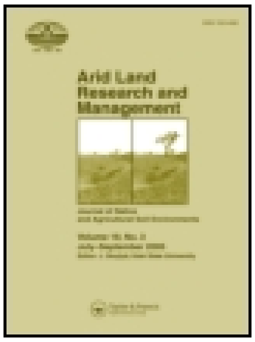

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Salinity fractionation of saline-sodic soils reclaimed by $CaCl_2$-amended brackish ice

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ABSTRACT

The amelioration of saline-sodic soil and the rational utilization of irrigation water resources are important environmental problems worldwide, particularly in the arid and semi-arid regions. In order to study the water-salt dynamics and reclamation effects of $CaCl_2$-amended brackish ice on saline-sodic soils, we conducted a laboratory experiment to study the salinity fractionation of brackish ice and the amelioration effects in different saline-sodic soils (ESP 20, 40, and 70) under four salinity levels (1, 1.6, 2.2, and 2.8 g/L) of brackish ice. Based on the analysis of soil pH, electrical conductivity (EC), sodium adsorption ratio (SAR), alkalinity, infiltration depth, and ionome, the results showed that the pH, SAR, and alkalinity of ESP 20 soil with a higher salinity (2.2 g/L, Na/Ca $\leq$ 1.14) of brackish ice could be improved. However, for high ESP soils (ESP 40 and 70), there was no significant difference among brackish ice treatments of 1, 1.6, 2.2, and 2.8 g/L, the 0–12 cm soil layer could be desalted, but more salts accumulated at the lower layer of the soil profile. We further determined an optimal brackish ice concentration to improve different ESP soils: 2.2 g/L brackish ice for ESP 20 soil, 1.6 g/L for ESP 40 soil, and 1 g/L for ESP 70 soil. $CaCl_2$-amended brackish ice can be used to ameliorate saline-sodic soil, this study provides invaluable supporting information on saline-sodic soil reclamation by optimizing brackish ice salinity and sodicity.

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Brackish ice; ESP; ionome; saline-sodic soil; salt leaching

Introduction

Soil salinization is a global problem in soil deterioration, especially in arid and semi-arid regions, which seriously affects the regional environment and agricultural development. The Songnen Plain is the main distribution area of saline-sodic soil in China, with a total area of salt-affected soils over 3.73 million hectares (Li 2000), and the Na_2CO_3 and $NaHCO_3$ are the dominant salts in this region (Xiao et al. 2017). Due to the excess amounts of Na^+ adsorbed on soil colloids, soil clay particles are dispersed when the soil gets wetted (Li, Cao, and Li 2004), which causes the extremely low soil permeability and nutrient availability (Ayers and Westcot 1976; Chi and Wang 2010;

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Wang 2004; Yang et al. 2016). The deteriorating soil properties adversely affect the germination and growth of crops (Kinraide 1999) and restrict the agricultural sustainability in this area.

The purpose of saline-sodic soil reclamation is to improve the soil hydraulic conductivity, thereby increase the leaching of salts, especially the excess Na^+ (Gangwar et al. 2020). Previous studies have shown that soil hydraulic conductivity was mainly influenced by the coupling effect of total electrolyte concentration (TEC) and exchangeable sodium percentage (ESP) in the fine-textured soil (Levy, Goldstein, and Mamedov 2005). When the TEC in the soil was higher than the critical flocculation concentration (CFC), the soil permeability could be improved (Warrence, Bauder, and Pearson 2002); otherwise, the clay particles would spontaneously disperse with increasing soil ESP (Sumner 1993). Therefore, the improvement of saline-sodic soil from the chemistry perspective mainly includes two aspects: to replace Na^+ by Ca^{2+} on the ion exchange sites (Pistocchi et al. 2017) and to increase the electrolyte concentration of the soil solution to improve soil permeability (Sumner 1993). The first method is mainly used to remove excess Na^+ adsorbed on the soil by adding calcium-based amendment, thereby improves the deteriorated physical structure of saline-sodic soil, and this method has been widely applied in engineering practices (Amezketa, Aragüés, and Gazol 2005; Hanay et al. 2004; Li et al. 2008, Qadir and Oster 2004). Irrigation with underground saline water could improve the soil conditions by increasing the electrolyte concentration (Shah 2014), inhibiting the soil dispersion, and leaching the salts from the upper soil layer. However, irrigation with saline water with excessive sodium concentration would lead to clay dispersion (Frenkel, Goertzen, and Rhoades 1978; Suarez, Wood, and Lesch 2006) and soil sodification (Heydari, Gupta, and Loof 2001; Sharma and Minhas 2005).

The processes of brackish water freezing and thawing can separate freshwater from saline water and greatly increase the electrolyte concentration of initial meltwater (Guo, Ju, and Feng 2016; Li, Liu, and Zhang 2008). When brackish ice melts, the initial meltwater contains more salts (Nakagawa, Maebashi, and Maeda 2010), which contributes to the increase of soil hydraulic conductivity and infiltration rate. Meanwhile, the late-melted low salinity water (or even freshwater) would leach salts out of the soil profile and further promote the formation of the desalinized soil surface layer (Gu et al. 2013; Li et al. 2008). It should be noted that brackish irrigation ice could also improve saline-sodic soil by protecting soil surface during cold winter in the cold region, thus improving the structure of surface soil and providing water during the dry spring period (Li et al. 2008; Ling and Zhang 2007). Therefore, the infiltration of saline ice meltwater is a feasible way to reclaim saline-sodic soils.

Currently, freezing saline water irrigation is mainly applied to improve the coastal saline soil constrained by NaCl (Shah 2014; Suarez, Wood, and Lesch 2006). However, there is a lack of information on the water movement and salt redistribution in different ESP saline-sodic soils applied with brackish ice (Wang et al. 2011). Moreover, the underground water in the saline-sodic soil area has a low electrolyte concentration and contains a high concentration of Na^+, and according to Fipps (2003) classification of irrigation water, this underground water presents a medium sodium hazard level and is not suitable for direct irrigation. After freezing and thawing, the electrolyte

Table 1. Properties of shallow groundwater at Da'an Station.

Units	pH	EC (dS/m)	Na^+ (mmol$_c$/L)	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	CO_3^{2-}	Cl^-	SO_4^{2-}	SAR
Value	8.81	1.60	15.89	0.054	2.30	0.58	10.93	4.23	2.86	1.9	13.24

concentration of meltwater is not enough to flocculate the soil particles. Therefore, how to increase the electrolyte concentration and reduce the Na^+ concentration of underground water has become the main research question for the amelioration of saline-sodic soils in this region.

