

Using HYDRUS to Simulate the Dynamic Changes of Ca^{2+} and Na^+ in Sodic Soils Reclaimed by Gypsum

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Abstract

Wang J., Bai Z., Yang P. (2016): Using HYDRUS to simulate the dynamic changes of Ca^{2+} and Na^+ in sodic soils reclaimed by gypsum. *Soil & Water Res.*, 11: 1–10.

Sodic soils are characterized by the occurrence of excess sodium to levels that can adversely affect soil structure. In recent years, with the advent of alternatives for reclaiming sodic soils, such as the addition of by-products of flue gas desulfurization, fly ash, phosphogypsum, etc., using CaSO_4 to reclaim sodic soil has again become a hot topic. In this study, cation exchange batch experiments and column leaching experiments were conducted to analyze the adsorption-exchange and dynamic changes of Ca^{2+} and Na^+ during the reclamation of sodic soils with CaSO_4 . The HYDRUS-1D software was subsequently used to simulate and predict dynamic changes in Ca^{2+} and Na^+ . The cation exchange batch experiments consisted of six treatments with six CaSO_4 rates (0, 0.25, 0.5, 1, 1.5, and 2 g/l), and the column leaching experiments consisted of two treatments with two CaSO_4 concentrations (0.5 and 1.5 g/l). The results of the static cation exchange batch experiments indicated that the ion adsorption-exchange coefficients $K_{\text{Ca-Na}}$, $K_{\text{Ca-Mg}}$, and $K_{\text{Ca-K}}$ were 1.9, 0.8, and 1.1, respectively. Applying CaSO_4 and leaching are efficient methods to reclaim sodic soil. The pH and electrical conductivity of the soil solution gradually decreased with longer leaching time in all of the treatments. HYDRUS-1D successfully simulated both the dynamic changes of the Ca^{2+} and Na^+ concentrations at different soil depths under different treatments and leaching time, and the effects of soil hydraulic conductivity and soil pH on the transport of Ca^{2+} and Na^+ . The correspondence between the observed and simulated variables was remarkable.

Keywords: cation exchange; ion transport; leaching; simulation; soil reclamation

Sodic soils occur in large areas worldwide. These soils are unsuitable for growing agricultural crops, and a number of such soils are unable to support any plant growth whatsoever. These barren lands severely limit agriculture production and negatively impact the ecosystem (QADIR *et al.* 2001a; WANG *et al.* 2008). Typical sodic soils contain an excess of exchangeable sodium (Na^+) in soil colloids, and the soluble carbonates are in the form of Na_2CO_3 and NaHCO_3 (CHUN *et al.* 2001). This results in soil with a high pH (> 8.5), clay dispersion, soil swelling, and overall poor physical properties, all of which can adversely affect soil structure and disturb the

availability of certain nutrients to plants (SUAREZ *et al.* 1984; QADIR *et al.* 2000). The physical and chemical properties of sodic soils can be improved by sodic soil reclamation (CHUN *et al.* 2001; QADIR *et al.* 2001b).

Sodic soil reclamation involves an increase in calcium (Ca^{2+}) on the cation exchange sites at the expense of Na (QADIR *et al.* 2001b). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has been known as a reclamation agent for sodic soils for more than 100 years (PRATHAPAR *et al.* 2005; SIVAPALAN 2005; MURTAZA *et al.* 2013); however, this method has rarely been used because of the high cost involved in the exploitation, transporta-

tion, and crushing of natural gypsum (SAKAI *et al.* 2004; WANG *et al.* 2008). In recent years, with the advent of alternatives such as the by-products of flue gas desulfurization (BFGD), fly ash, phosphogypsum, etc. (KUMAR & SINGH 2003), the mechanism for reclaiming sodic soils using gypsum has again become a hot topic (CHUN *et al.* 2001; WANG *et al.* 2008; CHI *et al.* 2012).

A series of complex physical and chemical processes, such as ion adsorption-exchange and precipitation-dissolution, are generated when sodic soils are reclaimed by gypsum, and the hydraulic conductivity of the soil changes dynamically during this process (SAHIN & ANAPALI 2005; SAHIN *et al.* 2011; NAYAK *et al.* 2013; WANG *et al.* 2014). Therefore, understanding the mechanism of ion transport and the dynamic changes during the process of using gypsum to improve sodic soils is important. Computer modelling to simulate the movement and reactions of salts in sodic soils has been a potentially useful complement to experimental data (SUAREZ 2001). In addition, computer modelling may help assess the economic viability of different soil amelioration methods, which is needed to extend the results broadly to other similar locations (QADIR *et al.* 2001b; SIMUNEK *et al.* 2012). These models are typically based on the numerical solutions of the Richards' equation for variably saturated flow, and analytical or numerical solutions of the Fickian equation based on the convection-dispersion equation for solute transport (SIMUNEK & SUAREZ 1997; GONCALVES *et al.* 2006). The UNSATCHEM model can be used to assess the chemical reactions for solutions with very high ionic strengths. The model also considers kinetic chemical reactions, such as the precipitation/dissolution of calcite and the dissolution of dolomite, and is suitable to simulate the ion dynamic change in sodic soils reclaimed by gypsum (RAMOS *et al.* 2011; SEAMAN *et al.* 2012). The UNSATCHEM model has recently been incorporated in the HYDRUS-1D software package (SIMUNEK *et al.* 2008, 2012). The HYDRUS-1D software may be used to analyze the movements of water and solute in unsaturated, partially saturated, or fully saturated homogeneous layered media (SIMUNEK *et al.* 2008; READING *et al.* 2012a).

