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Research article

Effective removal of sodium ion as efflorescence at soil surface using ammonium salts

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ABSTRACT

The existing methods for reclamation of saline-sodic soils are expensive, time-consuming, and require skilled engineering approaches. Therefore, new and fast techniques should be developed for the reclamation of these soils. This study was undertaken to evaluate if harvesting excessive salts via the soil with ammonium hexacyanoferrate (II) (AH) and ammonium perchlorate (AP) [0, 10, 20 and 40 mmol kg^{-1}] is possible through dendritic crystal growth above the soil surface. Application of crystallization inhibitors increased the concentration of salts on the outer surface and thereby increased pH_e at the top of the soil. Whereas the pH_e of 0–5 cm layers were obtained as 7.30, 7.36 and 7.84, it increased to 9.94, 9.84 and 8.45 in 15–20 cm layers with 10, 20 and 40 mmol kg^{-1} AH application doses, respectively. Except for 5–10 cm of control and 10 mmol kg^{-1} AP application, the lowest pH_e values were obtained from the 0–5 cm and gradually increased from bottom to top. For all AH and AP application doses, the highest electrical conductivity (EC_e) values were obtained from the 15–20 cm and significantly increased from bottom to top. Application of AH and AP have transformed exchangeable Na^+ to water-soluble Na^+ and this situation has caused an increase in the concentration of water-soluble Na^+ throughout the soil column. AH and AP applications have decreased exchangeable sodium percentage (ESP) in all of the layers. Whereas the ESP of control was 70.07% in 0–5 cm layer, it decreased to 62.44, 55.63 and 53.76% with 10, 20 and 40 mmol kg^{-1} AH application doses, respectively. Similar decreases were obtained for 5–10, 10–15 and 15–20 cm layers. Results obtained have shown that application of AH and AP to saline-sodic soil is an effective reclamation material to remove salts from soil surface within a short time, particularly in arid climates.

2. Introduction

Climate change and water scarcity issues in arid and semi-arid regions throughout the world have led to an increase in soil degradation (Ding et al., 2021). Soil degradation caused by salinization and sodification is considered as a major constraint for agricultural productivity. Of the 104-million km^2 habitable land area, only 50% (51-million km^2) is currently used for agriculture. However, only 23% (11-million km^2) of global agricultural land is used for crop production (Ritchie and Roser, 2019), and this land is expected to produce 82% of the world's calories and 63% of total protein (Poore and Nemecek, 2018). Irrigated agriculture, which accounts 40% of global food production, just covers 20% of cultivated land (2.75-milion km^2) (UNESCO, 2021), and nearly 20% of these areas are salt-affected to varying degrees. Along with primary (anthropogenic) sources, second (human-based activities) sources such as application of fertilizers, poor soil management, and unjustifiable use of water, vegetation and land are the main sources of salt-affected areas (Rengasamy, 2010; Nouri et al., 2017). Since, the focus on increasing the agricultural production per area is tried to be achieved, it is obvious that more areas will be threatened with salinity and/or sodicity problems in the next decades. Therefore, it is crucial to reclaim these areas with proper management strategies.

Several methods and techniques such as, leaching without amendment application to ameliorate gypsiferous sodic soils, leaching with high-electrolyte water, using chemical amendments, modifying soil profile through tillage, scrapping of salts and surface flushing, and

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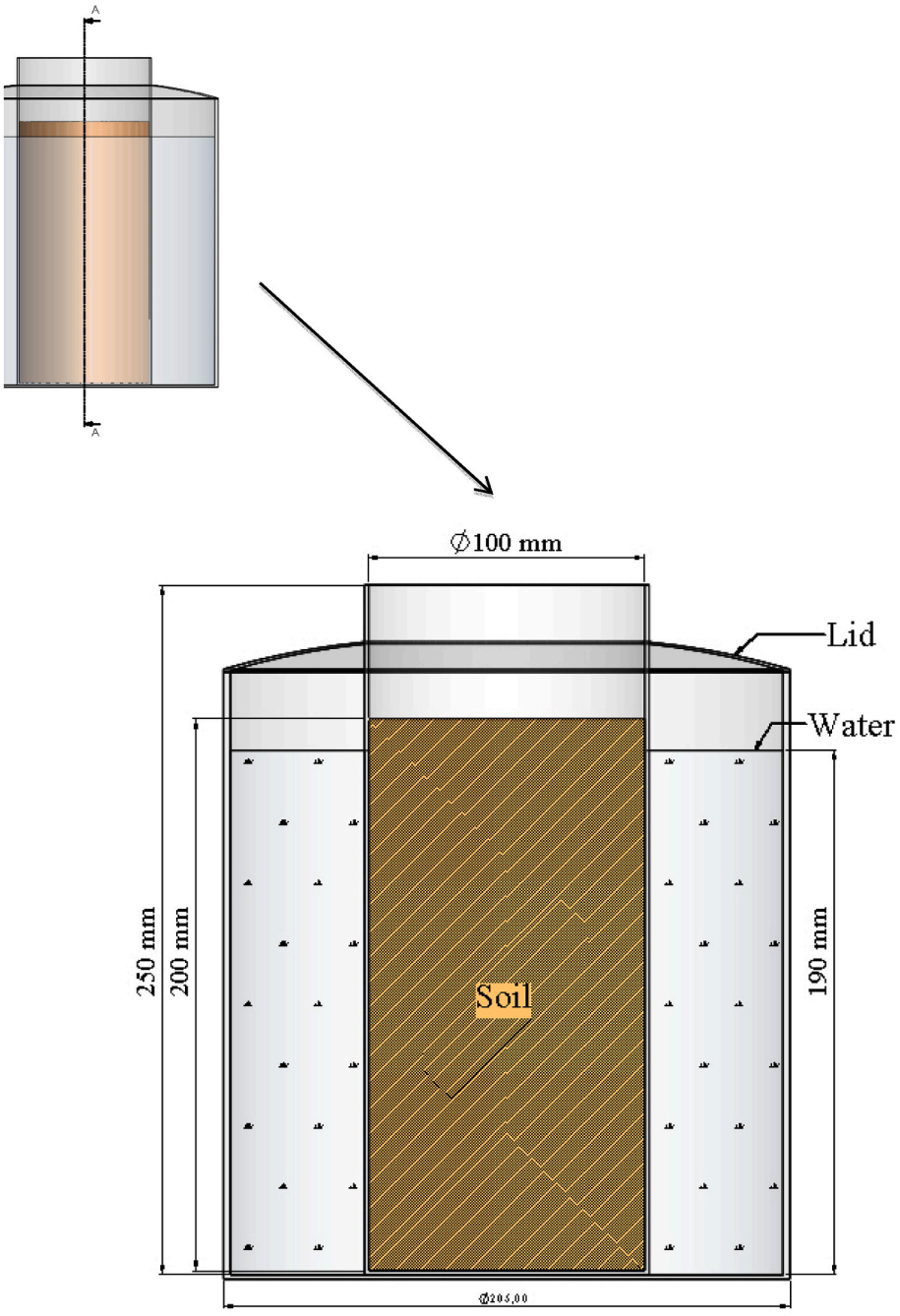

Fig. 1. Illustrated display of experimental setup.

phytoremediation are used for the reclamation of saline, sodic, and saline-sodic soils (Qadir et al., 1996, 2007; Pistocchi et al., 2017). However, these methods are expensive, time-consuming, and require skilled engineering approaches. Therefore, new and fast techniques should be developed for the reclamation of sodic and saline-sodic soils.

Development of methods and strategies for reclamation of sodic and saline-sodic soils has received considerable attention nowadays. Application of crystallization inhibitors is an emerging technique that uses some chemicals to disrupt salt precipitation within the porous media by preventing or delaying salt precipitation, and consequently, results in salt formations on the outer surfaces of the porous medium (Rodriguez-Navarro et al., 2002; Gupta et al., 2012; Daigh and Klaustermeier, 2016; Klaustermeier et al., 2017; Angin et al., 2019). The few experimental results published until now (Daigh and Klaustermeier, 2016; Klaustermeier et al., 2017; Angin et al., 2019; Swallow and O'Sullivan, 2019) suggest that iron (III) ferrocyanide $\{Fe_4[Fe(CN)_6]_3\}$ may have a positive effect on reclamation of saline, sodic and saline-sodic soils by enhancing salt transport towards the soil surface and thereby promoting the formation of efflorescences. Daigh and Klaustermeier (2016) and Klaustermeier et al. (2017) have reported a study in which the use of iron (III) ferrocyanide for sodium chloride (NaCl) removal on brine-contaminated soils is considered. They concluded that iron (III) ferrocyanide application at 0.01 M harvested 29–57% of salts from NaCl contaminated soils within 7 days. Angin et al. (2019) investigated the potential of using iron (III) ferrocyanide for the reclamation of saline-sodic soil and concluded that after 14 days of application the amount of total salts removed from soil was 12.2%, 26.6%, and 42.9% for 5, 10, and 15 mmol kg^{-1} application doses, respectively, and thus