Previous studies have shown that the application of calcium amendment (gypsum) in soil and irrigation with frozen saline water could improve the properties of saline-sodic soil (Xiao et al. 2014; Yang, Wang, and Xiao 2012). According to the principle that the freezing process could separate the fresh water and saline water, we assert that directly adding $CaCl_2$ amendment to the underground brackish water could increase the electrolyte concentration and reduce the sodium hazard level of underground water. Collectively, it is necessary to assess the optimal combination of different ESP saline-sodic soils and brackish ice salinity.

In this study, we tested the hypothesis that adding $CaCl_2$ to the underground brackish water would increase the electrolyte concentration and relieve the sodium hazard. After freezing and thawing, the initial melted high salinity water could increase the infiltration rate, replace excess Na^+ in clay. Therefore, in this experiment, we aimed to study the salt separation characteristics during the freezing-thawing process of underground brackish water with different amounts of $CaCl_2$ and the leaching effect of brackish ice with different electrolyte concentrations on saline-sodic soils. The objectives of this study were to determine an optimal brackish ice concentration for the amelioration of different ESP saline-sodic soils and provide technical support for the remediation of saline-sodic soil.

Materials and methods

Experimental design

There were two experiments conducted in this study. The first experiment aimed to characterize salt and ion fractionation during the freezing and thawing stages of $CaCl_2$-amended brackish water ("Freeze/Thaw Experiment"). The second soil column experiment studied the effects of $CaCl_2$-amended brackish ice with different concentrations on salt and ion distribution in three saline-sodic soils with different ESP values ("Infiltration/Leaching Experiment").

The water used in this experiment was pumped from the shallow groundwater (Table 1) of the Da'an Sodic Land Experiment Station, Chinese Academy of Sciences (45°35′58″N∼45°36′28″N, 123°50′27″E∼123°51′31″E). Soils with ESP 40 and ESP 70 were also collected in this station, and the ESP 20 soil was collected at Yaheng Animal Husbandry Co., Ltd, Baicheng, Jilin province, China (45°34′33″N∼45°33′36″N, 123°01′25″E∼123°02′24″E). The soil samples were air-dried and crushed through a 2 mm sieve, and their chemical properties are shown in Table 2.

Table 2. Particle size and chemical parameters of different ESP saline-sodic soils.

Soil sample property	Unit	ESP20	ESP40	ESP70
Clay (<0.002 mm)	%	7.45	10.32	37.60
Silt (0.002–0.02 mm)	%	16.51	21.28	39.14
Sand (0.02–2 mm)	%	76.04	68.40	23.26
pH		9.07	10.53	11.46
$EC_{1:5}$	dS/m	0.51	1.79	6.59
Na^+	$mmol_c/L$	5.28	18.61	67.26
K^+	$mmol_c/L$	0.10	0.05	0.04
Ca^{2+}	$mmol_c/L$	0.57	0.27	0.78
Mg^{2+}	$mmol_c/L$	0.04	0.06	0.03
HCO_3^-	$mmol_c/L$	3.47	3.36	22.56
CO_3^{2-}	$mmol_c/L$	1.01	0.67	19.54
Cl^-	$mmol_c/L$	1.20	13.10	19.84
SO_4^{2-}	$mmol_c/L$	0.17	0.39	8.60
$SAR_{1:5}$	$mmol_c/L$	9.56	45.81	105.69
$Alkalinity_{1:5}$	$mmol_c/L$	4.48	4.03	42.10

$EC_{1:5}$, $SAR_{1:5}$&$Alkalinity_{1:5}$: In 1:5 soil:water extract.

Freeze/thaw experiment

In this experiment, we prepared five concentrations of saline water (S1–S5) by adding different amounts of $CaCl_2$ to the brackish groundwater (Table 3). Each treatment was filled into a cylindrical plastic bottle with a volume of 500 mL (6 cm in diameter), and three plastic bottles were applied as replicates. All the bottles were placed vertically at −20 °C outdoor in the mid-winter to freeze naturally and then sampled by slicing (SQ) and thawing (SR). For the slicing method, every 3-cm-thick layer was cut and took as a sample, each sliced sample was naturally melted indoors (temperature: 19 °C), and the salinity and ion composition of each ice layer was measured. For the thawing method, the whole saline ice columns were naturally melted indoors (temperature: 19 °C), and each 80 mL volume of the thawed water was collected in sequence to observe the ion fractionation during the thawing process.

Infiltration/leaching experiment

Soils with three ESP values (ESP 20, 40, and 70) were tested in this experiment. Different amounts of $CaCl_2$ (0, 0.75, 1.40, and 2.15 g) were added to 1 L brackish groundwater, corresponding to the concentration of 1, 1.6, 2.2, and 2.8 g/L of brackish water and 5.19, 1.78, 1.14, and 0.80 of Na/Ca ratio, respectively (Table 4). The four concentration levels of brackish water were poured into plastic bottles and frozen at −20 °C in a refrigerator for 24 h. Afterward, the ice was removed from the plastic bottles (4.8 cm in diameter) and placed on the surface of the column at room temperature (19 °C). Each of the three ESP soils was treated with four concentrations of brackish ice. The volume of each brackish ice added to each soil column was 240 mL (equivalent to 1.5 pore volume and irrigation quantity of 122 mm) (Wang, Li, and Li 2019).

The cylindrical soil column was made of a transparent polymethyl methacrylate, with 25 cm in height and 5 cm diameter (Guo, Ju, and Feng 2016; Heydari, Gupta, and Loof 2001; Li, Liu, and Zhang 2008; Nakagawa, Maebashi, and Maeda 2010). The bottom of the column was covered with quartz sand and mesh for water filtering (Heydari, Gupta, and Loof 2001). Meanwhile, silicone grease was applied to the inner wall of the column

Table 3. Chemical parameters of water pre-freezing and thawing.

Treatments	$CaCl_2$ dosage g/L	SAR $(mmol_c/L)^{1/2}$	Salinity of brackish ice (g/L)	Net Ca^{2+} dosage (g/L)
S1 (SQ1, SR1)	7.79	3	8.48	2.71
S2 (SQ2, SR2)	2.47	5	3.17	0.78
S3 (SQ3, SR3)	1.02	7	2.39	0.52
S4 (SQ4, SR4)	0.42	9	1.57	0.18
S5 (SQ5, SR5)	0.11	11	1.00	0.00

S1–S5 indicates five concentrations of brackish ice. SQ1–SQ5 indicates five concentrations of sliced brackish ice and SR1–SR5 indicates five concentrations of thawed brackish ice.

Table 4. Chemical parameters of brackish ice.

