Soil & Tillage Research 149 (2015) 12–20

Contents lists available at ScienceDirect

Soil & Tillage Research

journal homepage: www.elsevier.com/locate/still

Improvement of hard saline–sodic soils using polymeric aluminum ferric sulfate (PAFS)

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ARTICLE INFO

Article history:
Received 25 November 2013
Received in revised form 30 November 2014
Accepted 23 December 2014

Keywords:
Polymeric aluminum ferric sulfate
Saline–sodic soils
Reclamation
Soil properties
Rice yield

ABSTRACT

Highly dispersed hard saline–sodic soils are important agricultural land reserves in the world. These soils are difficult to be ameliorated by conventional amendments because of poor soil properties. The objectives of this study are to screen a highly efficient inorganic polymer soil amendment using laboratory experiments and to evaluate its effectiveness in soil improvements and grain yield promotion under paddy field conditions using field experiments. Compared with control soils cultivated with rice for one year without PAFS treatment, the pH of the 0–8 cm and 8–16 cm layers of PAFS-treated soil decreased from 10.70 and 10.75 to 8.94 and 9.99, respectively, soil $CaCO_3$ contents decreased by 29.49% and 16.19%, respectively, and contents of silt-plus-clay particles decreased by 46.06% and 14.55%, respectively. Soil saturated hydraulic conductivity increased from 0.05 mm d^{-1} to 40.01 mm d^{-1} and soil bulk density decreased from 1.55 g cm^{-3} to 1.29 g cm^{-3} in the 0–8 cm soil layer. Soil exchangeable Na^+, exchangeable sodium percentage (ESP), and salinity (ECe) in the 0–8 cm soil layer were reduced by 61.92%, 63.23%, and 45.61%, respectively; in the 8–16 cm soil layer, the corresponding values decreased by 34.91%, 34.57%, and 37.47%, respectively. Rice yields with PAFS application in the first year of cultivation were as high as 4.66 t ha^{-1}. By contrast, rice yields without PAFS application were only 0.83 t ha^{-1} in plots cultivated with rice for one year and 1.55 t ha^{-1} in plots cultivated with rice for two years. Therefore, PAFS is effective for amending hard sodic soils.

1. Introduction

The scarcity of arable land has a significant negative effect on human livelihood. Saline–sodic soil reclamation is an important approach in replenishing arable lands. The Songnen Plain, located between N 42°30′ to 51°20′ and E 121°40′ to 128°30′, is one of the largest saline–sodic areas in the world (Wang et al., 2009). The saline–sodic area of soils in the Songnen Plain is about 3.42×10^6 ha. Most soils are hard saline–sodic (Li et al., 1998). To replenish the arable farmland lost during rapid urbanization and infrastructure expansion and maintain acceptable minimum areas of arable land, the Chinese government launched a large project to reclaim saline–sodic land in the west Songnen Plain. The project aimed to reclaim 3.05×10^5 ha of saline–sodic land and turn it into standardized paddy farmlands; this reclamation is currently the largest land reclamation project in China.

Today, all the irrigation and drainage pumping stations, canal systems, and field road systems in the project area were constructed. Root zone salinity and sodicity need to be significantly reduced as soon as possible.

Irrigated rice cropping is often practiced to reclaim saline–sodic soils in many parts of the world because flooded water is not only beneficial to rice growth but also necessary for leaching salts (Chi et al., 2012). The above-ground parts of rice plants can also consume alkalinity in alkaline soil (Van Asten et al., 2004). However, under single irrigated rice cropping without additional soil amelioration, rice yields are very low or even zero within the first three or four years (Luo and Sun, 2004). Thus, the use of available chemical amendments to accelerate soil reclamation is necessary.

Sodic soils are generally ameliorated by providing calcium (Ca^{2+}) to replace excess Na^+ in the cation exchange complex. The displaced Na^+, together with excess soluble salts, if present, is leached from the root zone through excessive irrigation water

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http://dx.doi.org/10.1016/j.still.2014.12.014

(Qadir et al., 2001). To reclaim slightly and moderately saline–sodic soils with good drainage property, leaching with freshwater or slightly saline water and modifying soil conditions through tillage and phytoremediation have been successfully used (Oster et al., 1996; Qadir et al., 2001; Li et al., 2004). However, most of the abovementioned traditional methods are unable to reclaim highly dispersed hard saline–sodic soils (Qadir et al., 1998; Ilyas et al., 1993).

The main chemicals reported for soil amelioration include gypsum, phosphogypsum, flue gas desulfurization gypsum, calcium chloride, sulfuric acid, sulfur, iron pyrite, and aluminum sulfate (Abrol et al., 1988; Ahmad et al., 2006; Mason et al., 1994; Amezketa et al., 2005; Scherer, 2001; Singh et al., 2010). Among these substances, gypsum-like solid Ca^{2+} amendments are the most common chemicals applied to large areas. Gypsum and desulfurized gypsum application followed by freshwater leaching ameliorates hard saline–sodic soils and enhances the grain yield of rice (Qadir et al., 1998; Chi et al., 2012). However, the dissolution rates of gypsum-like amendments are generally low, and their coagulation abilities for soil colloid particles require improvement. Several years may be necessary to effectively ameliorate hard saline–sodic soils.

Inorganic polymeric coagulating chemicals applied in water treatment can achieve rapid flocculation and sedimentation of colloidal particles in water bodies (Zouboulis et al., 2007). The modes of action of these chemicals are generally explained in terms of two distinct mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate ("sweep flocculation") (Duan and Gregory, 2003). These coagulation mechanisms may be used to overcome the high dispersion of hard saline–sodic soils and promote the formation of aggregate structures, thereby eventually improving soil porosity, water holding capacity, and permeability. Furthermore, many inorganic polymers can produce H^{+} ions by hydrolysis (Zouboulis et al., 2007), which results in considerable reduction in soil pH and facilitates the dissolution of $CaCO_3$ to provide Ca^{2+} ions for ameliorating saline–sodic soils.

