



Article Combined Application of Organic Amendments and Gypsum to Reclaim Saline–Alkali Soil

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Abstract: Saline–alkali soils have high sodicity, high pH, and high levels of soluble salts, as well as carbonates. This study aimed to evaluate the effect of cattle manure and chicken manure combined with gypsum at three levels on reclaiming a saline–alkali soil, through a soil column experiment. Combined treatments were more effective than those of sole gypsum in reducing the initial exchangeable sodium percentage (ESP) below 5%. Electrical conductivity (EC_e) was lowered below 1.6 dS m⁻¹ by all treatments, except the control. The higher effectiveness of manures combined with gypsum can be explained by their synergistic effect on Na⁺ displacement and subsequent soil structure improvement, leading to an enhancement in the leaching process, and then the salinity/sodicity reduction. Soluble salts and Na⁺ were considerably reduced in all treatments at the first leaching. Soil ESP and EC_e threshold values from the US Salinity Lab classification were reached by any treatment, except the control. The addition of cattle manure or chicken manure might enhance the reclamation effect of gypsum with leaching for some saline–alkali soils.

Keywords: saline-alkali soil; saline-sodic soil; cattle manure; chicken manure; gypsum; land use



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1. Introduction

Saline–alkali soils are characterized by a significant amount of soluble salts, and sodium (Na⁺) in the soil solution and cation exchange complex, as well as a high pH due to the soluble carbonates. Sometimes, the presence of sodium carbonates passes unnoticed when obtained from paste extract, due to a portion of the dissolved carbonates that reacts with Ca²⁺ and precipitates as CaCO₃; moreover, the high solubility of Na⁺ salts and the electroneutrality of aqueous solutions mean that the remaining Na⁺ charge is either balanced by sulfate ions or included into the exchange sites, which also permit the use of efflorescence crusts (pH > 8.4, Na/Cl ratio > 1) as indicators of sodium carbonates. [1]. Sodicity causes many adverse effects, such as changes in exchangeable and soil solution ions and soil pH, the destabilization of soil structure, the deterioration of soil hydraulic properties, increased susceptibility to crusting, runoff, soil erosion, and osmotic/specific ion effects on plants [2]. Soil salinity can be measured by the electrical conductivity (EC) of soil solution, and sodicity by the exchangeable sodium percentage (ESP); moreover, the sodium adsorption ratio (SAR) is used to characterize the presence of Na⁺ in irrigation water and soil solution. According to the criteria of the US Salinity Lab (USSL) [3], salinealkali soils developed in situ have an ESP > 15%, pH > 8.5 and EC_e > 4 dS m⁻¹. In addition, Chhabra [4] has proposed that if the ratios—expressed in mol m⁻³— of either (2CO₃^{2–} + $HCO_3^{-})/(Cl^{-} + 2SO_4^{2-})$ and/or Na⁺/(Cl⁻ + 2SO_4^{2-}) > 1, soils should be treated as natric and reclaimed with chemical amendments.

The amelioration of saline–sodic and sodic soils normally needs a source of soluble Ca^{2+} to replace the excess Na^+ from the cation exchange sites, and this is most effective with non-saline irrigation water [5]; then, the replaced Na^+ , together with the excess soluble salts, if present, are removed from the root zone through infiltrating water as a result of

excessive/regulated irrigation [6]. Gypsum (CaSO₄·2H₂O) application counters reduced hydraulic conductivity in Na⁺-dominated soils through Na⁺–Ca²⁺ exchange, the hydrolysis of Na⁺ through the ionic strength effect, and enhancing electrolytic concentration [7]. Due to the high pH of alkali soil, most likely as a result of Na₂CO₃, the addition of gypsum provides a source of Ca²⁺ which precipitates as CaCO₃ and Ca(HCO₃)₂, leading to a decrease in pH [8]. However, the chemical amelioration strategy itself has become cost-intensive as an effect of increases in amendment costs [6].