Treatments	$CaCl_2$ dosage (g/L)	Salinity of brackish ice (g/L)	Na/Ca $(mmol_c/L)^{1/2}$	Net Ca^{2+} dosage (g/L)
Underground brackish water	0	1	5.19	0.00
Underground brackish water + $CaCl_2$	0.75	1.6	1.78	0.22
Underground brackish water + $CaCl_2$	1.4	2.2	1.14	0.43
Underground brackish water + $CaCl_2$	2.15	2.8	0.80	0.65

to prevent the pipe wall effect (Gu et al. 2013). To obtain a homogenous soil bulk density (1.4 g/cm^3), the soil was filled into the soil columns in 4 cm thick sections, and the soil surface of the previously packed layer was stirred before filling the next increment (in order to prevent soil stratification within the soil column). In each column, the soil was packed to 20 cm in height. After infiltration (no water was observable on the surface of the soil), there was no water leaching from the bottom of the columns. Soil samples were collected from five layers (4 cm per layer) of each soil column, with a total of 180 soil samples (3 ESP × 4 salt concentration × 5 layer× 3 replicate).

Brackish water and soil chemical analysis

The wetting front was recorded every 30 min to determine the infiltration depth. Gravimetric soil moisture content was determined by the oven-drying method. Soil electrical conductivity ($EC_{1:5}$), $pH_{1:5}$ and water-soluble salts were determined by 1:5 soil:water suspension and glass electrodes (Shanghai Precision Scientific Instrument Co., Ltd)(Li 1986). The concentration of Na^+ was determined by flame photometer, and Ca^{2+} and Mg^{2+} contents were determined by EDTA titration (Wang and Yu 1993). The concentrations of CO_3^{2-} and HCO_3^- were determined by dilute acid titration. Sodium adsorption ratio (SAR) and alkalinity were calculated by the following equations, where the concentrations of cations are expressed in $mmol_c/L$ (same as milliequivalent per litre) (Xiao et al. 2014; Yang, Wang, and Xiao 2012).

$$\mathrm{SAR} = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}+Mg^{2+}]}{2}}}\ (\mathrm{mmol_c/L}) \tag{1}$$

$$Alkalinity = CO_3{}^{2-} + HCO_3{}^{-}(\mathrm{mmol_c/L}) \tag{2}$$

The relative variation ratio (R) of EC and Na^+ was calculated from Eq:

$$R(\%) = \frac{(C_0 - C_1)}{C_0} \times 100\% \tag{3}$$

The R (%) value is the relative variation ratio, C_0 is the content of salt or Na^+ before brackish ice freeze-thaw experiments, and C_1 is the final content of salt or Na^+ after brackish ice freeze-thaw experiments.

Statistical analysis

Statistical analyses were performed using the SPSS 23.0 software. The effects of ice salinity and soil layer on soil moisture, pH, EC, SAR, and alkalinity were evaluated using a two-way ANOVA test. To investigate the overall change of soil ionome (including Na^+, Ca^{2+}, Mg^{2+}, CO_3^{2-} and HCO_3^-) under different ice salinities and soil layers, principal coordinate analysis (PCoA) by Bray-Curtis distance was performed in R using package "vegan" and visualized by package "ggplot2." A permutational multivariate analysis of variance (PERMANOVA) test was used to verify the significance and relative contribution of the soil layer and salt content on the soil ionome in each soil type.

Results and discussion

Salinity fractionation in brackish ice

Distribution of salt and ions during brackish ice freezing process

The contents of Na^+ and HCO_3^- in groundwater accounted for 69.22% of the total salt of eight ions (Table 1), while Na^+ accounted for 84.41% of soluble cations and HCO_3^- content accounted for 54.87% of soluble anions. When the brackish water was completely frozen, the freshwater was separated from saline water in every treatment. The EC, Na^+ and HCO_3^- showed a trend of migration and accumulation from the top (0–3 cm) to the bottom (15–18 cm) after freezing, whereas the pH showed an opposite trend and decreased from the top to bottom (Figure 1). In contrast to the pre-freezing solution (Table 3), the EC at 0–3 cm ice layer decreased with 2.98, 1.20, 1.10, 1.00, and 0.56 dS/m for the treatments of SQ1-SQ5, respectively. Greater salinity of brackish water (larger $CaCl_2$ dose) led to a higher reduction of EC value. After freezing, the top layer of the brackish ice became desalinated. Salinity (EC) started accumulating at 12–15 cm layer. Compared with the pre-freezing solution of SQ1-SQ5 (Table 3), the EC at the bottom layer increased to 8.59, 3.11, 1.32, 0.93, and 0.89 dS/m, respectively, demonstrating that the freezing process could separate freshwater in the upper layer from the bottom saline water, with the salts accumulating at the bottom of the ice. During freezing, the ice crystals are initially formed from pure water, and the ions in front of the growing crystal front are excluded. Later, the increased ion concentration leads to the decrease of freezing point, and the remaining unfrozen liquid will freeze quickly with the low temperature (Beier et al. 2007). Additional factors include the effect of gravity between the dilute and concentrated fractions and the formation of brine channels (Zhang, Yang, and Yao 2016; Gu et al. 2013), which cause salts to move toward the bottom of the ice.