The objectives of this study were to analyze and simulate the dynamic changes of individual ion concentrations in sodic soils reclaimed by gypsum using the HYDRUS-1D software package, and to provide a theoretical basis for the field application of alternative reclamation techniques (such as BFGD).

MATERIAL AND METHODS

Material. This study included two experiments: a static cation exchange batch experiment and a column leaching experiment. The experiments were performed in the Soil Physics Laboratory of the China Agricultural University. The primary purpose of the static cation exchange batch experiment was to determine the adsorption-exchange coefficients among cations (Na^+ and Ca^{2+} , Mg^{2+} , and K^+) during sodic soil reclamation by gypsum. The purpose of the column leaching experiment was to study the variation in Na^+ and Ca^{2+} in the soil leachate, soil solution, and soil colloid during sodic soil reclamation by gypsum. The same materials were used in both experiments. Pure CaSO_4 was used to more precisely examine the mechanism of sodic soil reclamation.

The soil samples were derived from the Changsheng Experimental Station of the Baoyannur League Institute of Water Resources in northwest China (40°20'N, 108°31'E). According to the FAO soil classification system, the soil was classified as Kastanozem. The soil material was not only sodic, but also saline. The soil displayed a high pH and exchangeable sodium percentage, and low hydraulic conductivity with a high electrical conductivity (EC). It had a clay texture (for its physical and chemical properties see Table 1). The soil was air-dried, crushed, and passed through a 2 mm sieve before the experiments.

The pure CaSO_4 (molecular weight 136) was purchased from the Tianjin Wendaxigui Chemical Reagent Factory (Tianjin, P.R. China).

Cation exchange batch experiments. The cation exchange batch experiments were conducted in the Soil Physics Laboratory of the China Agricultural University in August 2005. Pure CaSO_4 was selected as the reagent, and distilled water was used to dissolve the CaSO_4 . The solubility of CaSO_4 is 2 g/l at room temperature. The experiments consisted of six treatments with six CaSO_4 concentrations (0, 0.25, 0.5, 1, 1.5, and 2 g/l, with Ca^{2+} concentrations of 0, 3.68, 7.35, 14.71, 21.06, and 29.41 mmol_c/l , respectively). Each treatment was replicated three times.

Eighteen 300 g soil samples were weighed and loaded into individual flasks divided into six groups. Next, 100 ml of the 0, 0.25, 0.5, 1.0, 1.5, and 2.0 g/l CaSO_4 solutions was added to the respective samples, and the flasks were then sealed with plastic sheeting. After mixing, the soil samples were stored at a stable temperature (nearly isothermal conditions) for 10 days to allow the solution to reach a balanced state. The

doi: 10.17221/14/2015-SWR

Table 1. Physical and chemical properties of the studied soils

Exchangeable cations (cmol _c /kg)					Soil bulk density (g/cm ³)	pH	
Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	CEC			
8.65	0.60	0.50	1.27	11.02	1.45	9.15	
Soluble cations (mmol _c /l)					Soluble anions (mmol _c /l)		
Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻
303.15	5.18	3.33	3.33	193.33	50.00	51.67	20.00
Particle size distribution (%)					EC (dS/m)	K _s (cm/h)	
2.0–0.02 (mm)		0.02–0.002 (mm)		< 0.002 (mm)			
23.2		34.7		42.1	12.95	0.25	

EC – electrical conductivity; K_s – saturated hydraulic conductivity; CEC – cation exchange capacity

soil sample solution was then extracted to analyze the Ca²⁺, Na⁺, K⁺, and Mg²⁺ content.

Column leaching experiments. The experimental device (Figure 1) was a 70 cm high plexiglass column with an inner diameter of 15 cm (the soil in the column reached as high as 55 cm). A Mariotte bottle was used to supply the water, and a device composed of a pumping system and magnetic head catheters was used to extract the soil solution. The experiments consisted of two treatments with CaSO₄ concentrations of 0.5 and 1.5 g/l, corresponding to Ca²⁺ concentrations of 7.35 and 21.06 mmol_c/l, respectively. The pure CaSO₄ was selected as the reagent and distilled water was used to dissolve the CaSO₄.