Organic amendments such as manure can be considered as an alternative, as well as a complement to chemical amendments. The addition of organic amendments in sodic soils binds fine particles together into large water-stable aggregates, increasing porosity, and thus improving the soil physical properties [9]. Fertilization with organic matter can be expected to improve salt-affected soils, regarding their chemical and physicochemical characteristics, by decreasing the exchangeable Na⁺ content, and improve their physical properties by increasing the aggregate stability [10]. Additionally, remediating saline–sodic soils with organic amendments is a cheaper and more sustainable alternative to inorganic materials [11]. Moreover, Mahmoodabadi et al. [12] suggested that the application of gypsum together with organic amendments, depending on their chemical composition, might promote some synergistic effects on soluble Na⁺ and K⁺ concentrations and have a positive impact on properties of calcareous saline–sodic soils. Furthermore, based on a revision, Diacono and Montemurro [13] concluded that most of the well-known effects of organic materials on the chemical, biological, and physical properties of salt-affected soils are relevant in terms of effectiveness.

Saline–sodic/alkali soils are abundant in the agricultural lands of the High Valley (Bolivia) [14], negatively affecting crop production. In addition to the fact that manures as organic amendments are locally and economically accessible, a previous screening of experiments under controlled conditions with similar soils from that area, carried out by Castellon and Andrade [15], Andrade Foronda [16], and Andrade et al. [17], showed that manures were more effective than biochar and peat, and that gypsum was more efficient than sulphur in decreasing soil sodicity and salinity. Thus, the objective of this study was to evaluate the combined effects of cattle manure, chicken manure and no-manure, with gypsum at three levels (50, 75 and 100% of requirement) and leaching, on reclaiming a saline–alkali soil.

2. Materials and Methods

The target soil (Table 1) was collected at a depth of ~25 cm from the High Valley of Cochabamba, Bolivia (17°32′38.6″ S, 65°51′41.9″ W, elevation of 2750 m). The experiment was carried out at the Faculty of Agricultural and Livestock Sciences, 'Universidad Mayor de San Simón' (17°27′2.9″ S, 66° 7′59.7″ W). Cattle manure (CA), chicken manure (CH) and gypsum (GY) were collected locally and analyzed for some properties (Table 2) related to the salt-term evaluation.

Following and adapting the protocol of Ahmad et al. [7], PVC tubes (height of 100 cm and \emptyset of 10 cm) as simulated soil columns were prepared, and 5 cm of gravel, glass fiber and plastic mesh were placed at their bottoms. The gypsum requirement (GR) at the 100% level (8 g GY kg⁻¹ soil) needed to reduce the initial soil ESP to 15%, was calculated through the equation used by Lebron et al. [18]. The saline–alkali soil, GY and manures were homogenized and sieved at 4, 2 and 6 mm, respectively. Manures were applied at 2% of organic matter on a dry weight basis (w/w). Each of the columns was filled with 3.6 kg of affected soil to a height of 35 cm based on bulk density, placing the treated soil in the upper layer (height of 20 cm).

Property	Value	Property	Value	_
Bulk density (g cm $^{-3}$)	1.3	$EC_e (dS m^{-1})$	24.1	
Clay (%)	17.8	pН	9.6	
Silt (%)	53.9	Na^+ (mmol _c L ⁻¹)	332.1 *	
Sand (%)	28.3	Ca^{2+} (mmol _c L ⁻¹)	0.5	
TOC (%)	0.3	Mg^{2+} (mmol _c L ⁻¹)	0.6	
Saturation (%)	29.2	K^+ (mmol _c L ⁻¹)	1.5	
CEC (cmol _c kg ⁻¹)	11.2 *	HCO_3^{-} (mmol _c L ⁻¹)	59.0	
Na^+ (cmol _c kg ⁻¹)	6.9 *	CO_3^{2-} (mmol _c L ⁻¹)	46.0	
Ca^{2+} (cmol _c kg ⁻¹)	4.9 *	Cl^{-} (mmol _c L ⁻¹)	104.0	
Mg^{2+} (cmol _c kg ⁻¹)	1.1 *	SO_4^{2-} (mmol _c L ⁻¹)	52.5	
K^+ (cmol _c kg ⁻¹)	0.1 *	$CaCO_3 (g kg^{-1})$	3.57	
ESP (%)	52.8			

Table 1. Chemical and physical properties of the saline-alkali soil before reclamation.