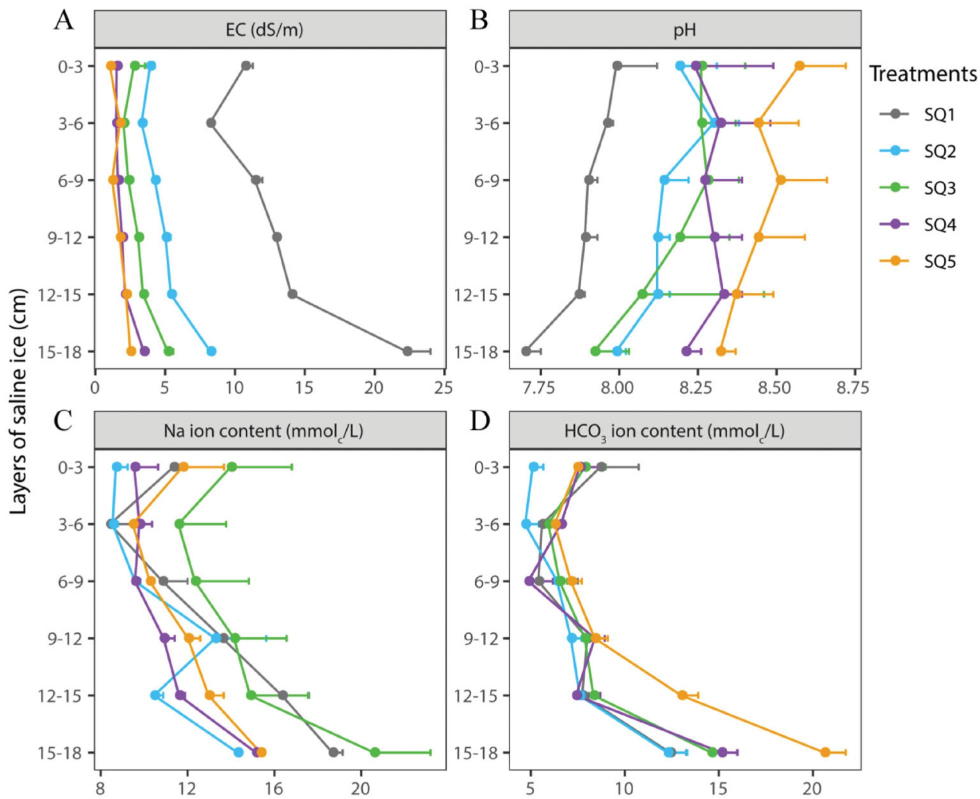

Figure 1. Distribution of salinity and ions in different brackish ice layers. The salt concentration from high to low is denoted as SQ1–SQ5 (See Table 3). (A) The EC values in different ice layers; (B) The pH values in different ice layers; (C) Na^+ content in different ice layers; (D) HCO_3^- content in different ice layers.

The content of Na^+ in the 0–15 cm ice layers was lower than in the initial brackish water (Na^+:15.89 mmol$_c$/L) in all treatments (Figure 1C). The observed reduction of Na^+ concentration in brackish ice could be attributed to the fact that ions moved downward during the freezing process. The contents of HCO_3^- in the 0–12 cm ice layers were also lower than in the initial brackish water (HCO_3^-:10.93 mmol$_c$/L) in all treatments (Figure 1D). The HCO_3^- contents in the 12–18 cm layer were the highest in the SQ5 treatment with the lowest $CaCl_2$ dose, and the value was significantly higher than in other treatments ($p < 0.05$). This demonstrated that the applied $CaCl_2$ amendment doses played a large role in determining the content of HCO_3^-in brackish underground water, and adding $CaCl_2$ could significantly decrease the content of Na^+ and HCO_3^-in brackish ice. Nevertheless, the pH changes were different from EC, Na^+ and HCO_3^-. The pH values in the upper layers were greater in all brackish ice treatments, but the pH levels in all of the ice layers were lower than in the initial brackish water (pH = 8.81). Cheng et al. (2011) obtained similar results, it was likely that Ca^{2+} reacted with CO_3^{2-} and HCO_3^- in solution to form $CaCO_3$, which resulted in a decrease in the pH and HCO_3^- concentration.

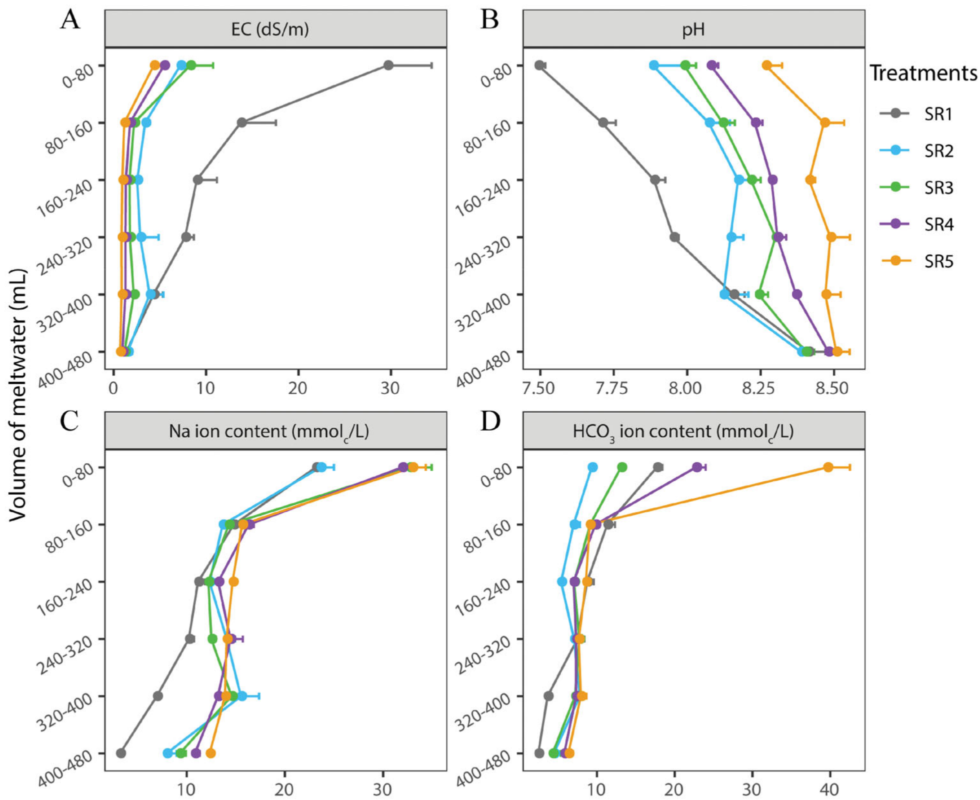

Figure 2. Distribution of salinity and ions in different brackish ice meltwater. The salt concentration from high to low is denoted as SR1–SR5 (See Table 3). (A) The EC values in meltwater; (B) The pH values in meltwater; (C) Na^+ contents in meltwater; (D) HCO_3^- contents in meltwater.

Distribution of salt and ions during brackish ice melting process

The distribution of brackish ice during the melting process follows the principle of the fractionation of salt and fresh water during the freezing process. It was showed that EC, Na^+, and HCO_3^- contents were extremely high in the initial meltwater and decreased with the increase of the meltwater volume (Figure 2). For the initial 80 mL (0–80 mL) meltwater, the EC of meltwater in SR1-SR5 treatments were 2.16, 1.41, 2.14, 2.15, and 2.69 times higher compared with the pre-freezing brackish water, respectively. It was reported that over 50% of the total amount of Ca^{2+}, Mg^{2+}, and Na^+ was released from the saline ice during the first 2 h of thawing (Guo and Liu 2014), which greatly increased the EC of the initial meltwater. And the melting process of salinity fractionation is guided by gravity and the preferential melting of brine pockets in saline ice (Gu et al. 2013). The salinity of brackish water was decreased with the melting process, and the EC in the final 80 mL meltwater fraction (400–480 mL) was negligible and similar across different treatments. The results indicated that the salt concentration of the final melted water was very low after the freezing-thawing process, and the desalination effect was obvious, irrespective of the salt concentration of the initial solution. Similarly, it was reported that the salt of seawater could be fractionated during freezing and melting processes, as indicated in the saline soil of a coastal area (Zhang, Yang, and Yao 2016).