The primary objectives of this study were to: (1) screen a highly efficient inorganic polymer soil amendment; (2) evaluate its improvements in soil properties under field conditions using the screened amendment; and (3) investigate the effectiveness of the screened amendment in increasing the grain yield of rice under field conditions. The study results are expected to provide useful information for the improvement and agricultural utilization of saline–sodic soils, particularly hard saline–sodic soils.

2. Materials and methods

2.1. Screening test of inorganic polymer soil amendments

2.1.1. Soil and amendments

Soil samples used for the lab screening test were randomly collected at a depth of 0–20 cm from a hard saline–sodic wasteland located at Honggangzi Township in Daan City, Songnen Plain. This town was included in the large reclamation project. The area of the soil sample collection site was $5 \times 5\,m^2$. Soil properties were determined after soils were air-dried and passed through a 2-mm sieve. The initial values of soil pH, exchangeable Na, ESP, and ECe were 10.83, 16.85 $cmol\,kg^{-1}$, 50.26, and 17.48 $dS\,m^{-1}$, respectively. Four inorganic polymers, namely, polymeric aluminum ferric sulfate (PAFS), polymeric aluminum sulfate (PAS), polymeric ferric sulfate (PFS), and polymeric aluminum ferric chloride (PAFC), were used as screening amendments, and their corresponding characteristics are listed in Table 1. A common chemical amendment, gypsum, was used as a reference.

2.1.2. Horizontal flushing experiment

Five hundred grams of air-dried soil (<2 mm) were weighed and placed in a 1000 mL beaker. All treatments were done in triplicate. Each amendment was mixed with soil prior to flushing at application rates (mass ratio of amendment to dried soil) of 0.2%, 0.4%, 0.6%, 0.8%, and 1.0%. Afterwards, 750 mL of distilled water was added to each beaker and the mixture was thoroughly stirred. After allowing to stand for 48 h, the supernatant was drained. The soil samples were air-dried after drainage and passed through a 2-mm mesh sieve for chemical analysis.

2.1.3. Soil column leaching experiment

When the best inorganic polymer soil amendment had been determined from the horizontal flushing experiment described above, the amendment was further evaluated via a soil column leaching experiment. Soil samples were packed into plexiglass cylinders (diameter: 9.6 cm, height: 60 cm) and placed vertically on brick stands. A 2 cm layer of sand was placed on the bottom of each column to facilitate leaching. The column was closed at the bottom except for a hole used to collect the leachate. Each cylinder was packed with 3.6 kg of dry soil to a depth of 40 cm. The dry bulk density of the packed column was 1.24 $g\,cm^{-3}$. The upper 20 cm layer was treated with the selected inorganic polymer soil amendment applied at a rate of 1.0%. Soils without any amendment and treated with gypsum were used as controls. The amendments were mixed with the soils before packing. Water was continuously added to the columns, and a 5-cm water head was maintained for about 10 days. The leachates were collected in storage bottles and placed below each column. Leachate volumes were measured continuously throughout the experiment to determine the effect of the amendment on soil permeability compared with the controls.

2.2. Field experiment

2.2.1. Experimental site

After a suitable amendment was successfully screened through the lab experiment, a saline–sodic wasteland site was chosen from the reclamation project area for the field experiment, based on irrigation and transportation conditions. The field experimental site (1.2 ha) was also located at the Honggangzi Township (45°37′13″N, 123°53′45″E) in Daan City, Songnen Plain, and was about 500 m away from the soil sample collection site for the lab screening test. The soil chemical properties of both sites were similar except for CEC and ESP. For the lab screening test soil, CEC was much higher than that in the field experiment, resulting in

Table 1
Basic characteristics and main components of the amendments.

Amendment	Shape	pH	Main component	Note
PAFS	Schistose	3.19	$\{Al(OH)_nSO_4\}_m\{Fe_2(OH)_nSO_4\}_m$	$n \le 5$, $m \le 10$
PAS	Schistose	3.20	$[A1_2(OH)_n(SO_4)_{3-n/2}]_m$	$1 \le n \le 6$, $m \le 10$
PFS	Powdery	2.05	$[Fe_2(OH)_n(SO_4)_{3-n/2}]_m$	$n < 2$, $m > 10$, $m = f(n)$
PAFC	Granular	4.32	$[Al_2(OH)_nCl_{6-n}{\cdot}xH_2O]_m{\cdot}[Fe_2(OH)_nCl_{6-n}{\cdot}xH_2O]_m$	$1 \le n \le 5$, $m \le 10$, $x < 12$
Gypsum	Powdery	5.96	$CaSO_4{\cdot}2H_2O$	–

pH was measured in 1 L of distilled water in which 1 g of amendment had been dissolved. n: the number of atoms or radicals, m: the number of molecules.

Table 2
Initial soil chemical properties of experimental site.

	0–8 cm soil depth (150 samples)		8–16 cm soil depth (150 samples)	
	Mean (range)	Median	Mean (range)	Median
pH	10.80 (10.63–11.12)	10.80	10.74 (10.61–11.24)	10.78
Exchangeable Na^+ (cmol kg^{-1})	15.50 (12.33–19.97)	16.39	15.65 (12.09–19.30)	17.23
ESP (%)	82.95 (60.45–98.11)	92.49	82.66 (65.02–99.52)	90.65
ECe (dS m^{-1})	16.42 (12.29–20.55)	17.24	14.39 (11.01–17.80)	16.96
CEC (cmol kg^{-1})	18.35 (14.34–21.96)	18.45	18.93 (14.75–23.24)	19.22
$CaCO_3$ (%)	8.29 (6.90–10.06)	8.45	8.12 (6.84–9.92)	8.26

lower ESP of soil for the lab screening test. Although soil ESP of both sites was different, their ESP was much higher than the average level of the reclamation project area of 3.05×10^5 ha because both of them were saline–sodic wasteland. Initial soil chemical properties of the filed experimental site are presented in Table 2. The local climate is temperate and semi-arid. The mean annual air temperature is approximately 5 °C, varying from −18 °C in January to 23 °C in July. The growing season lasts from May to September, and the average annual precipitation is 400 mm. Over 80% of the rainfall occurs in the summer.

