). The ecological risk posed by Pb and Cr was evaluated by the RAC method. The results showed that all the Pb and Cr in soils posed low ecological risk.

In the urban soil, the ecological risk from Pb increased at 10 and 15 FTCs. When comparing the control treatment after 10 and 15 FTCs to before freezing, for instance, the ecological values of Pb were 8.32 and 7.38% higher. In addition, the Pb ecological risk slightly increased with increasing water content. In the agricultural/pastoral and industry soils it increased in the first 5 FTCs to 1.66 and 4.60%, respectively, and then decreased. However, water content did not significantly affect the risk in these soils. The Pb risk in the mining area fluctuated during the FTCs; for instance, after 5 and 60 FTCs it increased by 2.92 and 3.51%, respectively. In the mining area it increased significantly with increasing water content. Freeze–thaw frequency and soil-water content did not impact the risk from Pb in the salt-lake area. The risk in the background area fluctuated during the FTCs, and the impact of water content was weak. The results indicate that the FTCs can increase the ecological risk from Pb in most soils of all areas except that of the salt-lake area.

After 10, 15 and 60 FTCs at 60% water content, the ecological risk from Cr in the urban area increased from 0.23 to 0.59, 0.41 and 0.51%, respectively. It reached a maximum value after 15 FTCs at 80%. Conversely, in the mining area it decreased with increasing FTCs and soil water content. In the industrial area it reached a maximum value of 6.52% after 1 FTC at 60%. The values of risk in soils of the agricultural and pastoral, salt-lake and background areas changed little, indicating that the impacts of different freeze–thaw treatments on the ecological risk from Cr were less obvious.

Compared with Pb, the ecological risk from Cr in soils was not significant.

Conclusions

It was shown that different FTC frequency and soil water content affected some soil physicochemical properties and fractions of Pb and Cr in the northeastern Qinghai–Tibet Plateau. The pH, CEC, texture and morphology of soils changed under different treatments. The pH of urban soil with 60 FTCs was 12.5% higher. CEC increased significantly in agricultural and pastoral soils with an increase of up to 5 FTCs. The sand proportion of soil in the urban area decreased at 60 FTCs, and that in the agricultural and pastoral, industrial and background areas decreased with freeze–thaw at different cycling times and water content.

The freeze–thaw treatment did not change the functional groups and mineral constituents of soils in the study area. The infrared peaks of soils under different conditions were very similar, but the relative intensity of the groups was affected by FTCs, indicating that repeated freeze–thawing increased or diminished the abundance of functional groups in the soils. Soils treated at different cycling times and water contents were mainly composed of quartz, calcite, muscovite, albite and dolomite. The freeze–thaw treatment can promote the mobility and bio-availability of Pb in soils in the urban, agricultural and pastoral, mining, industrial and background areas, but not the salt-lake area.

The freeze–thaw treatment affected the transformation of chemical fractions of Cr in a manner less obvious than for Pb. It could increase the ecological risk from Pb in most soils in the study area, while its impact on the risk from Cr was less obvious. The exchangeable Pb in the agricultural and pastoral area increased from 0.19 to 1.52 and 0.90% at 5 and 10 FTCs at 60% water content. The ecological values of Pb in urban soil were 8.32 and 7.38% higher at 10 and 15 FTCs compared to the control treatment. These results imply that FTCs can change the physicochemical properties of soil and enhance the mobilization of Pb and Cr. Further studies are

needed to investigate the migration mechanism of Pb and Cr in soils during FTCs.

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Data availability Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

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