The trends of Na^+ and HCO_3^- were similar to EC. The initial concentration of Na^+ and HCO_3^- were 15.89 and 10.93 mmol$_c$/L in the brackish water (Table 1). After freezing and melting, the initial meltwater contained an extremely high concentration of Na^+ and HCO_3^-, and the concentrations of Na^+ and HCO_3^- were reduced with the increase of meltwater volume (Figure 2). Remarkably, in the final 80 mL meltwater (400–480 mL), the contents of Na^+ and HCO_3^- were 3.21, 7.95, 9.29, 10.83, 12.33 mmol$_c$/L and 2.47, 4.47, 4.30, 5.80, 6.33 mmol$_c$/L for the treatments of SR1-SR5, respectively. This observation suggested that the brackish ice treatments with greater $CaCl_2$ amendment doses (SR1 > SR2 > SR3 > SR4 > SR5) resulted in lower Na^+ and HCO_3^- concentrations in the subsurface brackish water. The results verified our hypothesis: the alkalinity and salinity hazard level of underground brackish water can be reduced with the application of $CaCl_2$ amendment after the freezing-thawing process. When the hazard level has been reduced, the underground water can be applied for soil irrigation and leaching. The trend of pH in the melting process was similar to the freezing process. The pH of initial melting water was low and increased with the increase of meltwater volume.

Relative change rates of EC and Na^+ concentration during brackish water freezing and thawing

After freezing and melting the brackish water, the relative change rates of EC and Na^+ concentration were calculated (Figure 3). The desalination rate of brackish ice in the melting process was significantly higher than that of the freezing process (Figure 3A and C). During the brackish water freezing process, the average decrease and the maximum decrease of EC were 32.51% and 56.10% across treatments, respectively (Figure 3A), and the maximum decreased percentage of Na^+ was 47.43% (Figure 3B). However, for the brackish ice melting process, they were 52.52%, 92.65% (Figure 3C), and 79.99% (Figure 3D), respectively. The decrease of Na^+ was proportional to the dosage of $CaCl_2$. Higher doses of $CaCl_2$ amendment in brackish ice led to a higher decrease in Na^+ concentration (Figure 3B and D). Beier et al. (2007) conducted experiments at different ambient temperatures, salt concentrations, and mass flow rates, and they also proved that melting could concentrate salt more effectively than freezing. This phenomenon may be due to the changes in salt distribution in the ice after freezing, which resulted in different salt contents in different layers of saline ice. Different salt contents (concentration) led to different freezing points (Foldvik and Kvinge 1974), which caused different melting rates during the thawing process. Once again, salinity fractionation took place during ice thawing, and the desalination rate in the thawing process was higher than that during the freezing process.

Infiltration of thawed solutions and variations of salinity in soil profiles

Wetting front

When the brackish ice was placed on the surface of the soil in columns at room temperature, it started melting and gradually infiltrated into the soil profiles. At the end of the infiltration process, there was no leachate observed at the bottom of the soil column. In the early stage of infiltration, the wetting fronts among treatments showed no

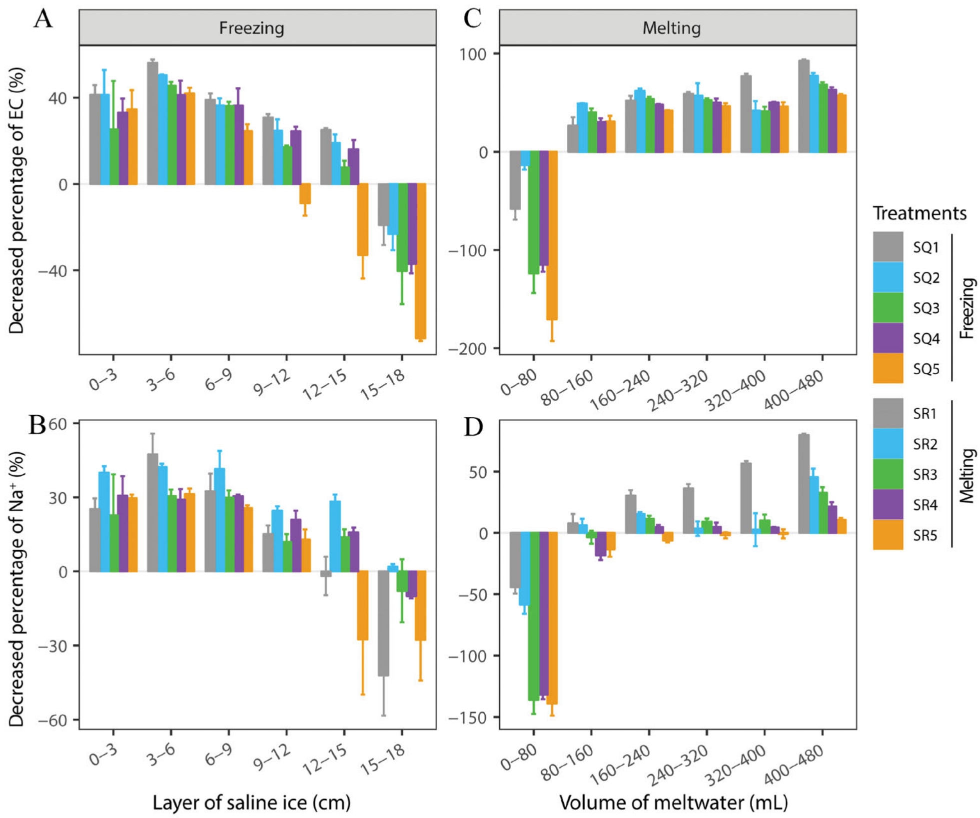

Figure 3. Percent decrease of EC and Na^+ concentration during brackish water freezing and thawing compared to initial concentration. The salt concentration from high to low was denoted as SQ1–SQ5 & SR1–SR5 (see Table 3). (A) The percent decrease of EC in different ice layers; (B) The percent decrease of Na^+ in different thawed solution fractions; (C) The percent decrease of EC in different ice layers; (D) The percent decrease of Na^+ in different thawed solution fractions.

significant difference. It might be due to the similar initial melting rate of saline ice, which leads to similar infiltration depth at the beginning. However, the wetting front varied considerably across treatments with the increase of meltwater volume (Figure 4). At the end of the recording (480 min), the final wetting front in ESP 20 saline-sodic soil was 7.0, 9.1, 13.6, and 15.1 cm for the treatments of 1, 1.6, 2.2, and 2.8 g/L brackish ice, respectively, which was higher than that in ESP 40 and ESP 70 soils (5.7, 6.5, 8.9 and 11.3 cm for ESP 40 soil, and 5.6, 6.5, 8.8 and 11.0 cm for ESP 70 soil). It demonstrated that the higher salinity of brackish ice led to a deeper depth of meltwater infiltration into saline-sodic soils with different ESP values. The melt-water with high electrolyte concentration originating from brackish ice with a larger $CaCl_2$ amendment dose could limit clay dispersion, improve aggregate stability and soil permeability and increase the infiltration depth (Ahmad et al. 2013). But, for brackish ice with the same salinity, saline-sodic soils with different ESPs showed different infiltration effects, and the wetting front was in the order of ESP 20 > ESP 40 > ESP 70, which could result from the fact that higher ESPs might cause aggregate dispersion, thus limited infiltration.