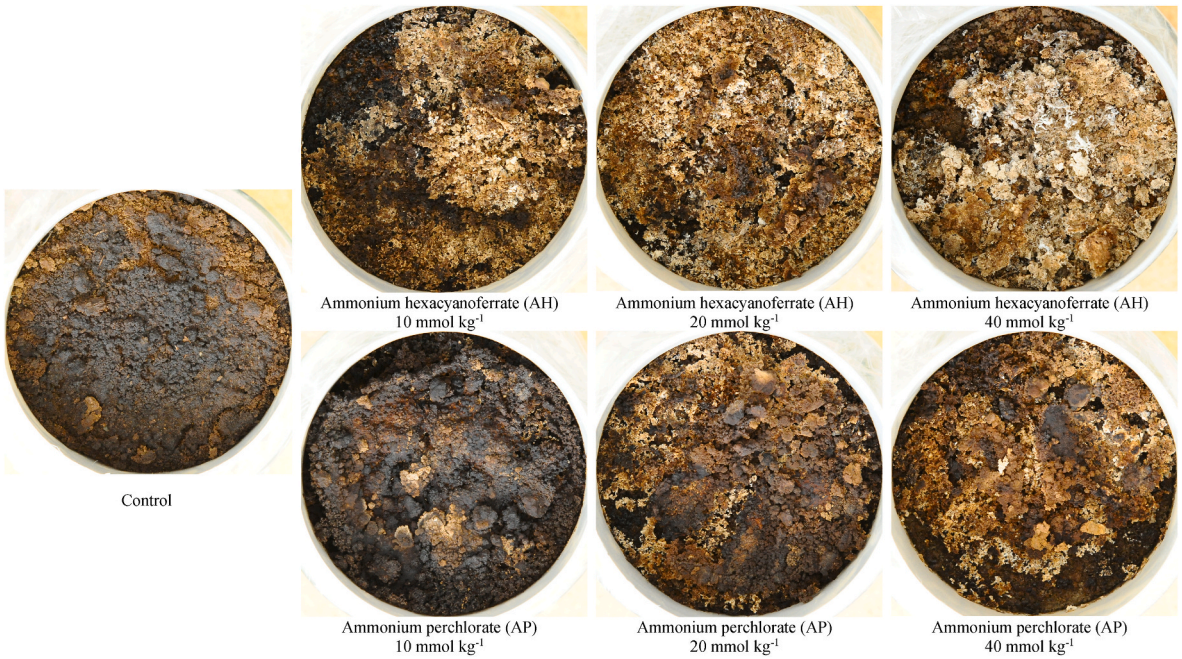

Fig. 2. Images of harvestable salt crystals deposited on the soil surface.

may be used for the amelioration of saline and saline-sodic soils. Unfortunately, iron (III) ferrocyanide is the only one crystallization inhibitor that is studied for the removal of Na^+ from soil.

The use of crystallization inhibitors is specific to the salt type that needs to be removed. While, Lubelli and van Hees (2007) have used sodium-ferrocyanide (NaFeC) and diethylenetriaminepentakis methylphosphonic acid (DTPMP) for sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) removal, Cassar et al. (2008) have used phospho-organic compound containing carboxylic moieties, and non-phosphorylated one for $NaSO_4$ removal. Selwitz and Doehne (2002), have investigated the potential of using potassium ferrocyanide, 1-Hydroxyethane-1, 1-diphosphonic acid (HEDP), ammonium sulfamate, methylenephosphonic acid, TRC, and polyaminopolyethermethylenephosphonic acid (PAPEMP) for sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) removal. The reason for selecting ferrocyanide in these studies is due to the structure of ferrocyanide molecule being nearly exact to that of a NaCl cluster. Results of these studies have revealed that a more detailed study is required to explore all aspects of different salt crystallization inhibitors in salt removal and inside the real porous material. Vincent et al. (2015) have reviewed immobilization of metal hexacyanoferrate ion-exchangers for the synthesis of metal ion sorbents and stated that metal hexacyanoferrates are very efficient sorbents for the recovery of alkali and base metal ions. Ammonium perchlorate (NH_4ClO_4) (AP), a water-soluble salt, is generally used as an explosive agent, oxidizing material, and etching compound in the industry. It is also preferred as a reagent in chemical analysis. It has been determined that the presence of sodium chloride (NaCl) strongly affects the physical properties of AP (Tanrikulu et al., 1998, 2000). Tanrikulu et al. (1998, 2000) reported that AP crystals are obtained with dendritic clusters if processed from their pure solution. It has also been denoted that the inclusion of NaCl in the crystallization solution blocks this dendritic orientation by decreasing both the growth and the dissolution rates of AP crystals. This case has been associated with the effect of both integration and diffusion steps on the overall growth rate of the AP crystals in NaCl containing aqueous solution (Tanrikulu et al., 1998). Hence, it is worth investigating remediation of saline-sodic soil using AP because AP is hypothesized to have the potential to decrease soil salinity by mixed crystal formation mechanism.

Therefore, the usability of crystallization inhibitors such as ammonium hexacyanoferrate (II) [$(NH_4)_4Fe(CN)_6$] (AH) and ammonium perchlorate [NH_4ClO_4] (AP) in saline-sodic soil reclamation should be investigated in detail. This study was undertaken to evaluate if harvesting excessive Na^+ via the soil with AH and AP is possible without a drainage system or undrained soil through dendritic crystal growth above the soil surface. The reason for selecting ammonium inhibitors in this study is not only due to its reaction and binding with organic matter and clay but also the attachment of ammonium ions on the soil cation exchange complex, thus easily replacement of Na^+.

2. MATERIALS and METHODS

A disturbed soil column study was conducted using a complete randomized block design with one factor (AH and AP) and three replicates under laboratory conditions with an average temperature of 25 ± 2 °C and a relative humidity of 60 ± 5%. The studies were done with a Typic Natrargid (Soil Survey Staff, 2014) sampled to a depth of 0–20 cm from Igdir plain, located in the northeast of Turkey. Soil was taken over an area of 10 ha using a grid sampling pattern (50 m × 50 m). The soil has 35.1% clay, 44.1% silt, and 20.8% sand with pH_e 9.02, 32.37 mS cm^{-1} electrical conductivity (EC_e), 1.04% soil organic matter, 8.84% calcium carbonate, and 83.21% exchangeable sodium percentage (ESP), respectively.

The soil was air-dried and crumbled to pass 8 mm sieve and was homogenized by thorough mixing. For each experiment 2150 g soil was transferred to 21 PVC columns (10 cm diameter and 25 cm depth). The bulk density (ρ_b) of soil was 1.22 g cm^{-3} and the length of the soil was 20 cm. The prepared samples were then placed into glass beaker reservoirs to obtain saturation throughout the experimental period (Fig. 1). The AH and AP (analytical reagent grade; Alfa Aesar) were added to reservoirs once as $(NH_4)_4Fe(CN)_6$ and NH_4ClO_4 solutions to obtain application doses of 0, 10, 20 and 40 mmol kg^{-1} for both. The experiment was ended when approximately three pore volume of water was evaporated from the soil column. After 10 months, dry dendritic crystals were gently removed from the surface (Fig. 2) and columns were opened longitudinally. The opened columns were sampled into 4 vertical intervals (0–5, 5–10, 10–15 and 15–20 cm) and 3 horizontal intervals (0–3.3, 3.3–6.7 and 6.7–10 cm), as a total of 12 samples from each column (Fig. 3). Collected samples were air-dried, crumbled and pass through a 2 mm sieve for further analysis. pH_e, electrical conductivity

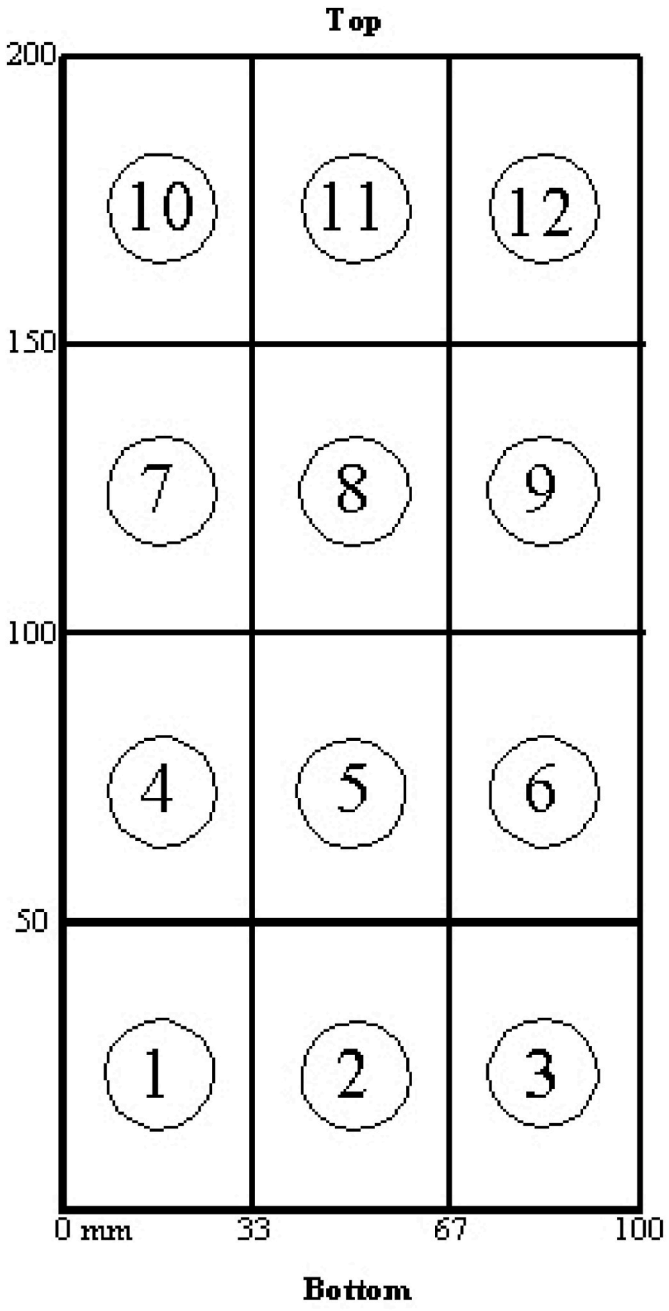

Fig. 3. Layout of soil sampling.

(EC_e), water-soluble Na^+, exchangeable Na^+ and cation exchange capacity (CEC) analysis were conducted in each collected samples and exchangeable sodium percentages (ESP) were calculated.