A 5 cm layer of quartz sand was placed on the bottom of each column as the filter layer. The tested soil samples were poured homogeneously into the plexiglass column at a dry soil bulk density of 1.45 g/cm³ to a depth of 55 cm. The soil was filled in 5-cm intervals and tamped to a desired height in respective layers. The surface soil was loosened before the next soil layer was filled. A ceramic plate was buried at 2.5, 10, 20, 32.5, and 47.5 cm to extract the soil solution.

The soil columns were saturated with distilled water from the bottom upwards. Once the soils were saturated, the surface water was quickly drained with a vacuum pump and the Ca²⁺ solution, that had been prepared in the Mariotte bottle, was immediately supplied. Soil solutions at heights of 2.5, 10, 20, 32.5, and 47.5 cm were extracted once every 48 h using a vacuum pump to measure Ca²⁺ and Na⁺ concentrations; the volume, pH, EC, and Ca²⁺ and Na⁺ concentrations of the leachate were also measured. After the experiments, soil samples from the depths of 2.5, 10, 20, 32.5, and 47.5 cm were also collected, and the Ca²⁺ and Na⁺ concentrations in the soil solution and the soil colloid were measured.

Analytical methods and statistical analyses. The soil samples were air-dried and passed through a 1 mm sieve. The EC, pH, soluble anions and soluble cations were measured using saturated soil extracts. Soluble cations were measured using an atomic absorption spectrophotometer (AA-6200, Shimadzu, Kyoto, Japan), soluble anions were determined by anion chromatography (ICS-2100, Dionex, Sunnyvale, USA), the soil pH was determined using the glass electrode method, and the EC was measured using a 1 cm conductivity cell, dip-type probe. Exchangeable cations were determined using a 1 M ammonium acetate (pH = 7) extraction. Following this extraction and a wash with 96% alcohol, the cation exchange capacity was determined by the removal of ammonium ions by distillation. Na⁺ and K⁺ were determined by flame emission spectroscopy (AP1200, Aopu, Shanghai, P.R. China) in the extract, and Ca²⁺ and Mg²⁺ were determined by atomic absorption spectrophotometry (TAS-986, Persee, Beijing, P.R. China). The concentrations of Na⁺ and Ca²⁺ in the leachate were measured using an atomic absorption

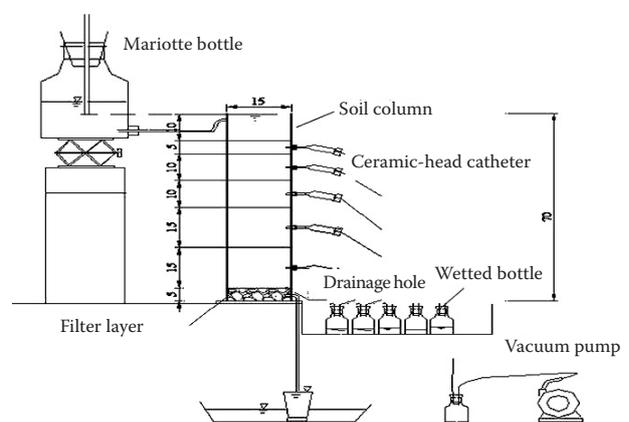


Figure 1. Scheme of the column experimental setup (in cm)

spectrophotometer, the soil pH was determined using the glass electrode method, and the EC was measured using a 1 cm conductivity cell, dip-type probe. The saturated hydraulic conductivity (K_s) was determined using a cutting ring and it was calculated by Darcy's law.

The sodium adsorption ratio of the soil solution was calculated as

$$\text{SAR} = \text{Na}^+ / \sqrt{\frac{\text{Ca}^{2+} + \text{Mg}^{2+}}{2}} \quad (1)$$

where:

SAR – sodium adsorption ratio
 Na^+ , Ca^{2+} , Mg^{2+} – ion concentrations in soil solution (mmol_c/l)

The chemical analysis was replicated three times. The Standard error of the mean (SEM) values of the three samples from each treatment were calculated. The variations between the treatments were analyzed using the SAS software (Statistical Analysis System, Version 9.1) and values of $P < 0.05$ were considered significant.

Criteria for model evaluation. To test the performance of the HYDRUS-1D model, comparisons were made between the simulated and observed values, and two statistical tests were performed: the mean bias error (MBE) and the root mean square deviation (RMSE). The MBE and RMSE were calculated using Eqs (2) and (3), respectively as follows:

$$\text{MBE} = \frac{1}{n} \sum_{i=1}^n (C_{si} - C_{oi}) \quad (2)$$

$$\text{RMSE} = \left[\frac{1}{n} \sum_{i=1}^n (C_{si} - C_{oi})^2 \right]^{1/2} \quad (3)$$

where:

n – total number of data
 C_{si} – i^{th} simulated datum
 C_{oi} – i^{th} observed datum
 C_o – mean of observed data

The MBE and RMSE values were compared separately for concentrations of Ca^{2+} and Na^+ for different soil depths. To increase the performance of the model, the adopted criteria were the lower value of the RMSE and the absolute value of the MBE (WILLMOTT 1982; WANG *et al.* 2013). In general, $\text{RMSE} \geq \text{MBE}$. The degree by which the RMSE value exceeds the MBE value is usually a good indicator of the presence and extent of outliers or the variance of the differences between the modelled and observed values.