CEC = cation exchange capacity, exchangeable cations (derived—ISO 22171 at pH of 7 and AAS); EC_e = electrical conductivity (paste extract); pH (water 1:5); ESP = exchangeable sodium percentage; soluble ions (paste extract and standard procedures of the USSL); TOC = total organic carbon; CaCO₃ (acid neutralization). * Remeasured values: excess soluble Na⁺ can be due to its accumulation at the soil collection site. Inherent error: difference between CEC and the sum of exchangeable cations.

The parameters of leaching water were: EC of 0.2 dS m⁻¹, pH of 8.1, and Na⁺, Ca²⁺ and Mg²⁺ concentrations of 0.9, 0.6 and 0.5 meq L⁻¹, respectively. The volume (1060 ml) of water was determined through the pore volume (PV) formula given by Kahlon et al. [19]. An initial 3/4 PV was added to saturate the soil, then four cycles (each of one PV) were applied until a relatively constant EC was reached in the leachates (Table A2), and then the reclaimed soil samples were collected to be analyzed.

Table 2. Some pertinent properties of organic amendments and gypsum.

Property	Cattle Manure	Chicken Manure	Gypsum *
Na^+ (mmol kg ⁻¹)	207.5	127.7	2.1
Ca^{2+} (mmol kg ⁻¹)	107.0	65.9	4247.2
Mg^{2+} (mmol kg ⁻¹)	45.2	33.5	7.8
$EC (dS m^{-1})$	11.4	5.2	2.6
pН	9.53	9.56	7.87
TOC (%)	33.1	34.2	0.08

Cations (Lakanen—Erviö, AA + EDTA, pH 4.65), pH (0.001 M CaCl₂) and EC (1:5 suspension). * Purity of gypsum: 91.7%.

Soil pH was determined in a 1:5 soil–water suspension (derived—ISO 10390). EC_e and soluble ions were measured from the paste extract through the standard procedures of Richards et al. [3]. Exchangeable cations were obtained at a pH of 7 (derived—ISO 22171) with atomic adsorption spectroscopy. The ESP was determined using the Formula (1) by Sumner et al. [20]. The estimated percentage of displaced Na⁺ was calculated through Equation (2).

$$ESP = \left(\frac{Na^{+}}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}}\right)100\tag{1}$$

where cations are expressed as a concentration in cmol_{c} kg⁻¹.

$$Na^{+}_{displaced} = 100 - \left(\frac{Na^{+}_{SA}}{Na^{+}_{AM} + Na^{+}_{SB}}\right)100$$
(2)

where $Na_{displaced}$ is Na⁺ (%), SA is soil after, AM is amendment, and SB is soil before.

The experimental design was completely randomized with four replicates. The treatments comprised 9 combinations of CA, CH, and no manure (NM) with GY levels (GY_{50} , GY_{75} and GY_{100}), and control (only leaching). The effects on soil ESP, EC_e, pH and displaced Na⁺, as response variables, were evaluated using the Scott–Knott clustering algorithm (p = 0.05). Statistical analysis was performed using R software (v.4.1.3) and RStudio (v.1.31093).

3. Results and Discussion

The soil ESP, pH and EC_e in reclaimed soil, as well as displaced Na⁺, differed significantly (p < 0.05) among the interactions, and between these and control. It should be mentioned that there was an absolute control (only leaching) which has not been taken into account for the comparisons of means in Figure 1, but is shown in those of Table A1 for reference purposes; since it received two cycles of leaching in 54 days, and because of the difference between groupings of means with and without the control. The soil ESP, EC_e and pH values of the control, decreased by 54, 79 and 8%, respectively, over the respective initial values; moreover, the threshold values of EC_e (4 dS m⁻¹) and ESP (15%) from the USSL classification were reached with any treatment, except for the control, however, that of soil pH (8.5) was only reached with CH at any dose of GY (Table A1).



Figure 1. Soil ESP (**a**), EC_e (**b**), pH (**c**) and displaced Na⁺ (**d**) for the interactions between manures/no manure and gypsum levels. Means sharing a letter are not significantly different, according to the Scott–Knott test (p = 0.05). The bars indicate the standard error.