Particle size analysis was performed by the Bouyoucos hydrometer method according to Gee and Or (2002). Soil pH and EC determinations were done in saturation extracts using glass electrode pH meter (Thomas, 1996) and standard EC electrode (Rhoades, 1996), respectively. Soil organic matter was determined using the Smith-Weldon method as described in Nelson and Sommers (1996). $CaCO_3$ content of soil was determined with the "Scheibler Calcimeter" as described by Loeppert and Suarez (1996). Water-soluble Na^+ concentration was determined from saturation extracts using a flame photometer (USSL, 1954). Ammonium acetate buffered at pH 7 was used to determine exchangeable Na^+ (Helmke and Sparks, 1996). Cation exchange capacity (CEC) was determined with a flame photometer (Jenway PFP-7, Essex, UK) using 1-M neutral ammonium acetate method (Sumner and Miller, 1996). The exchangeable sodium percentage (ESP) was calculated according to USSL (1954). Geostatistical analyses were performed using the GS^+ Version 10.0 geostatistical software (Gamma Design Software, 2015). The crystallographic structures of the efflorescence's were examined by powder X-ray diffraction (XRD) using a Rigaku (miniflex) X-ray diffractometer with Cu Kα radiation (λ = 1.5405 Å).

Statistical analysis was performed using SPSS Statistical Package v.20.0 (IBM, 2011). The data were subjected to one-way analysis of variance (ANOVA) followed by comparison of relevant means using Tukey's multiple comparison test method at 95% level of significance. Following checks of residuals, no data needed transformation.

3. RESULTS and DISCUSSION

Effects of AH and AP applications on soil pH_e are given in Tables 1 and 2, respectively. The pH_e variation patterns showed significant differences at different sampling points of the soil column (Fig. 4). While the pH_e of the control soil was 7.68 in 0–5 cm, it was found as 7.56, 9.13 and 9.85 for 5–10, 10–15 and 15–20 cm, respectively. In all AH application doses tested, the lowest pH_e values were obtained from the 0–5 cm of the soil column and gradually increased from bottom to top. Whereas the pH_e of 0–5 cm layers were obtained as 7.30, 7.36 and 7.84, it increased to 9.94, 9.84 and 8.45 in 15–20 cm layers with 10, 20 and 40 mmol kg^{-1} AH application doses, respectively. The range of variation was found as 2.29, 2.64, 2.48 and 0.61 units for control, 10, 20 and 40 mmol kg^{-1} AH application doses, respectively. The coefficient of variance (CV) for these application doses was found as 11.92, 13.15, 12.70 and 3.76%, respectively. The smaller variability which obtained under 40 mmol kg^{-1} AH application dose shows that pH_e variations among the soil column was almost similar and this dose is much more effective in pH_e decrease throughout the soil column (Fig. 4). Application of AP altered pH_e of the soil layers and almost same trend was seen as in AH application (Table 2). Except for 5–10 cm of control and 10 mmol kg^{-1} AP application, the lowest pH_e values were obtained from the 0–5 cm of the soil column and gradually increased from bottom to top (Fig. 4). This result is similar to the findings of Klaustermeier et al. (2017), who observed that soil pH increased with the application of inhibitor and ammonium hydroxide. The usual tendency of pH_e is to decrease from top to bottom because all current remediation methods involve the downward movement and extraction of salts through leaching. The addition of crystallization inhibitor increased the concentration of salts on the outer surface of the soil and thereby increased pH_e at the top of the soil. Gupta et al. (1989) have stated that soil pH usually increases with an increase in salinity, due to the effects of $NaHCO_3$ and associated salts. The use of crystallization inhibitor (AH and AP) have worked with the natural processes of evaporation thus transport of salts upward and efflorescence on the soil surface rather than displacing salts downward.

When layers were compared it is clearly seen that the highest pH_e value (7.84) for 0–5 cm was obtained from 40 mmol kg^{-1} AH treatment. The highest pH_e values for 5–10, 10–15 and 15–20 cm layers were obtained from 10 mmol kg^{-1} AH treatment as 8.46, 9.91 and 9.94, respectively. For AP treatment, the highest pH_e values for 0–5 cm (7.76), 5–10 cm (8.04), 10–15 (9.16) and 15–20 cm (9.85) layers were obtained from 10 mmol kg^{-1}, 20 mmol kg^{-1}, 20 mmol kg^{-1} and control, respectively. This situation may cause perception of control is better than AH and AP treatments on pH_e across layers. However, when exchangeable and water-soluble Na^+ values are investigated (Tables 1 and 2 and Figs. 6 and 7) it is clearly seen that exchangeable Na^+ contents were decreased in regard to an increase in water-soluble Na^+ contents with AH and AP treatments. While the amount of water-soluble Na^+ was determined to be 15.62 cmol kg^{-1} in control soil, it was determined as 21.89, 24.16 and 30.03 cmol kg^{-1} for 10, 20, and 40 mmol kg^{-1} AH applications, and 18.11, 19.58, and 22.73 cmol kg^{-1} for 10, 20, and 40 mmol kg^{-1} AP applications, respectively. AH and AP treatments have transformed exchangeable Na^+ to water-soluble Na^+ and hence, this situation has increased pH_e across layers due to an increase in dissolved

Table 1
Effects of AH applications on soil pH_e, electrical conductivity (EC_e), water-soluble Na^+ concentration, exchangeable Na^+ concentration and exchangeable sodium percentage (ESP).

Application dose (mmol kg^{-1})	Soil Layer (cm)	pH_e	EC_e (mS cm^{-1})	Water-soluble Na^+ (cmol kg^{-1})	Exchangeable Na^+ (cmol kg^{-1})	ESP (%)
Control	0–5	7.68 ± 0.13cAB£	2.27 ± 0.16bC	0.88 ± 0.04bD	19.88 ± 1.20bA	70.07 ± 1.27bA
	5–10	7.56 ± 0.12 cB	3.20 ± 0.34bC	1.22 ± 0.07bC	24.46 ± 0.70 aA	87.07 ± 3.82 aA
	10–15	9.13 ± 0.06bC	4.95 ± 0.68bB	2.89 ± 0.69bD	27.80 ± 0.36 aA	98.44 ± 0.64 aA
	15–20	9.85 ± 0.08 aA	69.44 ± 9.93 aA	57.50 ± 5.61 aA	16.01 ± 3.04bA	57.45 ± 10.86bA
	Mean	*8.56 ± 1.02B*	*19.96 ± 30.16C*	*15.62 ± 25.38C*	*22.04 ± 4.89A*	*78.26 ± 17.12A*
10	0–5	7.30 ± 0.37 cB	4.64 ± 0.44 dB	1.87 ± 0.09 dC	19.62 ± 0.92bA	62.44 ± 2.93bB
	5–10	8.46 ± 0.22bA	14.62 ± 1.04 cB	11.00 ± 1.60 cB	25.21 ± 1.70 aA	80.24 ± 5.43aAB
	10–15	9.91 ± 0.03 aA	36.72 ± 0.91bA	26.19 ± 0.28bC	25.66 ± 1.18 aA	81.67 ± 3.74 aB
	15–20	9.94 ± 0.02 aA	56.94 ± 1.53 aB	48.50 ± 1.72 aB	14.46 ± 1.55 cA	46.01 ± 4.92 cA
	Mean	*8.90 ± 1.17A*	*28.23 ± 21.16B*	*21.89 ± 18.46B*	*21.24 ± 4.93AB*	*67.59 ± 15.68B*
20	0–5	7.36 ± 0.20 cB	4.74 ± 1.26 dB	2.92 ± 0.53 dB	17.48 ± 1.00abAB	55.63 ± 3.19abBC
	5–10	8.12 ± 0.49bA	12.93 ± 2.67 cB	10.60 ± 2.17 cB	24.18 ± 0.97 aA	76.96 ± 3.09 aB
	10–15	9.65 ± 0.11 aB	36.91 ± 3.04bA	31.99 ± 2.07bA	19.89 ± 3.20abB	63.31 ± 10.18abC
	15–20	9.84 ± 0.04 aA	58.97 ± 3.88 aB	51.12 ± 4.40aAB	16.16 ± 3.80bA	51.43 ± 12.11bA
	Mean	*8.74 ± 1.11AB*	*28.39 ± 22.33B*	*24.16 ± 19.83B*	*19.43 ± 3.87B*	*61.83 ± 12.33B*
40	0–5	7.84 ± 0.18bA	18.84 ± 1.38 cA	15.55 ± 0.73 cA	16.89 ± 2.03 aB	53.76 ± 6.48 aC
	5–10	8.32 ± 0.22 abA	32.58 ± 1.81bA	27.71 ± 0.95bA	16.08 ± 0.68 aB	51.18 ± 2.17 aC
	10–15	8.41 ± 0.23 aC	34.87 ± 2.03bA	29.31 ± 1.64bB	16.20 ± 1.72 aC	51.57 ± 5.46aD
	15–20	8.45 ± 0.22 aB	46.09 ± 0.85 aC	47.53 ± 1.71 aB	5.73 ± 0.19bB	18.24 ± 0.58bB
	Mean	*8.25 ± 0.30C*	*33.10 ± 10.21A*	*30.03 ± 11.98A*	*13.73 ± 4.97C*	*43.69 ± 15.83C*

£While small letters followed in each column shows differences between layers for same soil, capital letters in each column shows differences between same layers of different application doses (Mean ± SD). Mean differences were tested at the level of $p < 0.05$.

Table 2
Effects of AP applications on soil pH_e, electrical conductivity (EC_e), water-soluble Na^+ concentration, exchangeable Na^+ concentration and exchangeable sodium percentage (ESP).