Saturated water flow movement

Soil water flow movement equation. The one-dimensional movement of water in a saturated rigid porous medium is described by a modified form of the Richards' equation (SIMUNEK & SUAREZ 1997):

$$\frac{\partial}{\partial z} \left[K_s \left(\frac{\partial h}{\partial z} + 1 \right) \right] = 0 \quad (4)$$

where:

h – water pressure head (cm)
 K_s – saturated hydraulic conductivity (cm/h)
 t – leaching time (h)
 z – spatial coordinate (positive upward)

The effect of the solution chemistry on the hydraulic conductivity is implemented as

$$K(h, \text{pH}, \text{SAR}, C_o) = r(\text{pH}, \text{SAR}, C_o)K(h) \quad (5)$$

where:

C_o – total salt concentration of the ambient solution (mmol_c/l)
 r – scaling factor related to the pH, SAR, and salinity

The overall scaling factor r was divided into two parts:

$$r(\text{pH}, \text{SAR}, C_o) = r_1(\text{SAR}, C_o)r_2(\text{pH}) \quad (6)$$

where:

r_1 – effect of the exchangeable sodium percentage and dilution of the solution on hydraulic conductivity
 r_2 – effect of the soil solution pH

r_1 and r_2 were taken from the results of others (SUAREZ *et al.* 1984).

Multicomponent solute transport

Solute transport equations. The partial differential equation governing one-dimensional advective-dispersive chemical transport under transient water-flow conditions in a partially saturated porous medium is as follows (SIMUNEK & SUAREZ 1997):

$$\frac{\partial \theta_w c_k}{\partial t} + \rho \frac{\partial \bar{c}_k}{\partial t} + \rho \frac{\partial \hat{c}_k}{\partial t} = \frac{\partial}{\partial z} \left[\theta_w D \frac{\partial c_k}{\partial z} - q_w c_k \right] \quad k = 1, 2, \dots, N_c \quad (7)$$

where:

c_k – total dissolved concentration of the aqueous species k (g/cm³) (for values in the initial conditions see Table 1)
 \bar{c}_k – total surface species concentration of the aqueous component k (g/g) (for values in the initial conditions see Table 1)

doi: 10.17221/14/2015-SWR

\hat{c}_k – total solid phase concentration of the aqueous component (g/g) (for values in the initial conditions see Table 1)

ρ – bulk density of the medium = 1.45 g/cm³

D – dispersion coefficient, in this study = 5.6 cm²/h

q_w – volumetric flux = 0.25 cm/h

N_c – number of the primary aqueous species CO₃²⁻, HCO₃⁻, Cl⁻, SO₄²⁻, Ca²⁺, Mg²⁺, K⁺, and Na⁺ that were considered in this study

Cation exchange and selectivity. The partition between the solid phase and the solution is described by the Gapon equation (SIMUNEK & SUAREZ 1997):

$$K_{ij} = \frac{\bar{c}_i^{y+}}{\bar{c}_j^{x+}} \frac{(c_j^{x+})^{1/x}}{(c_i^{y+})^{1/y}} \quad (8)$$

where:

y, x – valence of species i and j , respectively

K_{ij} – Gapon selectivity coefficient

The adsorption concentration is expressed in mol/kg of soil. The cation exchange capacity, \bar{c}_r (CEC), is assumed to be constant and independent of pH:

$$\bar{c}_r = \sum \bar{c}_i \quad (9)$$

RESULTS AND DISCUSSION

Cation adsorption-exchange coefficient

The concentrations of soluble cations and exchangeable cations in each treatment are shown in Table 2.

The cation adsorption-exchange coefficients K_{Ca-Na} , K_{Ca-Mg} , and K_{Ca-K} were calculated using Eq. (8) under different Ca²⁺ concentrations, and the results are shown in Table 3. The calculation assumed a constant CEC of 110.2 mmol_c/kg.

The average values of cation adsorption-exchange coefficients for K_{Ca-Na} , K_{Ca-Mg} , and K_{Ca-K} under different Ca²⁺ concentrations (1.91, 0.82, and 1.08, respectively) were selected as the starting point for the soil reclamation process.