Cattle manure (CA) and chicken manure (CH) combined with any level of gypsum (GY) were more effective than those of sole GY in lowering the ESP below 5%; moreover, CA-GY₁₀₀ and CH-GY₁₀₀ were the most efficient (Figure 1a). The soil before EC_e was decreased by over 90% with any combination, even with those of only GY at any dose, and CH-GY₁₀₀ was the most effective (Figure 1b). Combinations with CH were more effective than the rest of the treatments for reducing soil pH (Figure 1c). Because of the relatively low

Na⁺ contribution from amendments, the displaced Na⁺ values were highly congruent with those of the ESP from reclaimed soil, showing Na⁺ removals of over 93% by any combined treatment of manure and gypsum (Figure 1d).

These results are similar to those from other studies related to the effectiveness of organic amendments combined with gypsum: Chaganti et al. [11] reported that combined applications of gypsum and organic amendments (composts) were more effective than individual applications in improving soil properties such as sodium leaching, hydraulic conductivity, ESP, and SAR. As well, Prapagar et al. [21] found that gypsum application combined with partially burnt paddy husk and cow dung reduced the EC, SAR and pH more effectively, compared to applying gypsum alone. Moreover, Abdel-Fattah [22] observed that gypsum combined with water hyacinth compost or rice straw compost enhanced the reclamation process and caused a higher decrease in salinity and sodicity than gypsum alone, and in turn, than the control. However, some investigations differed from these results; as Hernández Araujo [23] found no differences among organic amendments (compost, vermicompost and *Lemna* spp.) at 1.5 or 3% w/w, nor combined with gypsum. Moreover, Manzano Banda et al. [24] reported that flushing water reduced the salinity and sodicity of two saline–sodic soils to satisfactory levels with and without the application of any amendment (cattle manure, gypsum and sulfuric acid).

The effectiveness of combined CA or CH with any level of GY at reducing the soil ESP and soluble salts from the saline–alkali soil (Figure 1a,b) can be explained by the positive impact of organic matter from manures and Ca²⁺ from GY on soil structure, leading to an enhancement in soil aggregation, porosity, infiltration, and subsequent leaching efficiency; furthermore, although the addition of GY by itself improved those characteristics, the superiority of combined treatments, independent of GY doses, suggests that the indirect effect of organic amendments on soil physical properties for removing Na⁺ and salts from the soil was significant. In this regard, Ahmad et al. [7] mention some factors that influence the leaching of salts and Na⁺, such as the difference between the soluble and exchangeable Na⁺ contents of soil, the quantity of gypsum added, soil texture, CEC, and the percolation time; coinciding partially with Shaygan et al. [25], who stated that the dynamics of hydraulic conductivity depend on the magnitude of cation exchange and the subsequent changes in the pore system. Likewise, Chaganti and Crohn [26] indicated that the chemical characteristics of composts are as important as those of biological factors in their potential for reclamation; therefore, to achieve a comprehensive physical and chemical amelioration of a saline–sodic soil, both factors must act synergistically.

The lower efficiency of treatments with sole GY compared with those combined with the manures in reducing salinity/sodicity (Figure 1) was probably due to the initial high exchangeable Na⁺ of soil, leading to lower availability of Ca²⁺ and to soil dispersion. However, the effect of sole GY was likely sufficient in promoting soil aggregation and subsequent leaching of soluble salts and Na⁺ from the soil, possibly boosted by the increased solubility of GY (~2–3 fold) in the presence of NaCl, meaning that relatively more Ca^{2+} could infiltrate the soluble form. This is in agreement with Gupta and Gupta [27], who stated that the solubility of gypsum in alkali soils is considerably higher than in normal soils, and is also increased if it is applied in conjunction with manures; and also coincides with Sim et al. [28], who found that NaCl largely increases the solubility of gypsum. In addition, Ahmad et al. [7] found that the increased addition of gypsum can improve the retention of $Ca^{2+} + Mg^{2+}$ and enhance leaching even for loamy sand and sandy loam soils. The order of effectiveness in lowering ESP for only gypsum treatments was: $GY_{100} > GY_{75} =$ GY_{50} > control (Figure 1a, Table A1); results coincide partially with those of Qadir et al. [29], who also included phytoremediation by *L*. *fusca* (LF): $GY_{100} > LF > GY_{50} > control.$ Because the three GY levels from the combinations with manures showed relatively low significant differences between them for lowering the soil ESP and pH—the same as between GY_{50} and GY_{75} from the gypsum-only treatments (Figure 1a,c)—manures with GY_{50} and GY_{75} could be considered as cost-efficient alternatives for further validations.