2.2.2. Experimental treatments and procedure

Performance of the most efficient inorganic polymer soil amendment screened in the laboratory experiment was evaluated under paddy field condition. According to the results of the soil amendment screening in the laboratory experiment, PAFS was the most efficient soil amendment and was evaluated in the paddy field. Since rice cultivation without any soil amendments was the common practice for hard saline–sodic soil amelioration in the Songnen Plain, rice cultivation for one year and two years were used as references.

The experiment was laid out in four blocks representing three controls and one treatment. Each treatment and control was split into three replicate subplots with an area of about 1000 m^2. The following controls and treatments were prepared:

1. Control, not reclaimed and no cultivation with rice (CK0).
2. Control, cultivated with rice for one year without PAFS treatment (CK1).
3. Control, cultivated with rice for two years without PAFS treatment (CK2).
4. Cultivated with rice for one year after PAFS treatment (T1).

For the PAFS treatment, the plots were plowed, disked, harrowed, and irrigated by surface flooding with a total of 30 mm fresh water from a canal. This irrigation amount was commonly used in local rice cultivation without PAFS treatment (Deng et al., 2006). The fields were then leveled and drained after 24 h. PAFS was applied at an application rate of 15 t ha^{-1} (approximately 0.6% of the dry weight of soil in the 0–16 cm soil layer) and mixed with the soil by a cultivator. 70–80 mm of water (Deng et al., 2006) was used to irrigate the soil, after which the electrical conductivity (EC) and pH of flooding water were measured using a conductivity meter and pH meter, respectively. When the recorded EC and pH values became constant after three days, the flooding water was drained and rice seedlings were transplanted. For the last two controls, all of the steps and operations applied in the PAFS treatment were followed except for addition of the amendment. The rice cultivar planted in this experiment was 'Dongdao 4', and all farming practices and field management were performed according to the common method of rice cultivation in the study area.

After the rice had been harvested, ten soil samples were taken from 0 to 8 cm and 8–16 cm depths from each plot. All soil samples were air-dried and passed through a 2-mm mesh sieve prior to analysis.

2.3. Analysis of soil chemical properties

Methods described by US Salinity Laboratory Staff (1954) were followed for chemical determination. Soil samples were analyzed for pH and EC using a 1:5 ratio of soil to water extracts. The EC of saturated paste extraction (ECe) was estimated from $EC_{1:5}$ (Chi and Wang, 2010):

$$ECe = 10.88EC_{1:5} \quad (1)$$

Exchangeable Na^+ and cation exchange capacity (CEC) were determined by extraction with ammonium acetate. Na^+ was determined using flame atomic absorption spectrophotometry (AA-7000, Shimadzu, Japan). The ESP was calculated from the ratio of exchangeable sodium to CEC, and soil $CaCO_3$ contents were determined using the gas-volumetric method (gravimetrically by neutralization of the carbonates with H_2SO_4).

2.4. Analysis of soil physical properties

2.4.1. Soil aggregate water stability

The wet sieving aggregate stability of the soil samples collected in the field was determined using a modified method by Elliott (1986) and Kemper and Rosenau (1986). Ten grams of air-dried soil were transferred to a 0.25-mm sieve that was then immersed for 5 min in a container filled with enough distilled water to cover the soil sample. The sieve was then lowered and raised with a vertical displacement of 1.3 cm at 30 cycles/min for 3 min. The fraction of soil that passed through the 0.25-mm sieve was transferred to a 0.053-mm sieve, and the sieving procedure was repeated. The amount of soil retained on each sieve after sand correction was dried at 105 °C for 24 h and expressed as relative weights of aggregates for three aggregate size fractions: (i) >0.25 mm (macro-aggregates), (ii) 0.053–0.25 mm (micro-aggregates), (iii) <0.053 mm (silt-plus-clay particles) (Kemper and Rosenau, 1986; Cambardella and Elliott, 1993).

2.4.2. Soil saturated hydraulic conductivity (Ks)

The Ks of soil was determined using a downward flow experiment with constant-head (Jury and Horton, 2004). Soil samples from 0 to 8 cm and 8–16 cm soil layer collected in the field plots were air-dried and passed through a 2-mm mesh sieve. 747 g of each soil sample was respectively added to a polyvinyl cylinder (diameter: 9.6 cm; height: 20 cm) to a depth of 8 cm and packed to a bulk density of 1.29 g cm^{-3}. The bottom of the cylinder was fixed with a nylon sieve and filter paper was put on the sieve. Soil in the cylinder was saturated by submerging it into distilled water for 24 h. The water depth above the soil surface was kept at 0.5 cm during submersion. 24 h later, the cylinder was taken out from water. When there was no leachate out from the bottom, distilled water was continuously added onto the soil surface in each cylinder. 3 cm water head was maintained for another 24 h. The leachate was collected and its quantity was then measured. The Ks of soil was reported in mm d^{-1} and calculated according to Darcy's law:

$$Ks = \frac{\Delta Q \times L}{A \times \Delta t \times (L + H)} \quad (2)$$

where ΔQ is the volume of leachate collected from the bottom of cylinder during a given time period Δt, and A is the cross-sectional area of the soil columns, L is the depth of soil sample, H is the height of constant water head.

2.4.3. Soil bulk density and microstructure

Soil bulk density was measured in the field by the undisturbed core method (Blake and Hartge, 1986). Soil microstructure was observed with a scanning electron microscope (SEM, Zeiss Gemini Ultra-55): soil samples collected from 0 to 8 cm soil layer in fields were passed through a 0.25-mm mesh sieve, all the aggregates (0.25–2 mm) were attached to copper mounts and coated with gold, and then were observed. IPP microstructure image analysis software (Image-Pro plus) was used for analysing the SEM images (Hu et al., 2013; Zhang et al., 2008). Through the method of image segmentation, SEM images can be converted to black and white binary image based on an intensity threshold (about 30 in this study). The black domains represent the soil matrix, and white domains represent pores. The SEM image soil porosity was the ratio of area of white domains to the area of whole image measured by IPP.