Application dose (mmol kg^{-1})	Soil Layer (cm)	pH_e	EC_e (mS cm^{-1})	Water-soluble Na^+ (cmol kg^{-1})	Exchangeable Na^+ (cmol kg^{-1})	ESP (%)
Control	0–5	7.68 ± 0.13cAB£	2.27 ± 0.16bC	0.88 ± 0.04bC	19.88 ± 1.20bA	70.07 ± 1.27bA
	5–10	7.56 ± 0.12cNS	3.20 ± 0.34bC	1.22 ± 0.69bC	24.46 ± 0.70 aA	87.07 ± 3.82 aA
	10–15	9.13 ± 0.06bA	4.95 ± 0.68bC	2.89 ± 0.70bC	27.80 ± 0.36 aA	98.44 ± 0.64 aA
	15–20	9.85 ± 0.08 aA	69.44 ± 9.93 aA	57.50 ± 5.61 aA	16.01 ± 3.04bB	57.45 ± 10.86bB
	Mean	*8.56 ± 1.02AB*	*19.96 ± 30.16B*	*15.62 ± 25.38C*	*22.04 ± 4.89A*	*78.26 ± 17.12A*
10	0–5	7.76 ± 0.09 cA	6.80 ± 1.18 cB	8.10 ± 1.06 cB	17.41 ± 0.83 cB	55.41 ± 2.63 cB
	5–10	7.61 ± 0.30cNS	8.79 ± 0.23 cB	10.05 ± 0.14 cB	22.39 ± 0.18bB	71.28 ± 0.58bB
	10–15	8.85 ± 0.14bB	18.10 ± 2.58bB	17.55 ± 2.02bB	23.52 ± 1.19abB	74.85 ± 3.79abB
	15–20	9.71 ± 0.04 aB	46.12 ± 4.35 aB	36.73 ± 2.94 aC	24.49 ± 0.37 aA	77.96 ± 1.18 aA
	Mean	*8.48 ± 0.91AB*	*19.95 ± 16.54B*	*18.11 ± 11.92B*	*21.95 ± 2.92A*	*69.87 ± 9.29B*
20	0–5	7.59 ± 0.14dAB	9.93 ± 1.12 dA	10.07 ± 1.06 dA	17.15 ± 1.11bB	54.58 ± 3.54bB
	5–10	8.04 ± 0.11cNS	13.51 ± 1.57 cA	13.23 ± 1.04 cA	21.83 ± 1.00 aB	69.48 ± 3.16 aB
	10–15	9.16 ± 0.03bA	20.86 ± 1.73 bAB	18.94 ± 1.11 bAB	23.88 ± 0.67 aB	75.99 ± 2.12 aB
	15–20	9.66 ± 0.07 aB	48.29 ± 0.59 aB	36.07 ± 0.74 aC	22.76 ± 0.95 aA	72.44 ± 3.04 aA
	Mean	*8.61 ± 0.87A*	*23.15 ± 15.75AB*	*19.58 ± 10.52B*	*21.40 ± 2.79A*	*68.12 ± 8.89B*
40	0–5	7.30 ± 0.37 cB	9.83 ± 0.75 cA	10.59 ± 0.71 cA	14.10 ± 0.74bC	44.89 ± 2.36bC
	5–10	7.69 ± 0.34cNS	13.07 ± 0.34 cA	14.10 ± 0.20 cA	19.11 ± 0.94 aC	60.81 ± 2.97 aC
	10–15	8.89 ± 0.02bB	21.88 ± 0.65bA	21.18 ± 0.66bA	19.78 ± 0.66 aC	62.96 ± 2.11 aC
	15–20	9.71 ± 0.05 aB	56.14 ± 3.18 aB	45.05 ± 2.52 aB	16.73 ± 2.64abB	53.25 ± 8.44abB
	Mean	*8.40 ± 1.03B*	*25.23 ± 19.25A*	*22.73 ± 14.09A*	*17.43 ± 2.65B*	*55.48 ± 8.45C*

£While small letters followed in each column shows differences between layers for same soil, capital letters in each column shows differences between same layers of different application doses (Mean ± SD). Mean differences were tested at the level of $p < 0.05$. NS: not significant.

inorganic solutes.

For all AH and AP application doses tested, the highest EC_e values were obtained from the 15–20 cm layer of the soil column and significantly increased from bottom to top (Tables 1 and 2 and Fig. 5). While the EC_e of control was 2.27 mS cm^{-1} in 0–5 cm layer, it increased to 69.44 mS cm^{-1} in 15–20 cm. When 0–5 cm layer is compared with 15–20 cm, it is seen that the EC_e values were increased from 4.64 to 56.94 mS cm^{-1} in 10 mmol kg^{-1} AH, 4.74 to 58.97 mS cm^{-1} in 20 mmol kg^{-1} AH, and from 18.84 to 46.09 mS cm^{-1} in 40 mmol kg^{-1} AH application doses. For AP treatments, the EC_e values in 0–5 cm layer increased from 6.80 to 46.12, 9.93 to 48.29 and 9.83 to 56.14 mS cm^{-1} in 15–20 cm layer for 10, 20 and 40 mmol kg^{-1} application doses, respectively. The reason for higher EC_e values throughout the soil column from bottom to top was due to the setup of the experimental design. This study has worked with the natural processes of evaporation thus the transport of salts upwards, hence accumulation of salts on the outer surface of the soil column (15–20 cm). Application of crystallization inhibitor allowed for the *in-situ* removal of effloresced salts from the soil

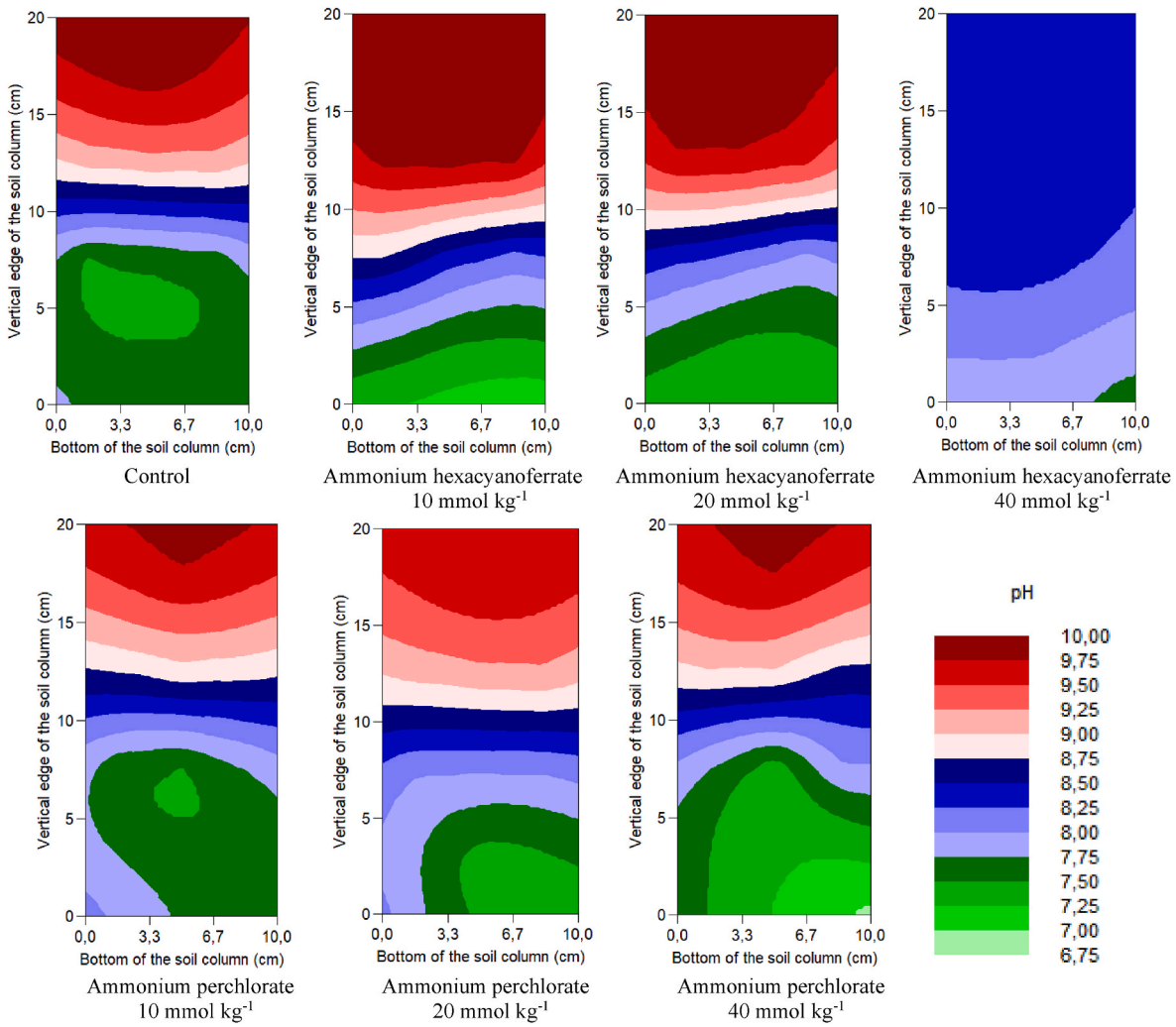

Fig. 4. Spatial variability distribution in soil pH at different soil depths of column (0–20 cm).

surface, thus EC of the upper layers were higher. While the EC_e values of 0–5, 5–10 and 10–15 cm layers in control were lower than that of AH and AP treatments, it was higher in 15–20 cm layer. This situation can be explained by the fact of water-soluble Na^+ contents of 0–5, 5–10 and 10–15 cm layers in control was lower than that of AH and AP treatments (Tables 1 and 2 and Fig. 6). As stated in pH_e, application of AH and AP have transformed exchangeable Na^+ to water-soluble Na^+ and this situation has caused an increase in the total concentration of water-soluble Na^+. Water-soluble Na^+ in control have accumulated in 15–20 cm layer, thus higher EC_e values than that of AH and AP treatments. While harvestable salt efflorescence with dendritic patterns above the soil surface was seen in AH and AP treatments it did not occur in any of the control soil column (Fig. 2). Application of AH and AP have increased the formation of dry dendritic crystals, hence easily harvest of salts from the outer surface of the soil column. In general, the higher the crystallization inhibitor, the higher the efflorescence produced (Klaustermeier et al., 2017; Angin et al., 2019). This result was in agreement with the finding of Klaustermeier et al. (2017), who observed no dendritic crystal growth in control soils without iron (III) ferrocyanide application.