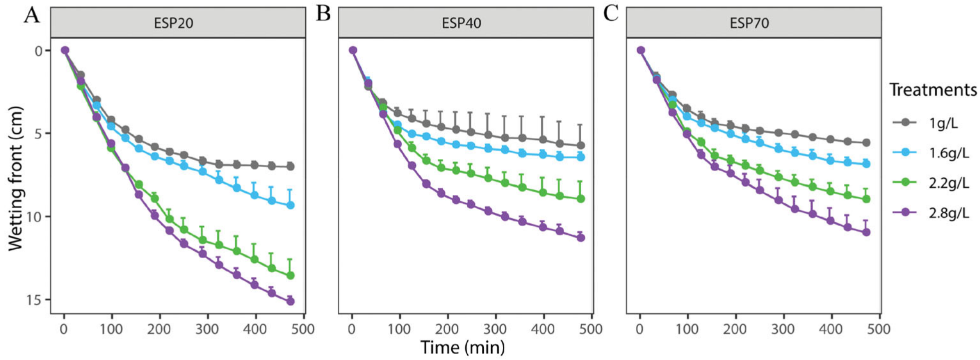

Figure 4. Effects of brackish ice on the wetting front of saline-sodic soils at different ESP values. (A–C) indicates the wetting front of ESP 20, 40, 70 soils with four levels of ice salinity, respectively.

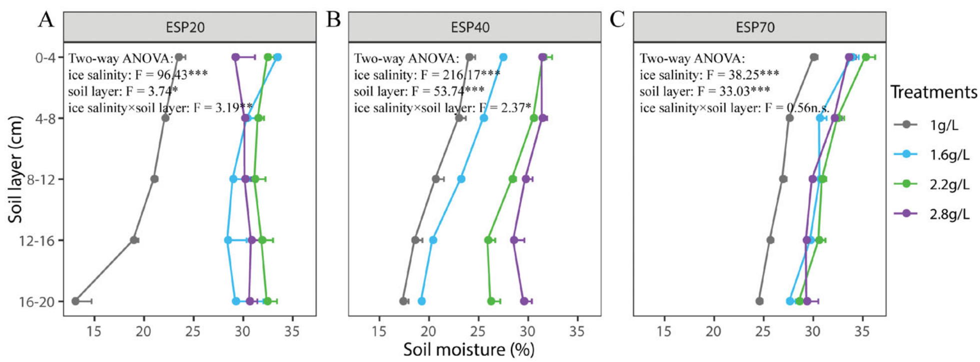

Figure 5. Effect of brackish ice on the gravimetric moisture content of saline-sodic soils with different ESP values. (A) The soil moisture of different soil layers at ESP 20 soil with four levels of ice salinity; (B) The soil moisture of different soil layers at ESP 40 soil with four levels of ice salinity; (C) The soil moisture of different soil layers at ESP 70 soil with four levels of ice salinity.

Soil moisture

The soil moisture was determined after the brackish ice meltwater infiltrated into the soil column (Figure 5). The two-way ANOVA results showed that both soil layers and ice salinity have a significant effect on soil moisture ($p < 0.05$), and ice salinity has a higher effect on soil moisture than the soil layer. There was a significant interaction between soil layer and ice salinity on ESP 20 and ESP 40 soils ($p < 0.05$), but the interaction between soil layer and ice salinity on ESP 70 soil was not significant. The lowest soil moisture was observed in the 1 g/L brackish ice treatment. This was mainly due to the fact that the electrolyte concentration of 1 g/L brackish ice treatment was lower than the critical flocculation concentration, which was not enough to inhibit clay dispersion and pore blockage, thereby reducing soil permeability and causing lower soil moisture (Li et al. 2008). For ESP 20 and 70 soils, no significant difference of soil moisture was observed between the 1.6, 2.2, and 2.8 g/L brackish ice treatments ($p > 0.05$). (Figure 5A and C). The soil moisture on ESP 70 soil treated with 1 g/L brackish ice was similar to that of 1.6 g/L brackish ice treatment on ESP 20 soil and 2.2 g/L brackish ice treatment on ESP 40 soil (Figure 5A–C). This is different from our hypothesis, and might be due

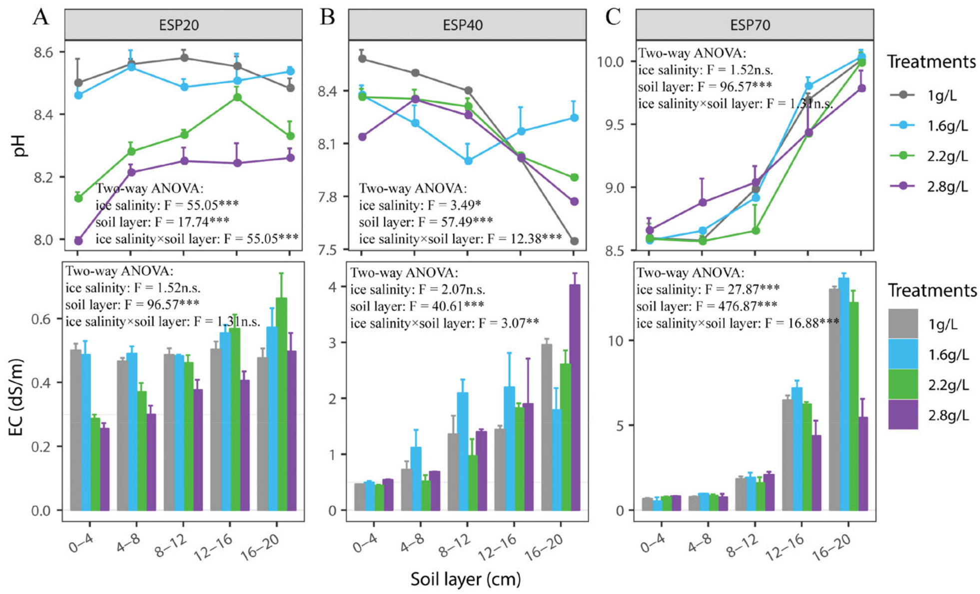

Figure 6. Effects of brackish ice on the pH and EC of saline-sodic soil at different ESP values. (A–C) indicates the pH and EC values at ESP 20, 40, 70 soils with four levels of ice salinity, respectively.

to the fact that ESP 70 soils contain a large concentration of salts (6.59 dS/m), the salts adsorbed on soil particles were also dissolved by the meltwater, thus resulted in a higher electrolyte concentration of soil solution, therefore promoted aggregate stability and soil moisture.