2.5. Rice grain yield measurement

Rice samples were picked from each treatment and control plots after rice maturing. Random sampling could not sufficiently reflect production because the growth of rice was quite uneven and some plots even showed no output. Thus, crop samples were collected according to the grades of rice growth conditions, and area percentage was regarded as a weighting coefficient to calculate the yield of rice using the weighted average method. The detailed calculations were as follows. First, based on careful observation of rice growth vigor, including leaf color, spikelet, plant height, and biomass, plants in each experimental plot were divided into the following grades: good, medium, and poor. Thereafter, the area of each grade in a single plot was measured, and 1-m^2 quadrants were set up for each grade. The yield components, including panicle number per square meter, grain number per panicle, percentage of filled grains, and 1000-kernel weight, were determined to calculate the rice yield of each grade. The grain yield of each plot was calculated as the sum of the grade yield multiplied by its area percentage.

2.6. Statistical analysis

Data were analyzed using SPSS 19.0. Average values in each subplot were subjected to one-way analysis of variance. Least significant differences were calculated for multiple comparisons among all treatments.

3. Results and discussion

3.1. Soil amelioration effects of inorganic polymers from screening test

The effects of the amendments on soil pH, exchangeable Na^+, ESP, and ECe of saline–sodic soils in lab experiments are presented in Fig. 1. All indices declined steadily with increasing dosage of the amendments except for ECe, which exhibited an inverse trend. The increase in ECe may imply that amendments and replaced Na^+ from soil particles are accumulated as a consequence of insufficient flushing of water. PAFS-treated soils exhibited the lowest pH, exchangeable Na^+ and ESP at any application rate. Soil ECe was also lower than most other treatments. Hence, among the four inorganic polymers, PAFS treatment improved the saline–sodic soils the most. However, soil ECe gradually increased when PAFS application rate was higher than 0.6%. Therefore, considering the cost and effectiveness of PAFS, approximately 0.6% of the dry weight of soil in the 0–16 cm soil layer was used in the paddy field experiment.

3.2. Effects of gypsum and PAFS on soil leaching

Data related to leachate volumes from soils treated with gypsum and PAFS are presented in Fig. 2. The leachate volume of PAFS treatment was higher than that of gypsum treatment at all time periods, and the total volume of the former was 1637.0 mL, which is approximately 3.8 times higher than that of the latter. These results show that PAFS has considerably better efficiency than gypsum for improving the permeability of saline–sodic soils. Soil permeability is a key factor for soil salinity leaching (Quirk et al., 1986). All of the results thus far indicate that PAFS performs best in ameliorating saline–sodic soils.

3.3. Effects of PAFS on field soil properties

3.3.1. Soil pH

The effects of PAFS on soil pH are presented in Fig. 3a. At 0–8 cm soil depth, pH decreased to 8.94 after PAFS treatment; by comparison, the pH of CK0 was 10.80. Similar results were found at 8–16 cm soil depth. No significant difference between the three controls at both soil depths was observed. These results indicate that PAFS was effective on lowering soil pH. pH usually does not decrease considerably in calcareous soils after phytoremediation because changes in pH are buffered by enhanced dissolution of $CaCO_3$ (Nelson and Oades, 1998; Van den Berg and Loch, 2000). The decrease in pH is attributed to H^+ produced by the polynuclear hydrolysis of PAFS. PAFS easily dissolves in water and forms Fe/Al hydroxides and H^+ by rapid hydrolysis (Duan and Gregory, 2003). Soil pH is also one of the most important factors affecting nutrient availability in the rhizosphere. The availability and uptake of some nutrient elements, such as P, Zn, Cu, Fe, and Mn, were significantly correlated with soil pH (Gardner et al., 1982; Sarkar and Wynjones, 1982). Hence, a rapid decrease in pH would significantly benefit the growth and yield of rice.

3.3.2. Soil $CaCO_3$

The effects of PAFS on soil $CaCO_3$ are presented in Fig. 3b. Soil $CaCO_3$ contents significantly decreased after PAFS treatment at both soil depths, which indicates that PAFS promotes the dissolution of $CaCO_3$ in saline–sodic soils. Dissolution of $CaCO_3$ further significantly reduced content of carbonate (CO_3^{2-}) in soil. When $CaCO_3$ dissolved during hydrolysis of PAFS, some CO_3^{2-} became CO_2 and escaped directly into atmosphere. The other CO_3^{2-} dissolved in soil solution and was leached from the root zone through excessive irrigation water. The decrease in carbonate was beneficial to decrease soil pH. Decrease in carbonate can also prevent dissolved calcium to form precipitated $CaCO_3$ again and produce excessive dissolved calcium sources. These excessive calcium sources were helpful to replace exchangeable sodium in soil. Phytoremediation could also promote the dissolution of soil $CaCO_3$ (Robbins, 1986; Qadir et al., 2005). However, no obvious difference was observed between CK1 and CK2, which suggests that the effects of phytoremediation are quite limited in hard saline–sodic soils. Ameliorating soils with PAFS before planting