Effects of AH and AP applications on water-soluble Na^+ and exchangeable Na^+ are given in Tables 1 and 2, respectively. In all application doses tested, the lowest water-soluble Na^+ values were obtained from the 0–5 cm of the soil column and gradually increased from bottom to top (Fig. 6). When 0–5 cm layer is compared with 15–20 cm, it is seen that the water-soluble Na^+ values were increased from 0.88 to 57.50 cmol kg^{-1} in control, 1.87–48.50 cmol kg^{-1} in 10 mmol kg^{-1} AH, 2.92–51.12 cmol kg^{-1} in 20 mmol kg^{-1} AH, and from 15.55 to 47.53 cmol kg^{-1} in 40 mmol kg^{-1} AH application doses. For AP treatments, the water-soluble Na^+ values in 0–5 cm layer increased from 8.10 to 36.73 cmol kg^{-1}, 10.07–36.07 cmol kg^{-1} and 10.59–45.05 cmol kg^{-1} in 15–20 cm layer for 10, 20 and 40 mmol kg^{-1} application doses, respectively. While water-soluble Na^+ contents of AH and AP applications in 0–5, 5–10 and 10–15 cm layers were higher than that of control, it was lower in 15–20 cm. The higher water-soluble Na^+ content in 15–20 cm of control could not only due to the transport and accumulation of salts to this layer but also harvest of salts from this layer in AH and AP applications. Also, application of AH and AP have transformed exchangeable Na^+ to water-soluble Na^+ and this situation has caused an increase in the concentration of water-soluble Na^+ (Tables 1 and 2). This hypothesis is consistent with exchangeable Na^+ values. While the amount of exchangeable Na^+ was determined to be 22.04 cmol kg^{-1} in control soil, it was determined as 21.24, 19.43 and 13.73 cmol kg^{-1} for 10, 20, and 40 mmol kg^{-1} AH applications, and 21.95, 21.40, and 17.43 cmol kg^{-1} for 10, 20, and 40 mmol kg^{-1} AP applications, respectively. In general, AH and AP applications have decreased exchangeable Na^+ values (Fig. 7). Ammonium forms [$(NH_4)_4Fe(CN)_6$ and NH_4ClO_4] found in solutions can be the main factor of these changes. The exchange complex is partially saturated with ammonium and this has caused replacement of Na^+ by ammonium. However, the replacing power of selected doses are insufficient to replace all of the Na^+ found in exchange complex. Exchangeable sodium percentage (ESP) of soils amended with AH and AP are presented in Tables 1 and 2, respectively.

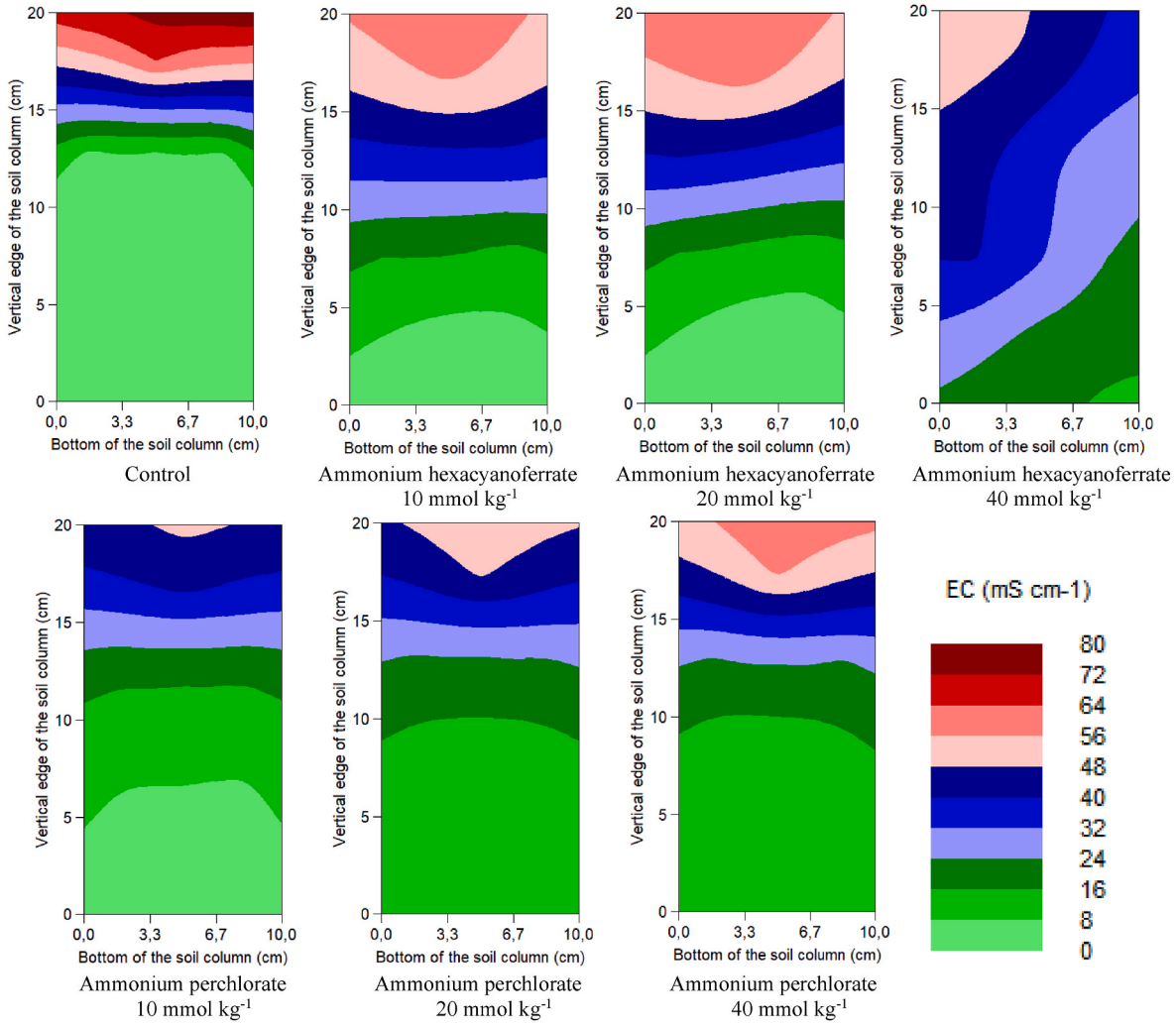

Fig. 5. Spatial variability distribution in soil EC at different soil depths of column (0–20 cm).

The ESP variation patterns showed significant differences at different sampling points of the soil column (Fig. 8). While the ESP of the control was 70.07% in 0–5 cm layer, it was found as 87.07, 98.44 and 57.45% for 5–10, 10–15 and 15–20 cm, respectively. When layers of control is compared with AH treatments it is clearly seen that the highest ESP values for 0–5, 5–10, 10–15 and 15–20 cm was obtained from control. As compared to control, AH applications have decreased ESP in all of the layers. Whereas the ESP of control was 70.07% in 0–5 cm layer, it decreased to 62.44, 55.63 and 53.76% with 10, 20 and 40 mmol kg^{-1} AH application doses, respectively. Similar decreases were obtained for 5–10, 10–15 and 15–20 cm layers. Except 15–20 cm layer of 10 and 20 mmol kg^{-1} AP treatments, ESP values of soils amended with AP had lower ESP values than that of control. While the mean ESP of control column was found as 78.26%, it decreased to 67.59, 61.83 and 43.69% with 10, 20 and 40 mmol kg^{-1} AH application doses, respectively. These values were found as 69.87, 68.12 and 55.48 with 10, 20 and 40 mmol kg^{-1} AP application doses, respectively. As compared with the control, the decreasing rates in ESP values for 10, 20, and 40 mmol kg^{-1} application doses were 13.6%, 21%, and 44.2% for AH, and 10.7%, 13%, and 29.1% for AP applications, respectively. As seen from the results presented, AH application is more effective than AP in ESP reduction. AH application in 40 mmol kg^{-1} have decreased ESP to 18.24% in 15–20 cm layer, which is close to accepted critical level. However, none of the treatment doses have decreased ESP to desired level (<15%). This situation indicates the necessity for reconsidering the doses applied. In addition to obtained results, it can be stated that this study is important to show that reduction of ESP with AH and AP applications can be achieved within a short time period, under arid conditions where leaching water is scarce and natural/artificial drainage systems are not available.

The main concern associated with AH and AP application is related to nitrate pollution. AH and AP application to soil requires careful and controlled use in terms of nitrification, because nitrate has a high mobility in soil. Amounts of N released with AH and AP applications varied between 140 and 2240 mg kg^{-1} in this study. High dosage of AH and AP application may cause eutrophication in the groundwater and surrounding watershed. However, these values are not the total N released to soil with AH and AP applications. The vast majority of N is taken as an efflorescence from the soil surface, thus released N is expected to be much lower than given by AH and AP applications. This issue warrants further investigation and is currently under research.