Changes in the physical and chemical properties of the soil and soil solution during treatment with CaSO₄

The pH of the soil solution. The measured values and simulation results of the pH in the soil solution at different soil depths and under different CaSO₄ application treatments are shown in Figure 2. The soil solution pH gradually decreased as the leaching time increased in all the treatments. The pH of the solution decreased further as the Ca²⁺ concentration in the supplied water increased. The pH of the topsoil decreased more than that of the subsoil. Because of the great soil depth, the poor physicochemical properties of sodic soil, and the low soil hydraulic conductivity, the Ca²⁺ in the supplied water first reacted with the Na⁺ in the soil colloids and the sodic salts of the topsoil. Despite the slight decrease in the pH of the subsoil solution, the magnitude of the decrease was much less than that of the topsoil. The solution pH

Table 2. The content of soluble and exchangeable cations after ion adsorption and exchange under different treatments

Experimental treatments (g/l)	Soluble cations (mmol/l)				Exchangeable cations (mmol _c /kg)			
	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺
T1/0	5.18	283.00	6.00	13.5	4.5	102.1	1.4	2.1
T2/0.25	5.19	284.25	15.05	13.4	4.5	101.8	1.7	2.1
T3/0.5	5.21	285.83	20.51	13.4	4.4	101.7	1.9	2.1
T4/1	5.22	287.17	23.15	13.5	4.4	101.6	1.9	2.1
T5/1.5	5.23	289.83	28.79	13.6	4.4	101.5	2.0	2.1
T6/2	5.22	290.75	33.82	13.6	4.4	101.4	2.1	2.1

Table 3. Calculated results for ion adsorption and exchange coefficients

Gapon constants	Experimental treatments						
	T1	T2	T3	T4	T5	T6	average
K_{Ca-Mg}	0.82	0.79	0.82	0.83	0.82	0.83	0.82
K_{Ca-Na}	1.89	1.78	1.83	1.92	1.95	2.00	1.91
K_{Ca-K}	1.08	1.03	1.09	1.08	1.09	1.10	1.08

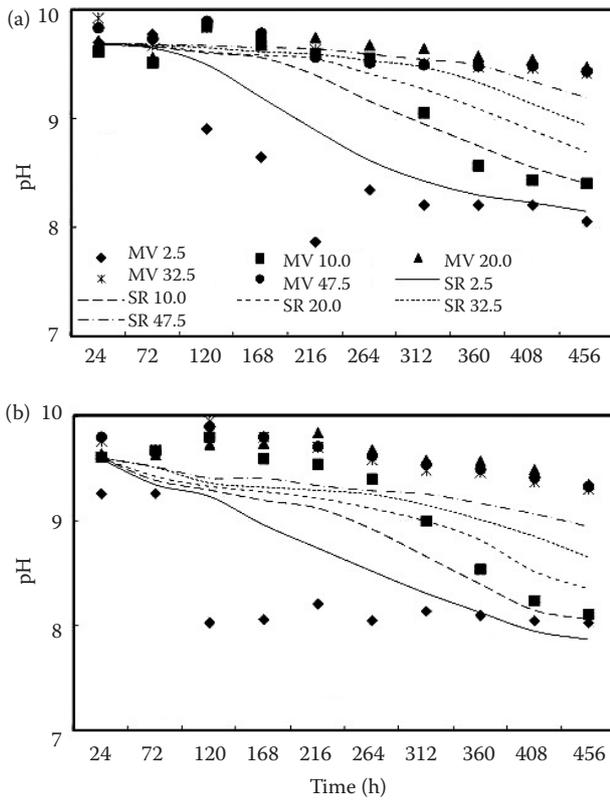


Figure 2. Changes in the soil solution pH at different soil depths with leaching time: 0.5 g/l (a); 1.5 g/l (b); MV – measured values; SR – simulation results (in cm)

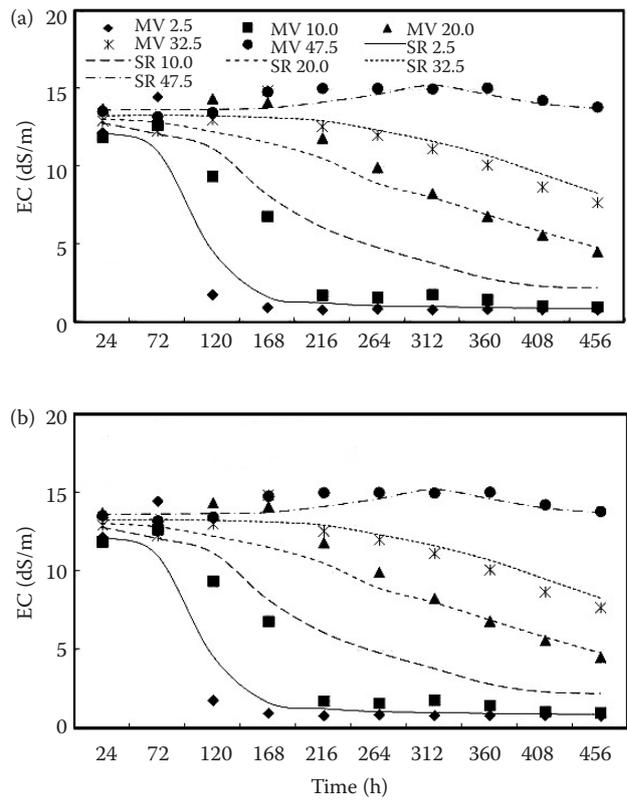


Figure 3. Changes in the soil solution electrical conductivity at different soil depths with leaching time: 0.5 g/l (a); 1.5 g/l (b); MV – measured values; SR – simulation results (in cm)

of the soil at a depth of 0–15 cm was less than 8.5, which is still classified as a moderately sodic soil level.