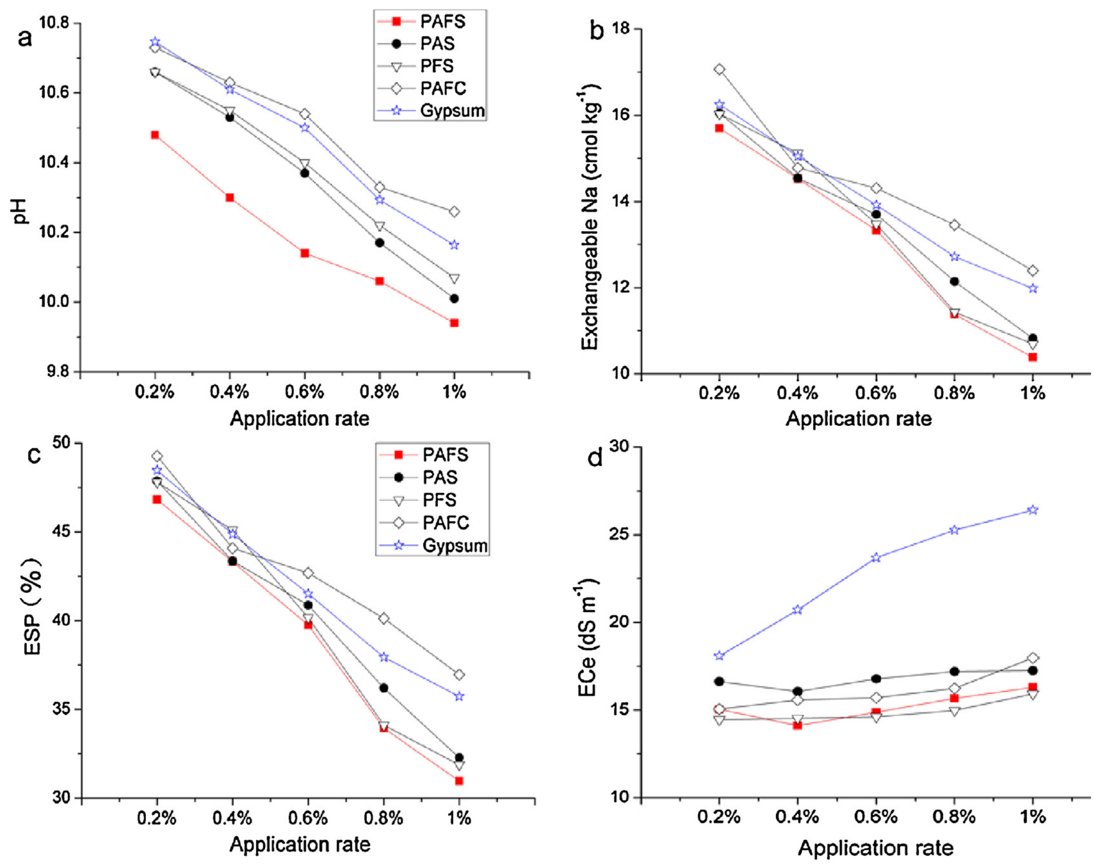

Fig. 1. Effects of amendments on soil pH (a), exchangeable Na^+ (b), ESP (c), and ECe (d) of saline–sodic soils in lab experiment. Application rate is the mass ratio of amendment to dried soil.

rice would provide more Ca^{2+} to replace Na^+ in soil exchangeable sites by the dissolution of soil $CaCO_3$.

3.3.3. Soil exchangeable sodium and ESP

The effects of PAFS on soil exchangeable Na^+ and ESP are presented in Fig. 3c and d. Soil exchangeable Na^+ and ESP observed after PAFS treatment were considerably lower than those in controls at both soil depths. Soil exchangeable Na^+ and ESP were generally lower at the 0–8 cm layer than at the 8–16 cm layer. For example, the soil ESP after treatment with PAFS was 28.68, which is considerably smaller than the ESP values of 82.95, 78.00, and 65.16 observed in CK0, CK1, and CK2, respectively. The decrease in sodicity facilitates improvements in soil physical properties (Ruiz-Vera and Wu, 2006).

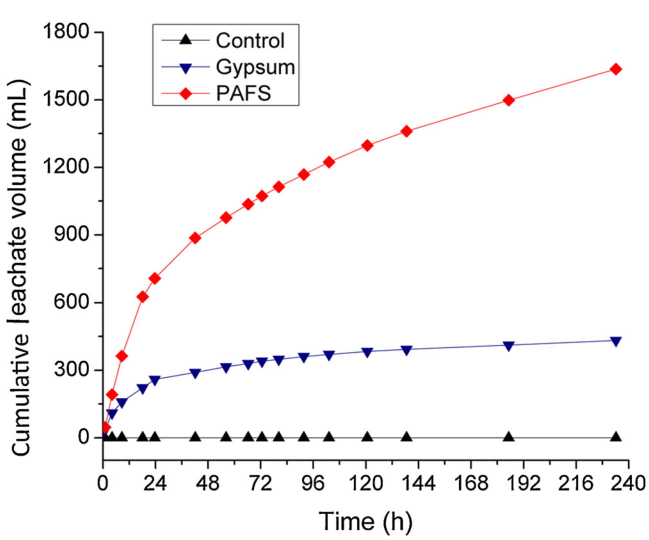

Fig. 2. Volume variation of leachate from soils treated with gypsum and PAFS in lab soil column leaching experiment.

3.3.4. Soil aggregate water stability

The effects of PAFS on the water stability of aggregates of hard saline–sodic soils are presented in Table 3. More significant decreases of silt-plus-clay particles were found after PAFS treatment than in controls at both soil depths. For example, the relative weight of silt-plus-clay particles decreased from 25.28% in CK0 to 15.82% in PAFS-treated soil at the 0–8 cm soil depth. These results indicate that PAFS could improve the water stability of soil aggregates. PAFS can cause aggregation of particles either by polymer bridging or charge neutralization (including “electrostatic patch” effects) (Gregory, 1996). In addition, Al/Fe hydroxide precipitates tend to have a rather open structure, so that binding (“bridging”) of particles by precipitated hydroxide may result in stronger aggregates (Duan and Gregory, 2003). The silt-plus-clay particles in the plot cultivated with rice for two years significantly increased compared with those in CK0 and CK1. This phenomenon is attributed to the effect of electrolyte concentration. Intermittent applications of rainwater or irrigation may lower the electrolyte concentration below a threshold value, after which clay dispersion and reductions in soil permeability occur (Ben-Hur et al., 2009).