The significant reduction in soil pH by combined treatments (Figure 1c), despite the previous high pH of manures and soil, could have been partially caused by the displacing of sodium salts, agreeing with Wong et al. [8], who affirmed that the high initial pH of soil, most likely as a result of Na₂CO₃, can be reduced through the addition and dissolution of gypsum as a source of Ca^{2+} which precipitates as $CaCO_3$ and $Ca(HCO_3)_2$, resulting in a direct decrease in soil pH and later proton generation for further reductions. In addition, Chaganti et al. [11] and Wong et al. [8] concluded that adding composts likely increases the partial pressure of CO_2 due to increased microbial activity during incubation and/or leaching, which can lead to the formation of inorganic and organic acids for further soil pH reductions. However, for the treatments with only GY, the soil pH after reclamation showed minimal variation compared to the initial pH (Figure 1c), likely because of the initial high ESP and soluble Na⁺, leading to soil dispersion, which probably counteracted the Ca²⁺ contribution from GY.

The percolation time for the control (two cycles in 54 days) was considerably longer than that of the rest of the treatments (four cycles in a range of 10–35 days), as shown in Figure 2. This behavior can be due to soil dispersion caused by the high exchangeable Na⁺ in the soil before reclamation, which can also explain the higher effectiveness of sole gypsum at all levels compared to the control (only affected soil with leaching) in decreasing soil ESP and EC_e (Table A1). Moreover, Shaygan et al. [25] suggested that an increased percolation time and a greater rate of cation exchange were associated with greater leaching efficiency.



Figure 2. Percolation time in accumulated days according to the applied cycles of leaching as pore volumes. Cycles of leaching: 1 = first, 2 = second, 3 = third, and 4 = fourth.

Soluble salts expressed as EC (Table A2) and SAR (Figure A1) in the leachates were considerably high for all treatments in the first leaching cycle; therefore, up to two cycles of leaching could be sufficient to reclaim this type of soil, at least under controlled conditions. This behavior can be related to the increased leaching rate triggered by amendments and soil flocculation, which counteracted the soil dispersion caused by the high sodicity of soil before reclamation; this agrees with Abdel-Fattah [22], who mentions that the first cycle of leaching can readily leach salts and mobile ions, whether the soils are amended or not. This also concurs with Ahmad et al. [7] and Hassan et al. [30], who reported a higher removal of Na⁺ in the first leaching cycle than that in the following leachates, coinciding with higher hydraulic conductivity. They also concluded that the maximum salts and Na⁺ could come from the dissolved part, while the forthcoming fraction could come partially

from the reactions taking place through the Na^+ – Ca^{2+} exchange and from the high initial EC_e of soils that keeps them flocculated to pass the solution [5].

Following the conceptualization of this study, further research could assess different soil textures, other GY levels below 75%, and lower rates of manures. Moreover, other studies could evaluate: a two-step process of washing with GY followed by organic amendment, similar to that of Sastre Conde et al. [31]; the influence of mulch with GY, as investigated by Zhao et al. [32]; or the inclusion of phytoremediation techniques, as studied by Qadir et al. [29].