The higher salinity of brackish ice led to higher values of soil moisture for saline-sodic soils with different ESP values (Figure 5). This trend was consistent with the trend of wetting front, and the infiltration of brackish ice meltwater increased soil moisture.

pH and EC

pH and EC are important parameters of soil salinity and sodicity. Through infiltration and leaching of brackish ice meltwater, the pH in all soil layers was far below the pre-experiment values (from 9.07 to 11.46) for all treatments. Ice salinity, soil layer, and their interaction all had significant effects on soil pH of ESP 20 and 40 soils ($p < 0.05$). The effect of ice salinity on soil pH of ESP 20 soil was higher than that of soil layers, but the trend was the opposite in ESP 40 soil. The soil layer had a highly significant effect on the soil pH of ESP 70 soil ($p < 0.001$), but ice salinity and its interaction with the soil layer had no significant effect on the pH of ESP 70 soil. Compared to the ESP 40 and 70 soils, the pH values in ESP 20 soil were relatively stable across different layers (Figure 6). For ESP 20 soil, 2.2 and 2.8 g/L brackish ice treatments decreased the pH value of each soil layer by 0.62 ∼ 0.94 and 0.81 ∼ 1.08, respectively, which were more effective than that of the 1 and 1.6 g/L brackish ice treatments (Figure 6A). For the ESP 70 soil, no significant pH difference was observed in 0–4 cm among the 1, 1.6, 2.2, and 2.8 g/L treatments ($p > 0.05$). Based on the soil moisture and wetting front in the ESP 70 soil, this could be due to the fact that less meltwater reached the bottom of the ESP

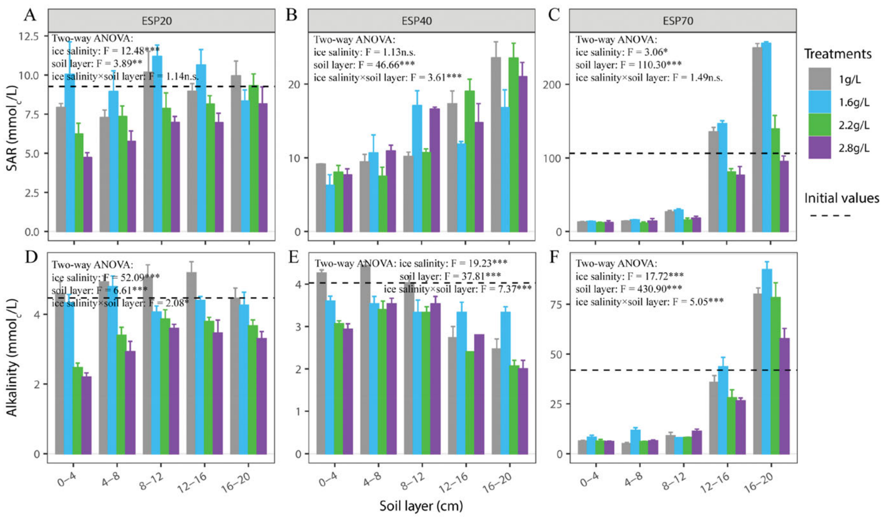

Figure 7. Effects of brackish ice on the SAR & Alkalinity of saline-sodic soil in different ESP values. (A–C) means the SAR of ESP 20, 40, and 70 soils with four levels of ice salinity, respectively; and (D–F) means the sodicity of ESP 20, 40, and 70 soils with four levels of ice salinity, respectively.

70 soil column and the improvement effect was incomplete at the bottom of the soil column.

Brackish ice meltwater infiltration promotes the mobility and leaching of salts. In the three different ESP soils, the soil EC was mainly affected by the soil layer ($p < 0.001$). The ice salinity had a significant effect on soil EC in ESP 70 soil, but no significant effect was observed on ESP 20 and ESP 40 soils. With the exception of the treatment of ESP 20 soil combined with 1 and 1.6 g/L brackish ice treatments, it could be observed that the EC was increased with the increase of soil depth, and salts were significantly removed from the upper layer of soil, while they accumulated in the bottom layer (16–20 cm) (Figure 6). Furthermore, in our experiment, the EC value in all layers of the ESP 20 soil with 1 and 1.6 g/L brackish ice treatments was higher than the initial value. This is probably due to the lower salinity of ESP 20 saline-sodic soil, in which the electrolyte concentration of irrigation water must have been increased in order to keep the soil flocculated. But the net addition of Ca^{2+} in 1 and 1.6 g/L brackish ice was not enough to replace the content of Na^{+} in ESP 20 soil, so the soil particles were still dispersed and the effect of salt leaching was limited. Application of 1, 1.6, 2.2, and 2.8 g/L brackish ice efficiently decreased the EC value of ESP 40 and ESP 70 soils in the 0–4 cm layers with 74.16%, 72.35%, 75.59%, 69.93%, and 89.87%, 91.94%, 88.34%, 87.55%, respectively. Nevertheless, EC was not significantly different ($p > 0.05$) among the four brackish ice treatments at 0–4 cm for the ESP 70 soil, thus suggesting that the four brackish ice treatments had a similar effect in reducing the soil EC in the upper layers of saline-sodic soil with high ESP.