3.3.5. Soil saturated hydraulic conductivity

Effects of PAFS on soil Ks are presented in Table 4. The Ks of PAFS-treated soil was much higher than those in controls at both

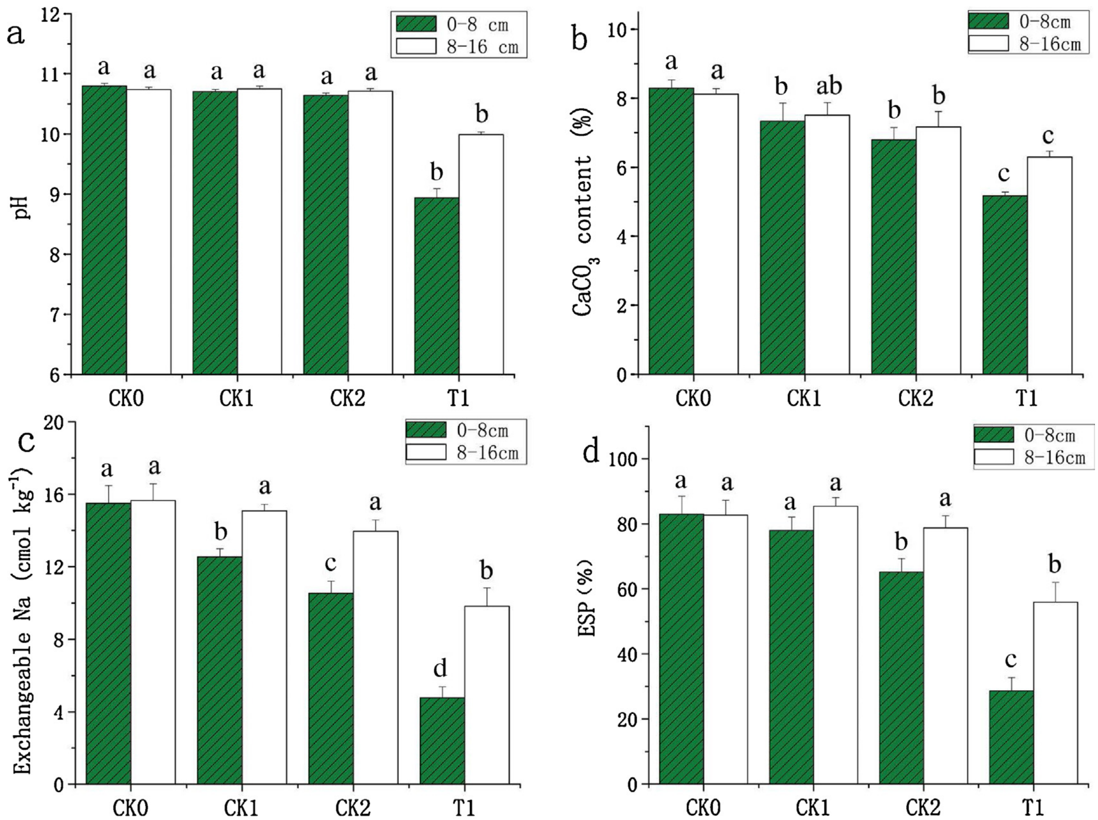

Fig. 3. Effects of PAFS on soil pH (a), $CaCO_3$ (b), exchangeable Na^+ (c), and ESP (d) in field experiment. CK0: unreclaimed, CK1: plot cultivated with rice for one year without PAFS treatment, CK2: plot cultivated with rice for two years without PAFS treatment, T1: PAFS treatment during the first year of rice cultivation. Vertical bars indicate standard errors. Different letters above the same soil depth indicate significant differences at $P < 0.05$.

soil depths. The Ks of PAFS-treated soil from 0 to 8 cm and 8–16 cm soil layer was as high as 40.01 and 22.17 mm d^{-1}, respectively. However, the soils from both depths in controls were almost impermeable. Soil saturated hydraulic conductivity was controlled by soil porosity and pore size. In our Ks measurement experiment, soils in each cylinder were packed into the same bulk density and had the similar soil porosity. Therefore, remarkable change of Ks after PAFS treatment was mainly attributed to the increase of soil micro-aggregates and the formation of soil big pores. Agassi et al. (1981) and Kazman et al. (1983) showed that the soil permeability is influenced by ESP, electrolyte concentrations, and the composition of the applied water. As discussed in Section 3.3.3, significant decreases in soil ESP after PAFS treatment were observed, which was in line with the considerable increase in soil saturated hydraulic conductivity.

3.3.6. Soil bulk density and microstructure

The effects of PAFS on soil bulk density are presented in Table 5. More significant decreases of soil bulk density were found after PAFS treatment than in controls at both soil depths. For example, the bulk density decreased from 1.55 g cm^{-3} in CK0 to 1.29 g cm^{-3} in T1 at the 0–8 cm soil depth. The bulk density decrease suggested an improvement in soil structure.

The effects of PAFS on soil microstructure are presented in Fig. 4. Results showed that soil pore size in T1 increased and soil aggregate surface became rougher compared with controls, and many irregular lamellar particles were observed at 10,000× magnification in T1 soils (Fig. 4a and b). With converting the SEM image at 1000× magnification to black and white binary image (Fig. 4c), the calculated SEM image soil porosity of T1 was 26.12%, much bigger than CK0 (2.96%), CK1 (2.57%) and CK2 (4.19%). The increased large soil pores (pore size approximately greater than 10 μm) were beneficial to increase soil hydraulic conductivity.

3.3.7. Soil salinity (ECe)

The effects of PAFS on soil ECe are presented in Fig. 5. Significant reductions in soil salinity were observed after PAFS treatment compared with CK0, CK1, and CK2. In the upper 8 cm soil layer, the

Table 3
Effects of PAFS on the water stability of aggregates observed in the field experiment.