Powder XRD technique has been performed to evaluate soil remediation. Fig. 9 illustrates XRD data of pure materials as well as treated soil with different concentrations of AP and AH. Observed XRD peaks of all samples have also been determined as represented in Table 3. The XRD of the control sample contains various diffraction peaks, indicating a polycrystalline crystal structure of the soil. The most intensive peak for control is observed at $2\Theta = 31.7°$, which is very close to previously published work (Fitzpatrick, 2008). The XRD spectra and peak analyses of the salts performed for soil remediation have been shown in Fig. 9 and Table 3, respectively. The XRD pattern of AP is associated with the American Society for Testing and Materials (ASTM) code of

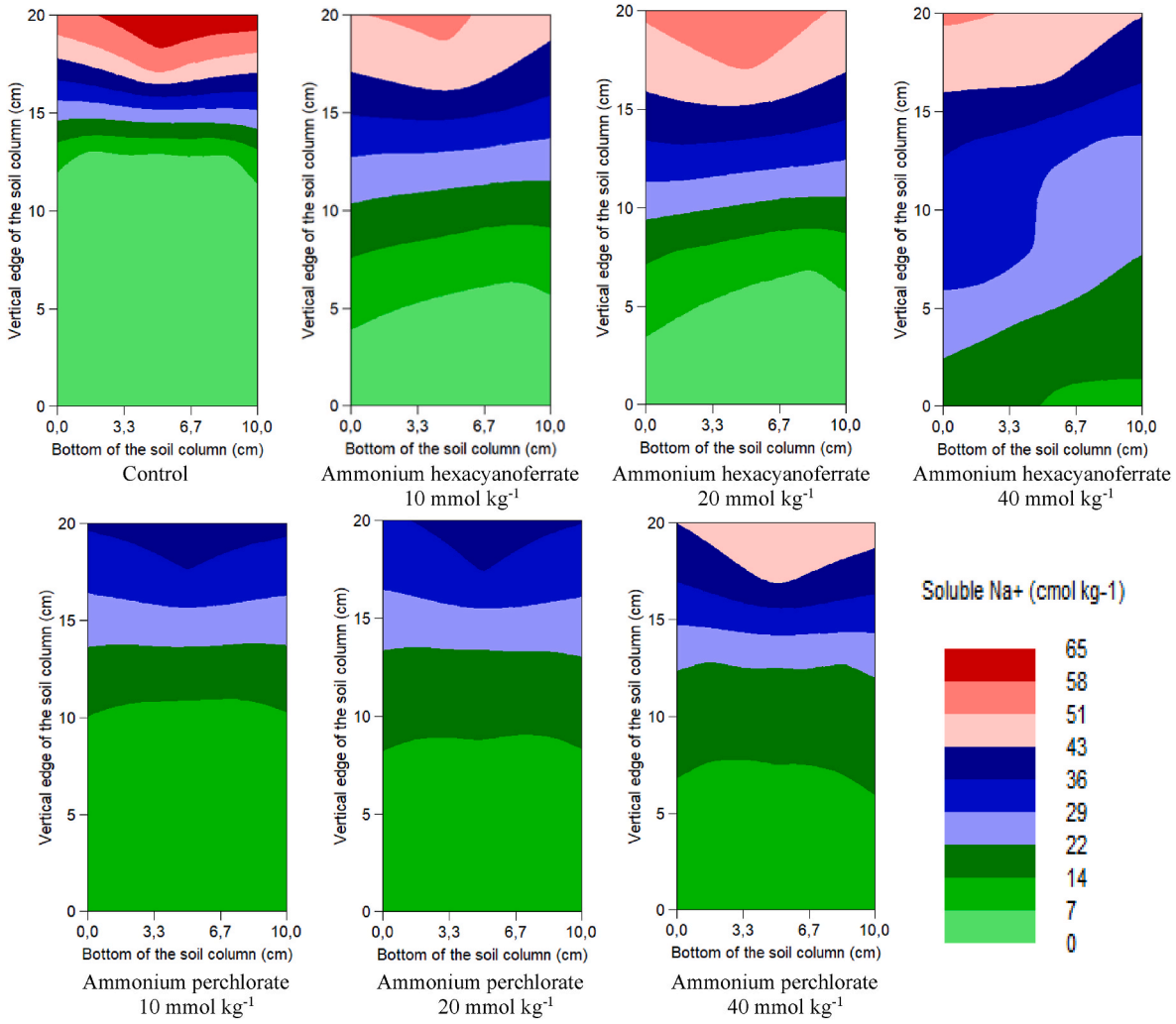

Fig. 6. Spatial variability distribution in water-soluble Na^+ at different soil depths of column (0–20 cm).

00–008-0451 (Hosseini et al., 2021) After treatment of the soil with 10 mmol kg^{-1} of AP, collected samples from the surface of the soil exhibited different XRD peaks as seen in Table 3. For this sample, only two peaks were assigned to the soil, while two peaks were also associated with AP. For this sample, 14 new XRD peaks arise which can be attributed to the mixed crystal structure of perchlorate salts with different cations such as sodium, potassium, magnesium, and calcium.

After treatment the soil samples with ammonium salt solutions, direction of water evaporation is expected through the surface of the soil, which results in the formation of nuclei of the crystallites (Dai et al., 2016). Crystallization of both AH and AP in the soil samples, which contain large amount of sodium ion are supposed to take place with mixed crystal formation by following mechanisms;

$$(NH_4)_4Fe(CN)_6(s) + xNa^+(aq) \rightarrow (NH_4)_{4-x}Na_xFe(CN)_6(s) + xNH_4{}^+(aq) \quad (1)$$

$$NH_4ClO_4(s) + yNa^+(aq) \rightarrow (NH_4)_{1-y}Na_yClO_4(s) + yNH_4{}^+(aq) \quad (2)$$

Elapsing time, transport of salts from inner side of the soil toward surface occurs by diffusion because of formation of solid phase at the surface. Then, nuclei start to grow to yield large crystals (efflorescences) on the soil surface.

Running more AP did not change remediation performance because almost the same XRD patterns were obtained for 20 and 40 mmol kg^{-1}. The treatment of the soil with AH indicated interesting results. The usage of 10 and 20 mmol kg^{-1} of AH demonstrated similar remediation performance, presenting peaks of soil, AH, and mixed crystal. The operation by 40 mmol kg^{-1} of AH yielded additional peaks, showing better soil remediation efficiency of AH than AP at the higher dose. This situation can be explained by taking redox abilities of the used salts. The perchlorate is an oxidant, while hexacyanoferrate (II) shows a reducing agent role based on the following redox reactions.

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-} \quad (3)$$

$$ClO_4{}^- + 2H^+ + 2e^- \rightarrow ClO_3{}^- + H_2O \quad (4)$$

The standard electrode potential values for reaction 3 and 4 are 0.37 V (Rock, 1965) and 1.19 V (Ujvari and Lang, 2011), respectively. Hence, it can be deduced that oxidative force of perchlorate is very high and hexacyanoferrate (II) can be classified as a weak reductant. Therefore, side redox reactions of perchlorate ion as oxidant are anticipated in soil samples which decrease the possibility of Na^+ integration during crystallization, while redox of hexacyanoferrate (II) is supposed with a very low probability. Moreover, sodic soils contain high amount of potassium ion besides sodium. Potassium hexacyanoferrate (II) salt is water soluble, while AP reveals precipitation reaction with K^+ yielding solid $KClO_4$ in the soil because its solubility product constant (Ksp) is 1.05×10^{-2} at 298 K (Guo et al., 2022) The precipitation of $KClO_4$ also reduces the possibility of removal of Na^+ by using AP.

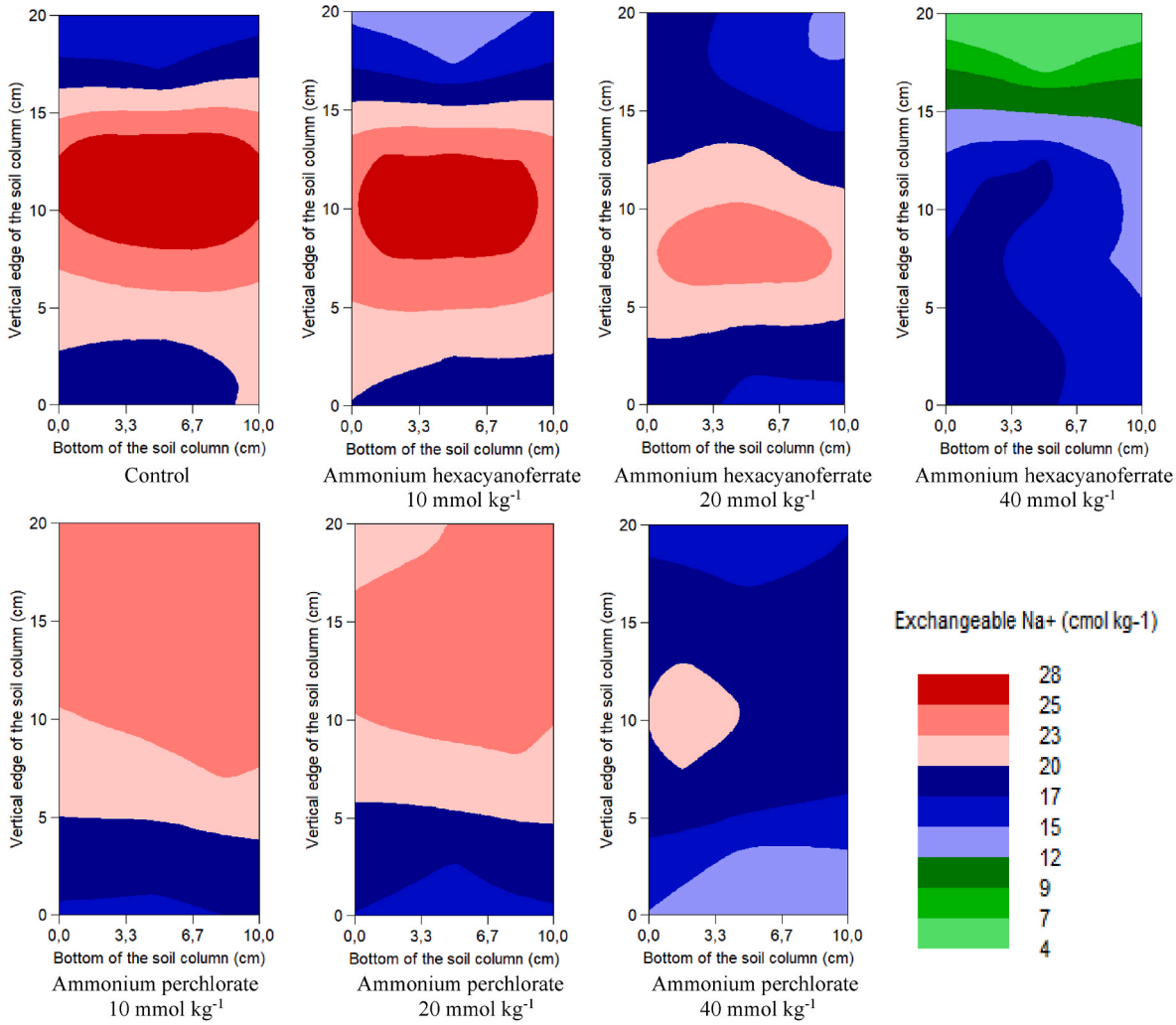

Fig. 7. Spatial variability distribution in exchangeable Na^+ at different soil depths of column (0–20 cm).