The EC of the soil solution. The measured values and simulation results of EC in the soil solution at different soil depths and under different CaSO_4 application treatments are shown in Figure 3. In the initial stage, the solution EC slightly increased. As the sodic soil constantly improved, the solution EC at each soil depth began to decrease, and the solution EC of the topsoil decreased more than that of the subsoil. As the concentration increased in the supplied water, the soil hydraulic conductivity also increased. However, the effect of the concentration increase in the supplied water was lower than that of the increase in soil hydraulic conductivity. Therefore, when the Ca^{2+} concentration in the supplied water was higher, the EC exhibited a stronger decrease. When the concentrations of supplied water were 0.5 and 1.5 g/l, the soil depths, at which the solution EC was lower than 4 dS/m, were 0–15 and 0–25 cm after 480 h, respectively.

The soil hydraulic conductivity. The changes in the soil hydraulic conductivity (K) under different CaSO_4 application treatments are shown in Figure 4.

The soil solution K gradually increased as the leaching time increased in all the treatments. When treated with higher concentrations, the soil K was better than when treated with lower concentrations. This may be because CaSO_4 application decreased soil solution pH, increased aggregation stability, and improved the soil hydraulic conductivity properties. The efficiency of Ca^{2+} application to improve

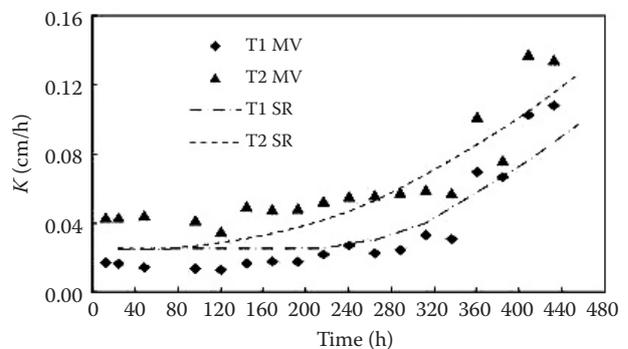


Figure 4. Changes in hydraulic conductivity (K) with leaching time: treatment 1 (T1) – 0.5 g/l; treatment 2 (T2) – 1.5 g/l; MV – measured values; SR – simulation results (in cm)

doi: 10.17221/14/2015-SWR

permeability of sodic and saline-sodic soils was demonstrated previously (SUAREZ *et al.* 1984; READING *et al.* 2012a). The change of soil K under different treatments with leaching time can be simulated by HYDRUS-1D, which reflects the measured result.

Changes and simulations of cations at different soil depths during treatment with CaSO_4

The Ca^{2+} in soil solution. The measured values and simulation results of Ca^{2+} in the soil solution at different soil depths and under different CaSO_4 application treatments are shown in Figure 5. The Ca^{2+} concentration in the topsoil solution increased rapidly under different treatments. The Ca^{2+} concentration in the subsoil solution had a slight decrease in the initial stage and then slowly increased. The trend at the site closest to the soil surface was more obvious than that at sampling site farther from the soil surface.

The change in Ca^{2+} concentration at different soil depths under different treatments as a function of leaching time can be simulated by HYDRUS-1D in a way reflecting the measured result. In the 0–5 cm

soil layer, the Ca^{2+} concentration in the soil solution increased rapidly as the supply of CaSO_4 increased. In the 5–15 cm soil layer, the Ca^{2+} concentration in the soil solution slightly decreased in the initial stage and then slowly increased. In the 15–55 cm soil layer, the Ca^{2+} concentration gradually decreased in all the soil layers, but the magnitude of this decrease was very low. The Ca^{2+} concentration at the site closer to the soil surface decreased more than that in the site more distant from the soil surface.