	Relative weight of water stable aggregates (%)					
	0–8 cm soil depth			8–16 cm soil depth		
	>0.25 mm	0.053–0.25 mm	<0.053 mm	>0.25 mm	0.053–0.25 mm	<0.053 mm
CK0	9.15 ± 0.29 a	65.57 ± 1.23 b	25.28 ± 0.97 b	3.73 ± 0.26 a	60.59 ± 1.15 b	35.68 ± 1.09 b
CK1	1.60 ± 0.06 c	69.07 ± 0.75 b	29.33 ± 0.73 b	0.63 ± 0.09 c	62.74 ± 0.67 b	36.63 ± 0.73 b
CK2	1.80 ± 0.15 c	53.97 ± 0.63 c	44.23 ± 0.50 a	1.00 ± 0.20 c	46.87 ± 1.16 c	52.13 ± 1.23 a
T1	6.83 ± 0.15 b	77.35 ± 1.83 a	15.82 ± 0.87 c	1.87 ± 0.09 b	66.83 ± 1.05 a	31.30 ± 0.96 c

CK0: unreclaimed, CK1: plot cultivated with rice for one year without PAFS treatment, CK2: plot cultivated with rice for two years without PAFS treatment, T1: PAFS treatment during the first year of rice cultivation. Different letters in a column indicate significant differences at $P < 0.05$.

Table 4
Effects of PAFS on soil Ks measured with soil columns.

Soil depth	Soil Ks (mm d^{-1})			
	CK0	CK1	CK2	T1
0–8 cm	0.09 ± 0.01 b	0.05 ± 0.01 c	0.00 ± 0.00 d	40.01 ± 3.45 a
8–16 cm	No flow	No flow	No flow	22.17 ± 1.77

CK0: unreclaimed, CK1: plot cultivated with rice for one year without PAFS treatment, CK2: plot cultivated with rice for two years without PAFS treatment, T1: PAFS treatment during the first year of rice cultivation. Different letters in a row indicate significant differences at $P < 0.05$.

Table 5
Effects of PAFS on soil bulk density in the field experiment.

Soil depth	Soil bulk density (g cm^{-3})			
	CK0	CK1	CK2	T1
0–8 cm	1.55 ± 0.03 a	1.50 ± 0.03 ab	1.45 ± 0.04 b	1.29 ± 0.07 c
8–16 cm	1.59 ± 0.04 a	1.55 ± 0.02 a	1.56 ± 0.06 a	1.36 ± 0.07 b

CK0: unreclaimed, CK1: plot cultivated with rice for one year without PAFS treatment, CK2: plot cultivated with rice for two years without PAFS treatment, T1: PAFS treatment during the first year of rice cultivation. Different letters in a row indicate significant differences at $P < 0.05$.

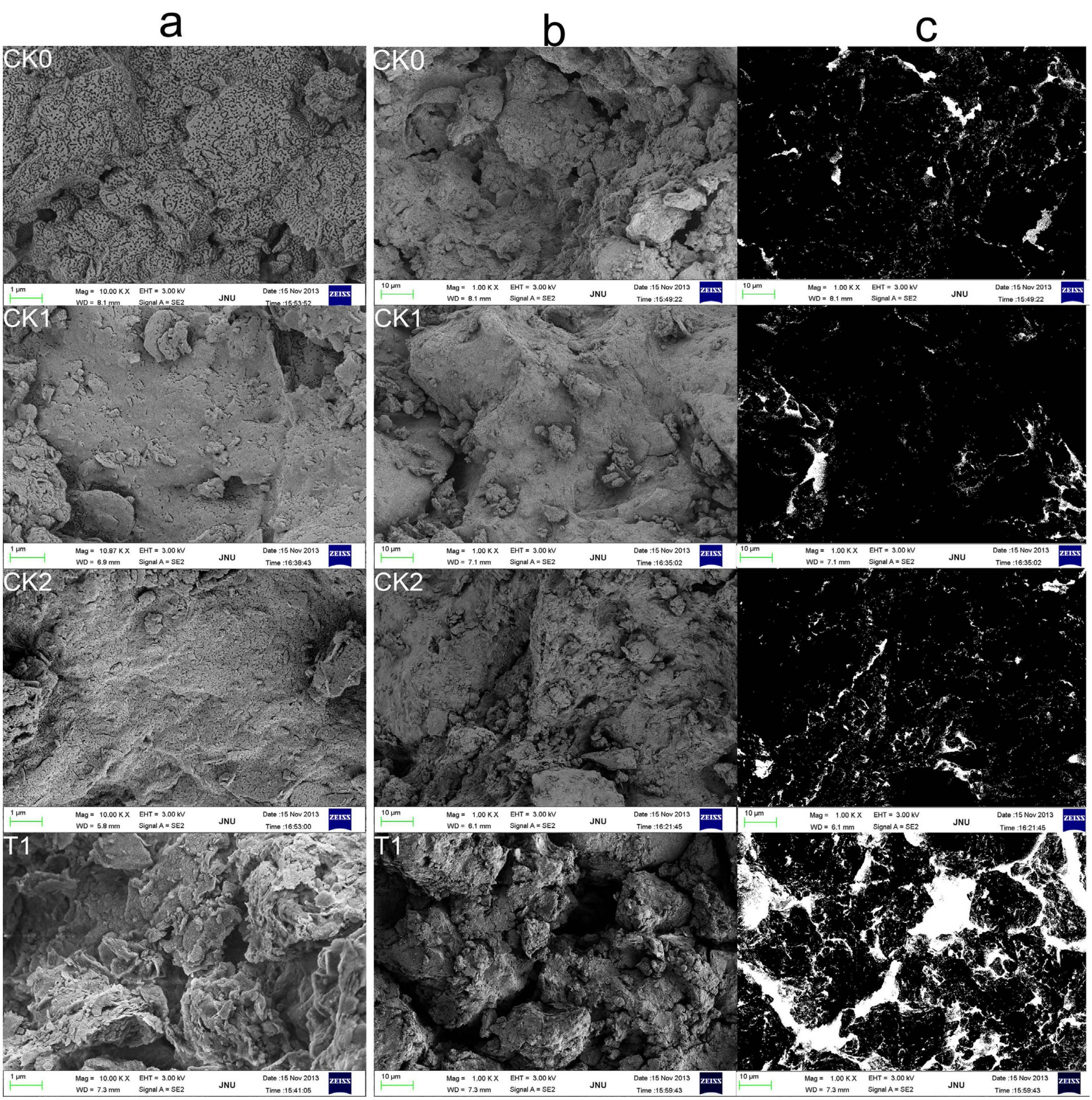

Fig. 4. Effects of PAFS on soil microstructure in field experiment. (a) Soil images observed at 10,000× magnification, (b) soil images observed at 1000× magnification, (c) black and white binary images converted by b. CK0: unreclaimed, CK1: plot cultivated with rice for one year without PAFS treatment, CK2: plot cultivated with rice for two years without PAFS treatment, T1: PAFS treatment during the first year of rice cultivation.