4. Conclusion

This study evaluated if harvesting excessive salts via the soil with AH and AP is possible through dendritic crystal growth above the soil surface. AH and AP treatments have transformed exchangeable Na^+ to water-soluble Na^+ and hence, this situation has increased pH_e and EC_e across layers due to an increase in dissolved inorganic solutes. Whereas the pH_e of 0–5 cm layers were obtained as 7.30, 7.36 and 7.84, it increased to 9.94, 9.84 and 8.45 in 15–20 cm layers with 10, 20 and 40 mmol kg^{-1} AH application doses, respectively. Application of AP have also altered pH_e of the soil layers and almost same trend was seen as in AH application. The reason for higher pH_e and EC_e values throughout the soil column from bottom to top was due to the setup of the experimental design, which has worked with the natural processes of evaporation thus the transport of salts upwards, hence accumulation of salts on the outer surface of the soil column. While the amount of exchangeable Na^+ was determined to be 22.04 cmol kg^{-1} in control soil, it decreased to 21.24, 19.43 and 13.73 cmol kg^{-1} in 10, 20, and 40 mmol kg^{-1} AH applications, and 21.95, 21.40, and 17.43 cmol kg^{-1} in 10, 20, and 40 mmol kg^{-1} AP applications, respectively. Not only decrease in the concentration of exchangeable Na^+ but also increase in the concentration of water-soluble Na^+ have decreased ESP. While the response was dependent on application doses, AH application was found much more effective. As compared with the control, the decreasing rates in ESP values for 10, 20, and 40 mmol kg^{-1} application doses were 13.6%, 21%, and 44.2% for AH, and 10.7%, 13%, and 29.1% for AP applications, respectively. Results obtained have shown that application of AH and AP to saline-sodic soil have enhanced salt transport towards the soil surface and thereby promoted the formation of efflorescences, hence easily harvest of salts from the outer surface of the soil column within a short time. Results suggested that application of AH and AP could be an effective tool to remove salts from the outer surface of soil, where leaching water is scarce and natural and/or artificial drainage system is not available.

Credit authorship contribution statement

Ilker ANGIN: Investigation, Methodology, Analysis, Data curation, Writing – original draft, review & editing. Ekrem Lutfi AKSAKAL: Methodology, Analysis, Data curation, Writing – original draft, review & editing. Serdar SARI: Analysis, Writing – review & editing. Murat ALANYALIOGLU: Methodology, Analysis, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

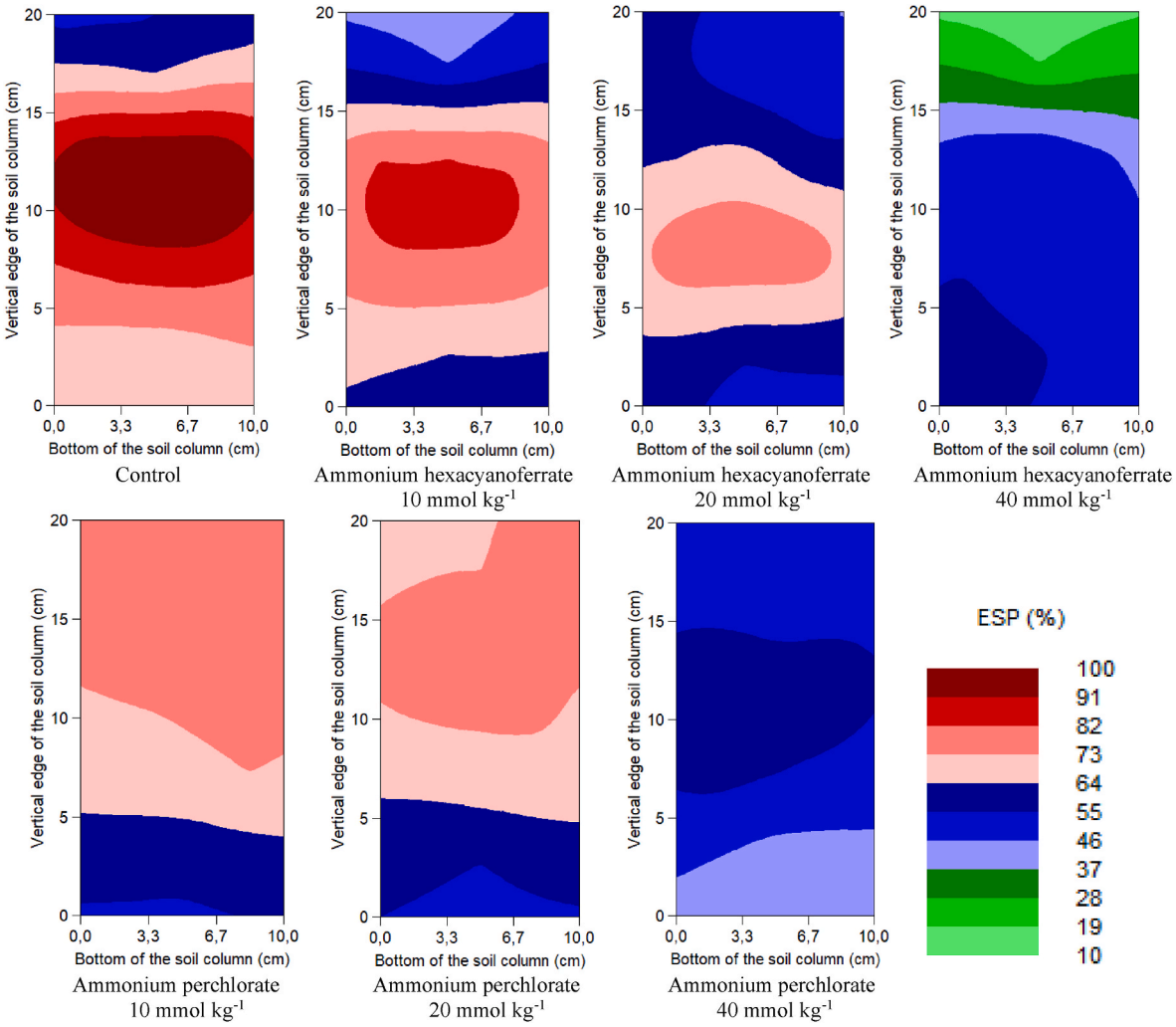

Fig. 8. Spatial variability distribution in ESP at different soil depths of column (0–20 cm).

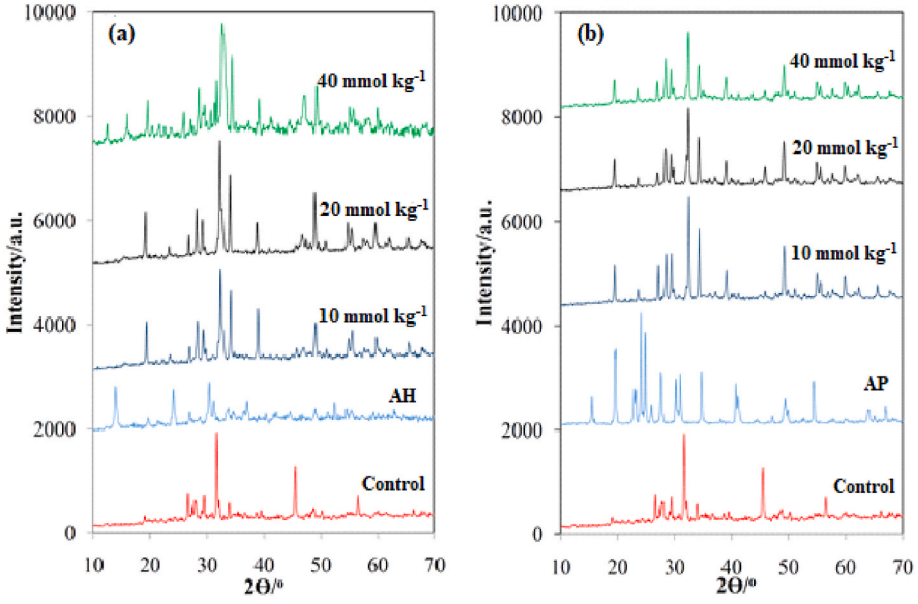

Fig. 9. Powder XRD patterns of control (a, b), Ammonium hexacyanoferrate (AH) (a), Ammonium perchlorate (AP) (b) and soils treated with various concentrations of AH (a) and AP (b) solutions.

Table 3
XRD peak maximum values (2Θ) of various samples obtained from Fig. 9[Ψ].