The Ca^{2+} decrease observed at soil depths of 5–15 cm may be due to the following reasons: the permeability is poor for sodic soils, and the transport of Ca^{2+} down into the 5–15 cm soil layer in the supplied water takes time (MZEZEWA *et al.* 2003; READING *et al.* 2012b). At the same time, the Ca^{2+} in the supplied water will react with the sodic salts in the soil solution and the exchangeable sodium in the soil colloid, which will consume a portion of the Ca^{2+} in the soil solution (QADIR *et al.* 2002; SINGH *et al.* 2013). Although the Ca^{2+} in the supplied water did not supply this soil layer, the Ca^{2+} in this soil layer penetrates to the soil layer underneath. Therefore, in the initial stages, the Ca^{2+} in the topsoil layer was not sufficiently supplying Ca^{2+} to the 5–15 cm soil layer, and the Ca^{2+} concentration in this soil layer gradually decreased. The extent of Ca^{2+} in the supplied water reaching down into the bottom soil layer gradually increased as the above soil layers improved. The Ca^{2+} concentration in the supplied water in treatment T2 was higher than that in T1; therefore, the trend in T2 was more obvious than that in T1. The changing trend of the Ca^{2+} concentration in the 15–55 cm soil layer should be consistent with that in the 5–15 cm, but the poor hydraulic conductivity of sodic soils led to the change in concentration that showed a trend that was slower than expected.

The Na^+ in the soil solution. The measured values and simulation results of Na^+ in soil solution at different soil depths under different CaSO_4 application treatments are shown in Figure 6. The Na^+ concentration in each soil solution constantly decreased under different treatments, and the Na^+ concentration in the topsoil solution decreased faster than in the subsoil. The rate at which the concentration decreased at the site closer to the soil surface was faster than that in the site farther from the soil surface. When the soil was treated with a higher supplied solution concentration, the rate at which the Na^+ concentration decreased in the soil solution was faster. The change of Na^+ concentration at different soil depths

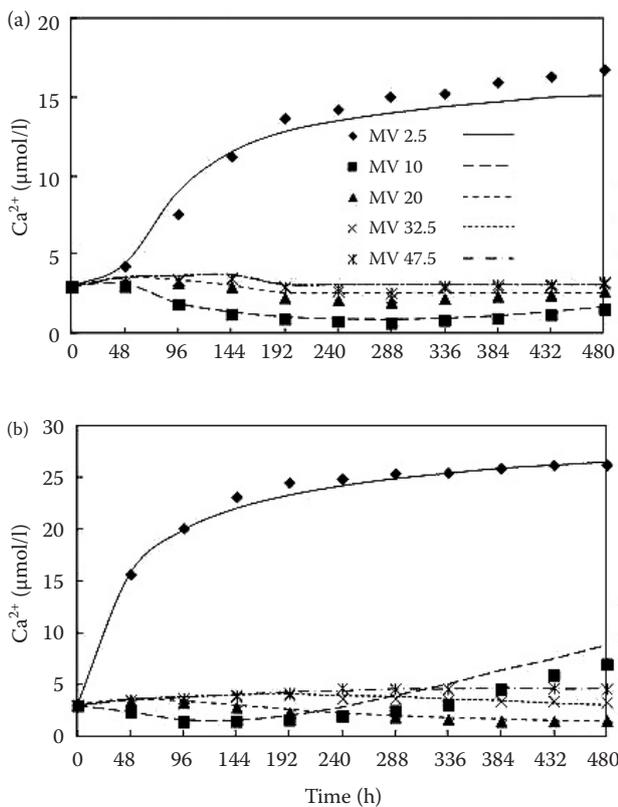


Figure 5. Ca^{2+} concentration at different soil depths with different supply solution: 0.5 g/l (a); 1.5 g/l (b); MV – measured values; SR – simulation results (in cm)

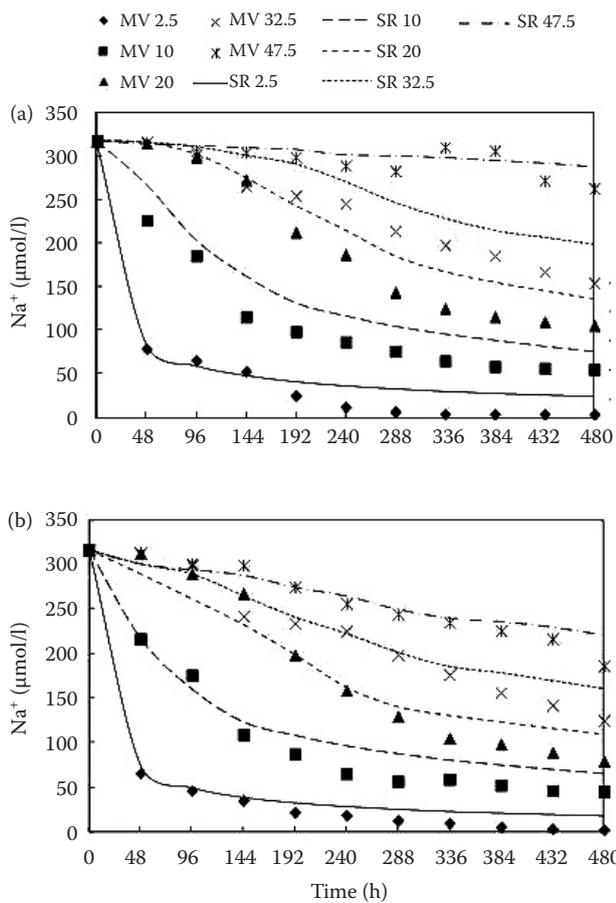


Figure 6. Na⁺ concentration at different soil depths with different supply solution: 0.5 g/l (a); 1.5 g/l (b); MV – measured values; SR – simulation results (in cm)

under different treatments with leaching time can be simulated by HYDRUS-1D, which reflects the measured result.