SAR and alkalinity

After leaching with brackish meltwater, the SAR of all soil treatments and soil layers was dramatically reduced (Figure 7A–C). Ice salinity had a significant effect on soil SAR

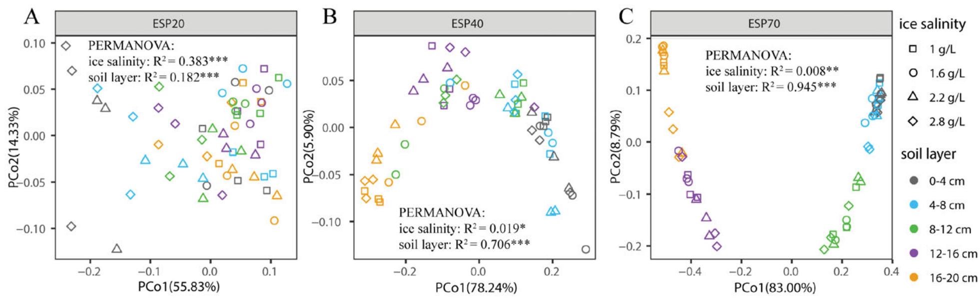

Figure 8. Principle coordinate analysis of soil ionome. where R^2 represented the relative importance of the variant on soil ion contents, and the star (*) indicated the significant effect of the variant. "*" represented $p < 0.05$, "**" represented $p < 0.01$ and "***" represented $p < 0.001$. Layer 1: 0–4 cm, Layer 2: 4–8 cm, Layer 3: 8–12 cm, Layer 4: 12–16 cm, Layer 5: 16–20 cm.

of ESP 20, but had a minor effect on SAR of ESP 40 and ESP 70 soils. The soil layer greatly determined soil SAR across the three different ESP soils ($p < 0.01$), and the effect of the soil layer increased with the increase of soil ESP. With a $CaCl_2$ dosage lower than 2.2 g/L, the amount of Na^+ removed from the exchange sites by Ca^{2+} was lower, which resulted in soil SAR values of 1 and 1.6 g/L brackish ice variants higher than that of the 2.2 and 2.8 g/L brackish ice treatments (Figure 7A–C).

The trend of alkalinity was consistent with SAR. For soil alkalinity, both ice salinity and soil layer had significant effects on ESP 20, 40, and 70 soils ($p < 0.05$). The effect of ice salinity on alkalinity in ESP 20 soil was greater than soil layer, but soil alkalinity was more determined by soil layer in ESP 40 and 70 soils than ice salinity. At the 0–4 cm soil layer, the alkalinity of ESP 20 soil with 1 g/L brackish ice treatment was significantly higher ($p < 0.05$) than that of ESP 20 soil with 2.2 and 2.8 g/L brackish ice treatments, and up to 2.1 times higher than the ESP 20 soil treated with 2.8 g/L brackish ice treatment (Figure 7D). Because the salinity level of the ESP 70 soil was high enough (EC = 6.59 dS/m), when the meltwater of low salinity (1 and 1.6 g/L) brackish ice was infiltrating, the salts in the soil were dissolved and the electrolyte concentration reached the salinity threshold required for improved soil leaching, similar to the effect with 2.2 and 2.8 g/L brackish ice treatments (Ahmad et al. 2013; Qadir and Oster 2004).

Soil ionome

Principal coordinate analysis of soil ionome (including Na^+, Ca^{2+}, Mg^{2+}, $CO_3{}^{2-}$ and $HCO_3{}^-$ ion) further confirmed that both brackish ice treatments and soil layer significantly affected the distribution of soil ionome in three different ESP soils (Figure 8). The effects of brackish ice salinity on soil ionome of ESP 20, ESP 40, and ESP 70 were $R^2 = 0.383$***, $R^2 = 0.019$* and $R^2 = 0.008$**, respectively. This result suggested that the amelioration effect of ice salinity on low ESP soil was more effective than that on high ESP soil. By contrast, the different salinity levels of brackish ice had a similar reclamation effect on the high ESP soil, and the soil layer explained the variance of ion distribution in two high ESP soils ($R^2 = 0.706$*** in ESP 40 soil and $R^2 = 0.945$*** in ESP 70 soil). This result was consistent with the improvement effect of soil pH, EC, SAR, and alkalinity. Interestingly, the results indicated that the ion pattern of bottom layers (12–20 cm) in high ESP soils clearly separated from top layers (0–12 cm), which might partially be attributed to the low infiltration and water availability of the bottom layers. Moreover, the percentage can be explained by the gradual increase in the salinity of brackish ice and soil layer from low ESP (sum of $R^2 = 0.565$) to high ESP soils (sum of $R^2 = 0.725$ in ESP 40 soil and 0.953 in ESP 70 soil), indicating that the two variables explained the most variance of ion distribution. Overall, the high salinity of brackish ice favored the ion removal of low ESP soil but had a marginal effect on improving high ESP soils, where the volume of brackish ice should be increased to improve the leaching of salts to the bottom soil.

Conclusion

With the $CaCl_2$ amendment applied to underground brackish water, the fractionation of salts and ions during the freezing and thawing processes were studied through a brackish water freezing/thawing experiment. The soil column experiment revealed the effects of brackish ice meltwater infiltration on saline-sodic soil with different ESPs. It was observed that the responses of saline-sodic soils with different ESPs to brackish ice were different. After 1 and 1.6 g/L brackish ice were melted and infiltrated into the ESP 20 soil, the amelioration effect of soil EC was not obvious, and the pH, SAR, and alkalinity of soil were lower than the initial value, but the amelioration effects were lower than with 2.2 and 2.8 g/L brackish ice treatments. For ESP 70 saline-sodic soil, the salinity and sodicity indicators were significantly reduced in the 0–12 cm soil layers but increased in the 12–20 cm soil layers, and a consistent result was also obtained from the principal component analysis of soil ionome. Therefore, we have drawn the following conclusions: (1) The effect of excessive amounts of salts and Na^+ in underground water can be alleviated through adding $CaCl_2$ amendment and freezing-thawing process. (2) Soil column experiment revealed that brackish ice meltwater leaching could increase the infiltration depth (wetting front), as well as reduce the soil pH, EC, SAR and alkalinity. (3) For low ESP saline-sodic soils (ESP 20), a certain amount of calcium amendment was needed to override the excess Na^+ in underground brackish water, and the Na/Ca ratio (in brackish ice) should be less than 1.14. Otherwise, the irrigation water would increase the content of Na^+ in the soil and have adverse effects. (4) For high ESP soils (ESP 40 and ESP 70), a little $CaCl_2$ amendment would achieve a good amelioration effect, with the recommended combination for ESP 40 soil being 1.6 g/L brackish ice and 1 g/L brackish ice for ESP 70 soil. Given that the 1.5 PV irrigation quantity is not enough to leach and ameliorate the tilth layer of ESP 70 soil (only 0–12 cm soil layer can be improved), further amelioration should increase the amount of irrigation brackish ice.

The results of this study indicated that using saline underground water in conjunction with freezing-thawing and calcium amendment is a feasible approach to ameliorate saline-sodic soil. This result not only provides new approaches for the amelioration of saline-sodic soil but also provides theoretical support for the rational utilization of water resources in this region and promotes the amelioration and reuse of marginal water and degraded soils.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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