Control	Pure AH	AH-10	AH-20	AH-40	Pure AP	AP-10	AP-20	AP-40
19.1	13.9	19.4	19.2	12.5	15.5	19.5	19.5	19.5
26.7	19.7	23.5	23.3	16.0	19.7	23.6	23.6	23.5
27.4	21.4	27.0	26.8	19.6	22.9	27.2	27.0	27.0
28.0	24.1	28.3	28.2	20.4	23.2	28.5	28.4	28.4
29.5	27.0	29.3	29.2	21.7	24.1	29.5	29.4	29.4
31.7	28.7	29.8	29.6	22.5	24.9	29.9	29.9	29.9
32.2	30.4	32.5	32.3	23.7	26.0	32.6	32.5	32.5
33.9	31.2	34.2	34.0	25.9	27.6	34.3	34.2	34.3
36.8	33.7	38.9	38.8	27.2	30.3	39.1	39.0	39.0
38.7	34.6	45.7	45.6	28.6	31.0	45.9	43.7	43.7
39.5	37.0	47.0	46.7	29.5	34.7	49.2	45.9	45.9
45.5	40.3	49.1	48.9	30.7	40.7	55.0	49.2	49.2
48.8	44.6	51.0	50.8	31.4	41.1	55.7	54.9	55.0
50.2	49.0	54.9	54.7	31.7	47.2	57.8	55.6	55.6
56.5	52.4	55.5	55.3	32.7	49.4	59.9	57.7	57.7
66.3	54.5	59.7	59.6	34.4	49.9	62.3	59.8	59.8
	55.3	65.4	65.3	39.1	54.4	65.6	62.3	60.4
	62.8			41.2	64.1	67.9	65.7	62.3
				44.5	65.1		67.9	65.6
				47.2	67.0			67.8
				49.3				
				55.0				
				55.7				
				59.9				

[Ψ] Peak matches has been applied considering 2Θ values with variation of ±0.2°. AH-10: Ammonium Hexacyanoferrate (II) 10 mmol kg^{-1}; AH-20: Ammonium Hexacyanoferrate (II) 20 mmol kg^{-1}; AH-40: Ammonium Hexacyanoferrate (II) 40 mmol kg^{-1}; AP-10: Ammonium Perchlorate 10 mmol kg^{-1}; AP-20: Ammonium Perchlorate 20 mmol kg^{-1}; AP-40: Ammonium Perchlorate 40 mmol kg^{-1}

References

Angin, I., Sari, S., Aksakal, E.L., Tohumcu, F., 2019. The use of iron (III) ferrocyanide soil amendment for removing salt from the soil surface. Arid Land Res. Manag. 33 (1), 91–96.

Cassar, J., Marrocchi, A., Santarelli, M.L., Muscat, M., 2008. Controlling crystallization damage by the use of salt inhibitors on Malta's limestone. Materials de Construcción 58 (289–290), 281–293.

Dai, S., Shin, H., Santamarina, J.C., 2016. Formation and development of salt crusts on soil surfaces. Acta Geotechnica 11, 1103–1109.

Daigh, A.L.M., Klaustermeier, A.W., 2016. Approaching brine spill remediation from the surface: a new in situ method. Agricultural and Environmental Letters 1 (1), 150013.

Ding, Z., Kheir, A.M.S., Ali, O.A.M., Hafez, E.M., ElShamey, E.A., Zhou, Z., Wang, B., Lin, X., Ge, Y., Fahmy, A.E., Seleiman, M.F., 2021. A vermicompost and deep tillage system to improve saline-sodic soil quality and wheat productivity. J. Environ. Manag. 27, 111388.

Fitzpatrick, R.B., 2008. Nature, distribution, and origin of soil materials in the forensic comparison of soils. In: Tibbett, M., Carter, D.O. (Eds.), Soil Analysis in Forensic Taphonomy. CRC Press, Boca Raton, FL, pp. 1–28.

Gamma Design Software, 2015. In: GS^{+} Geostatistics for the Environmental Sciences. GS + User's Guide, Version 10.0. Plainwell, MI, USA.

Gee, G.W., Or, D., 2002. Particle-size analysis. In: Dane, J.H., Topp, G.C. (Eds.), Methods of Soil Analysis. Part 4, Physical Methods, vol. 5. SSSA Book Series, Madison, WI, pp. 255–293.

Guo, X., Liu, Y., Zhang, X., Ju, Z., Li, Y., Mitlin, D., Yu, G., 2022. Revealing the solid-state electrolyte interfacial stability model with Na-K liquid alloy. Angew. Chem., Int. Ed., e202203409

Gupta, R.K., Singh, R.R., Abrol, I.P., 1989. Influence of simultaneous changes in sodicity and pH on the hydraulic conductivity of an alkali soil under rice culture. Soil Sci. 147 (1), 28–33.

Gupta, S., Terheiden, K., Pel, L., Sawdy, A., 2012. Influence of ferrocyanide inhibitors on the transport and crystallization process of sodium chloride in porous building materials. Cryst. Growth Des. 12 (8), 3888–3898.

Helmke, P.A., Sparks, D.L., 1996. Lithium, sodium, potassium, rubidium, and cesium. In: Sparks, D.L. (Ed.), Methods of Soil Analysis. Part 3, Chemical Methods, vol. 5. SSSA Book Series, Madison, WI, pp. 551–574.

Hosseini, S.G., Nouri, M., Bahri, M.M., Bazrafshan, E., 2021. Investigation of the effective parameters on the preparation of ammonium perchlorate particles using a cooling crystallization process. Propellants, Explos. Pyrotech. 46 (7), 1060–1069.

IBM, 2011. In: IBM Statistics for Windows, Version 20.0. IBM Corporation, Armonk, New York.

Klaustermeier, A.W., Daigh, A.L.M., Limb, R.F., Sedivec, K., 2017. Crystallization inhibitors and their remediation potential on brine-contaminated soils. Vadose Zone J. 16 (4), 1–10.

Loeppert, R.H., Suarez, D.L., 1996. Carbonate and gypsum. In: Sparks, D.L. (Ed.), Methods of Soil Analysis. Part 3, Chemical Methods, vol. 5. SSSA Book Series, Madison, WI, pp. 437–474.

Lubelli, B., van Hees, R.P.J., 2007. Effectiveness of crystallization inhibitors in preventing salt damage in building materails. J. Cult. Herit. 8, 223–234.

Nelson, D.W., Sommers, L.E., 1996. Total carbon, organic carbon, and organic matter. In: Sparks, D.L. (Ed.), Methods of Soil Analysis. Part 3, Chemical Methods, vol. 5. SSSA Book Series, Madison, WI, pp. 961–1010.

Nouri, H., Chavoshi Borujeni, S., Nirola, R., Hassanli, A., Beecham, S., Alaghmand, S., Saint, C., Mulcahy, D., 2017. Application of green remediation on soil salinity treatment: a review on halophytoremediation. Process Saf. Environ. Protect. 107, 94–107.

Pistocchi, C., Ragaglini, G., Colla, V., Branca, T.A., Tozzini, C., Romaniello, L., 2017. Exchangeable sodium percentage decrease in saline sodic soil after basic oxygen furnace slag application in a lysimeter trial. J. Environ. Manag. 203, 896–906.

Poore, J., Nemecek, T., 2018. Reducing food's environmental impacts through producers and consumers. Science 360 (6392), 987–992.

Qadir, M., Qureshi, R.H., Ahmad, N., 1996. Reclamation of a saline-sodic soil by gypsum and *Leptochloa fusca*. Geoderma 74, 207–217.

Qadir, M., Schubert, S., Badia, D., Sharma, B.R., Qureshi, A.S., Murtaza, G., 2007. Amelioration and nutrient management strategies for sodic and alkali soils. CAB Reviews: Perspectives in Agriculture, Veterinary Science, Nutrition and Natural Resources 2 (21), 13.

Rengasamy, P., 2010. Soil processes affecting crop production in salt-affected soils. Funct. Plant Biol. 37 (7), 613–620.

Rhoades, J.D., 1996. Salinity: electrical conductivity and total dissolved solids. In: Sparks, D.L. (Ed.), Methods of Soil Analysis. Part 3, Chemical Methods, vol. 5. SSSA Book Series, Madison, WI, pp. 417–435.

Ritchie, H., Roser, M., 2019. Land use. Published online at OurWorldInData.org. Retrieved from: https://ourworldindata.org/land-use. Nov. 2, 2021.

Rock, P.A., 1965. The standard oxidation potential of the ferrocyanide-ferricyanide electrode at 25° and the entropy of ferrocyanide ion. J. Phys. Chem. 70, 576–580.

Rodriguez-Navarro, C., Linares-Fernandez, L., Doehne, E., Sebastian, E., 2002. Effects of ferrocyanide ions on NaCl crystallization in porous stone. J. Cryst. Growth 243 (3–4), 503–516.

Selwitz, C., Doehne, E., 2002. The evaluation of crystallization modifiers for controlling salt damage to limestone. J. Cult. Herit. 3 (3), 205–216.

Soil Survey Staff, 2014. In: twelfth ed. Keys to Soil Taxonomy. USDA Natural Res. Cons. Service, Washington.

Sumner, M.E., Miller, W.P., 1996. Cation exchange capacity and exchange coefficients. In: Sparks, D.L. (Ed.), Methods of Soil Analysis. Part 3, Chemical Methods, vol. 5. SSSA Book Series, Madison, WI, pp. 1201–1229.

Swallow, M.J.B., O'Sullivan, G., 2019. Biomimicry of vascular plants as a means of saline soil remediation. Sci. Total Environ. 655, 84–91.

Tanrikulu, S.U., Eroglu, I., Bulutcu, A.N., Ozkar, S., 1998. The growth and dissolution of ammonium perchlorate crystals in a fluidized bed crystallizer. J. Cryst. Growth 194, 220–227.

Tanrikulu, S.U., Eroglu, I., Bulutcu, A.N., Ozkar, S., 2000. Crystallization kinetics of ammonium perchlorate in MSMPR crystallizer. J. Cryst. Growth 208, 533–540.

Thomas, G.W., 1996. Soil pH and soil acidity. In: Sparks, D.L. (Ed.), Methods of Soil Analysis. Part 3, Chemical Methods, vol. 5. SSSA Book Series, Madison, WI, pp. 475–490.

Ujvari, M., Lang, G.G., 2011. On the stability of perchlorate ions against reductive attacks in electrochemical systems and in the environment. J. Electrochem. Sci. Eng. 1 (1), 1–26.

UNESCO, 2021. World Water Assessment Programme (UNESCO WWAP). Retrieved from: http://www.unesco.org/new/en/natural-sciences/environment/water/wwap/facts-and-figures/all-facts-wwdr3/fact-24-irrigated-land/. Nov. 2, 2021.

USSL, 1954. In: Diagnosis and Improvement of Saline and Alkali Soils. United States Department of Agriculture, Washington. Agriculture Handbook No: 60.

Vincent, T., Vincent, C., Guibal, E., 2015. Immobilization of metal hexacyanoferrate ion-exchangers for the synthesis of metal ion sorbents-a mini-review. Molecules 20 (11), 20582–20613.