The source of Na⁺ in the soil solution consisted mainly of two parts: one was the Na⁺ contained in

soil in the original state, and the other was the Na⁺ exchanged by Ca²⁺ in the soil solution from the soil colloid (QADIR *et al.* 2005; YAZDANPANAHI & MAHMOODABADI 2013). The Na⁺ concentration might decrease due to the following: no Na⁺ was present in the supplied water, although Na⁺ was being constantly exchanged from the soil colloid (LI *et al.* 2004; LI & KEREN 2008), but the relative amount of Na⁺ was low. Because the Na⁺ in the soil solution leached out of the soils, the soil levels constantly decreased. Because Na⁺ was transported from the surface soil layer to the bottom soil layer, and the Na⁺ at the surface soil layer was supplementary to the bottom soil layer, the rate of decrease of Na⁺ in the bottom soil layer was slower than that in the surface soil layer.

Validation of the HYDRUS-1D model

As shown in Table 4, the values of the MBE and RMSE between the measured and simulated Ca²⁺ concentrations ranged from 0.01 to 0.91 and 0.71 to 1.13, respectively; the values for the measured and simulated Na⁺ concentrations ranged from 10.15 to 59.78 and 11.45 to 70.93. The RMSE and the absolute value of MBE between the simulated and measured Ca²⁺ and Na⁺ concentrations at the five soil depths were relatively low, and the RMSE was more than the MBE for Ca²⁺ and Na⁺ concentrations at different soil depths under different treatments. However, the degree, at which the RMSE value exceeded the MBE, was relatively low.

These data indicate that Hydus-1D can be used to confidently simulate the dynamic changes of Ca²⁺ and Na⁺ concentrations at different soil depths under different treatments with leaching time (WILLMOTT

Table 4. Statistical parameters indicative of model performance

Soil depth (cm)	CaSO ₄ (g/l)							
	0.5				1.5			
	Ca ²⁺ concentration		Na ⁺ concentration		Ca ²⁺ concentration		Na ⁺ concentration	
	RMSE	MBE	RMSE	MBE	RMSE	MBE	RMSE	MBE
2.5	0.63	> -0.01	18.54	-13.99	0.59	0.33	11.45	-10.15
10	0.12	-0.11	52.25	-48.81	1.22	-0.94	39.34	-35.70
20	0.70	-0.58	62.97	-50.50	0.15	-0.10	47.43	-30.54
32.5	0.42	0.25	70.93	-59.78	0.21	-0.09	50.99	-40.04
47.5	1.13	0.91	22.11	-17.11	0.12	-0.01	29.04	-18.17

RMSE – root mean square deviation; MBE – mean bias error

doi: 10.17221/14/2015-SWR

1982; SIMUNEK *et al.* 2012). Overall, the simulated Ca^{2+} and Na^+ concentrations values obtained with the HYDRUS-1D software were in agreement with the measured values, despite some discrepancies (Figures 5 and 6). The agreement was good, particularly considering the complexity of conditions to which the model was subjected, including the cation adsorption-exchange coefficient, the effects of the exchangeable sodium percentage, of the dilution of the solution on hydraulic conductivity, and of the soil solution pH (SIMUNEK *et al.* 2008).

CONCLUSION

The following conclusions can be drawn from our findings:

- (1) The ion adsorption-exchange coefficients $K_{\text{Ca-Na}}$, $K_{\text{Ca-Mg}}$, and $K_{\text{Ca-K}}$ were 1.9, 0.8, and 1.1, respectively, according to the static cation exchange batch experiments.
- (2) Applying CaSO_4 and leaching are both efficient methods to reclaim sodic soil. The soil solution pH and sodium adsorption ratio gradually decreased as the leaching time increased in all the treatments.
- (3) The HYDRUS-1D software was able to successfully simulate both the dynamic changes of Ca^{2+} and Na^+ concentrations at different soil depths under different treatments with leaching time and the effects of soil hydraulic conductivity and soil pH on the transport of Ca^{2+} and Na^+ . The correspondence between the observed and simulated variables was remarkably accurate.

Acknowledgements. This research was supported by the National Natural Science Foundation of China (No. 50749032), Fundamental Research Funds for the Central Universities of China (No. 2652012072), and Beijing Higher Education Young Elite Teacher Project.

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Received for publication January 27, 2015

Accepted after corrections May 5, 2015

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