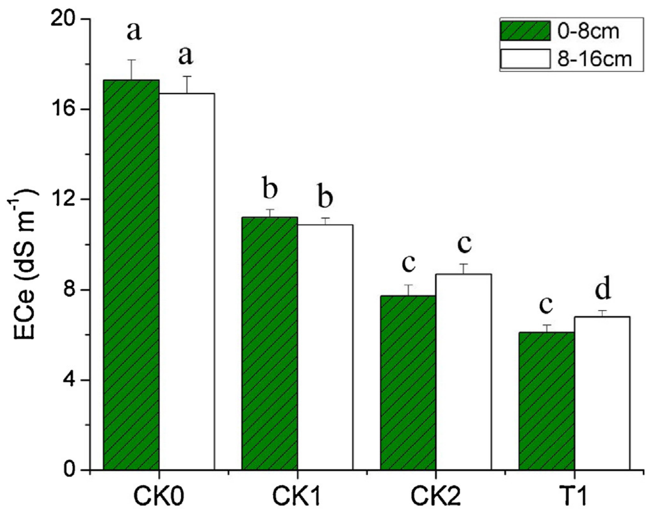

Fig. 5. Effects of PAFS on soil ECe in field experiment. CK0: unreclaimed, CK1: plot cultivated with rice for one year without PAFS treatment, CK2: plot cultivated with rice for two years without PAFS treatment, T1: PAFS treatment during the first year of rice cultivation.Vertical bars indicate standard errors. Different letters above the same soil depth indicate significant differences at $P < 0.05$.

ECe of soil was only 7.56 dS m^{-1} after PAFS treatment, while 16.42 dS m^{-1} in CK0 and 9.39 dS m^{-1} in CK1, respectively. Soil ECe obviously decreased as rice cultivation years increased. Soil ECe after PAFS treatment was even lower than that in two years rice cultivation. H^+ ions produced by the hydrolysis of PAFS effectively promote the dissolution of $CaCO_3$ and provide more Ca^{2+} for exchanging with Na^+ in flushing water. The high coagulation ability of PAFS is advantageous in preventing soil clay dispersion, increasing the water stability of soil aggregates, and promoting soil permeability for water and salt transport (Gu and Doner, 1993; Li, 2006). Given improvements in soil properties after PAFS treatment, rice exhibits better growth, and CO_2 partial pressures, proton release by plant roots, and salt and Na^+ uptake by crops might be enhanced during phytoremediation (Qadir et al., 2005). All these factors would ultimately facilitate the leaching of soil ECe.

3.4. Rice yield

The effects of PAFS on rice yield are presented in Table 6. All yield components in PAFS treatment were significantly higher than the corresponding results observed in CK1 and CK2. The yield components contributed to the ultimate grain yield (Saqib et al., 2008). Rice yield in PAFS treatment was 4.66 t ha^{-1}, increased by 461.4% compared with the yield in CK1 and increased by 200% compared with the yield in CK2. Luo and Sun (2004) obtained low yields and even no output in the initial one to two years after cultivating rice in hard saline–sodic land; yields reached 4.25 t ha^{-1} in the fourth year after addition of large amounts of fresh water to the soil to wash away salts. The good yields imply that hard saline–sodic soils show overall improvements with the application of PAFS. Improvements in soil properties benefited the availability of nutrients for crop growth (Gardner et al., 1982; Sarkar and Wynjones, 1982). If rice is continuously planted in PAFS-treated fields, higher yields in the second year may be expected.

Table 6
Effects of PAFS on rice yield.

Parameter	CK1	CK2	T1
No. of panicle m^{-2}	159.62 ± 34.12 b	206.89 ± 9.61 b	302.68 ± 14.26 a
No. of grains per panicle panicle^{-1}	43.85 ± 4.32 b	45.00 ± 2.31 b	66.97 ± 5.56 a
Filled grains (%)	56.57 ± 4.28 c	75.80 ± 6.04 b	93.72 ± 1.83 a
1000-kernel weight (g)	20.96 ± 0.96 b	22.66 ± 0.29 b	24.53 ± 0.20 a
Yield (t ha^{-1})	0.83 ± 0.32 b	1.55 ± 0.11 b	4.66 ± 0.57 a

CK1: plot cultivated with rice for one year without PAFS treatment, CK2: plot cultivated with rice for two years without PAFS treatment, T1: PAFS treatment during the first year of rice cultivation. Different letters in a row indicate significant differences at $P < 0.05$.

4. Conclusions

Among the inorganic polymers PAFS, PAS, PFS, and PAFC, PAFS was the best soil amendment for hard saline–sodic soils. By producing H^+ through hydrolysis, PAFS rapidly reduced soil pH and promoted the dissolution of $CaCO_3$ to provide Ca^{2+} for replacing exchangeable Na^+ in saline–sodic soils. The excellent coagulation performance of PAFS also significantly increased the water stability and permeability of soil aggregates. Improvements in the soil structure facilitated the leaching of exchanged Na^+ and salts and contributed to rapid decreases in sodicity and salinity in hard saline–sodic soils during rice cultivation. PAFS amendment of hard saline–sodic soils resulted in higher yields in the first year of rice cultivation. The results confirm that using PAFS as a soil ameliorant is an effective way to quickly improve hard saline–sodic soils for rice cultivation.

Acknowledgments

This study was supported by the Fundamental Research Funds for the Central Universities (No. 21613105) and the Chinese National Science and Technology Key Project (No. 2009BADB3B03).

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