4. Conclusions

Combined treatments (cattle or chicken manure with gypsum at any level) were more effective than those of sole gypsum in reducing the initial soil ESP below 5%, and both manures with GY_{100} were the most efficient. The soil before EC_e and ESP levels decreased below 1.6 dS m^{-1} and 14%, respectively, with any (combined and sole gypsum) treatment, except the control. Any combination of manure and gypsum lowered the pH below 8.7. The effectiveness of combining organic amendments with gypsum can be explained by their synergistic effect on Na⁺ displacement and soil flocculation, resulting in the subsequent improvement in soil porosity and infiltration, leading to an enhancement in the leaching process. The relative effectiveness of sole gypsum treatments was likely due to the Ca²⁺ contribution from gypsum and the influence of NaCl on its solubility. Manures with GY_{50} and GY_{75} could be cost-efficient alternatives for remediation in further validations. The control was less efficient in facilitating the percolation and lowering soil salinity/sodicity. Soluble salts and sodium were considerably lowered in all treatments at the first cycle of leaching. The ESP and ECe threshold values from the USSL classification were reached with all treatments except the control, and the pH threshold was only reached by chicken manure with gypsum. Overall, the study suggests that the addition of cattle manure or chicken manure might enhance the effectiveness of gypsum with leaching for the reclamation of some saline-alkali soils.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Treatment	ESP (%)	EC _e (dS m ⁻¹)	рН	Leached Na ⁺ (%)
CH-GY ₁₀₀	1.23 a (98.2)	0.82 a (96.6)	8.45 a (12.0)	97.25 a
CH-GY ₇₅	2.40 a (96.5)	1.00 a (95.9)	8.45 a (12.0)	94.16 b
CH-GY ₅₀	2.95 a (95.6)	1.14 a (95.3)	8.44 a (12.1)	93.45 b
CA-GY ₁₀₀	1.14 a (98.3)	0.92 a (96.2)	8.58 b (10.6)	97.71 a
CA-GY ₇₅	3.05 a (95.5)	0.98 a (95.9)	8.69 c (9.5)	93.21 b
CA-GY ₅₀	2.69 a (96.0)	1.23 b (94.9)	8.58 b (10.6)	94.80 b
NM-GY ₁₀₀	6.31 b (90.7)	0.90 a (96.3)	9.15 e (4.7)	86.85 c
NM-GY ₇₅	12.74 c (81.2)	1.35 b (94.4)	9.53 f (0.7)	72.91 d
NM-GY ₅₀	13.81 c (79.6)	1.57 b (93.5)	9.46 f (1.5)	73.83 d
Control	31.34 d (53.6)	5.00 c (79.3)	8.83 d (8.0)	40.78 e

Table A1. Effect of manures combined with gypsum levels on soil properties, compared to control.

CH = chicken manure, CA = cattle manure, NM = no manure, GY = gypsum. Means sharing a letter are not significantly different according to the Scott-Knott test (p = 0.05). Values in parenthesis indicate the decrease (%) over the respective value of soil before reclamation.

Appendix **B**

Appendix B.1. Electrical Conductivity

Table A2. Evolution of soluble salts as EC (dS m^{-1}) in the leachates at each cycle of leaching (pore volume).

	Cycle of Leaching				
Treatment	1	2	3	4	
Control *	83.0 (2.4)	31.6 (2.2)	_	_	
NM-GY50	71.5 (3.3)	5.3 (1.7)	4.3 (0.7)	2.4 (0.5)	
NM-GY75	67.5 (5.8)	5.4 (0.8)	4.6 (0.4)	2.6 (0.4)	
NM-GY100	69.3 (4.5)	6.2 (2.2)	4.6 (1.0)	2.8 (0.8)	
CA-GY50	78.4 (3.8)	5.7 (0.2)	3.6 (0.5)	1.5 (0.7)	
CA-GY75	78.2 (6.6)	5.1 (0.2)	3.9 (0.2)	2.3 (0.2)	
CA-GY100	77.0 (6.9)	6.3 (0.1)	3.5 (0.3)	2.2 (0.2)	
CH-GY50	75.4 (1.3)	6.7 (0.5)	4.3 (0.4)	2.2 (0.4)	
CH-GY75	81.9 (2.6)	6.0 (0.3)	3.5 (0.4)	2.6 (0.4)	
CH-GY100	72.5 (1.1)	8.5 (0.7)	3.4 (0.2)	2.3 (0.3)	

Values in parenthesis indicate the standard deviation. * Two cycles of leaching were applied to the control due to the length of its percolation time (Figure 2).

Appendix B.2. Sodium Adsorption Ratio

The SAR was determined using the Formula (A1) by Richards et al. [3].

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Ma^{2+}}{2}}}$$
 (A1)

where cations are expressed as concentration in $mmol_c L^{-1}$.



Figure A1. Evolution of sodium adsorption ratio (SAR) in the leachates at each cycle of leaching.

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